

Structure-Property Relationships of Polyester Regioisomers and Pendant Functionalized Polyetherimides

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ABSTRACT

Step-growth polymerization enabled the synthesis of novel polyester regioisomers and pendant functionalized polyetherimides (PEI)s. Novel monomers incorporated at targeted mol % produced series of polyesters and PEIs, suitable for systematic analysis of key polymer properties. Subsequent compositional, thermal, mechanical, and rheological characterization forged structure-property relationships to further understand the influence of composition on performance. Altering regiochemistry is a subtle way to maintain the same polymer composition but tune desired properties. Similarly, introducing functional pendant groups expands the property profile of common industrial polymers and installs a handle for secondary chemistry after synthesizing the main polymer. Both altering regiochemistry and adding pendant groups alters polymer properties without the need for large changes in synthetic requirements or reaction conditions, ideal for industrial adoption.

Incorporation of a kinked bibenzoate (BB)-based diester monomers into the commonly utilized linear regioisomer afforded processable amorphous and semi-aromatic (co)polyesters. BB-(co)polyesters with ethylene glycol (EG) possessed improved barrier performance compared to poly(ethylene terephthalate) (PET) while improving on mechanical properties, including tensile and flexural modulus/strength, rivaling bisphenol-A polycarbonate (BPA-PC). Replacement of EG with 1,4-cyclohexanedimethanol (CHDM) improved thermal properties closer to BPA-PC, while enabling melt rheological

analysis due to its amorphous morphology. Time-temperature superposition (TTS) analysis produced master curves provided insight into the entanglement molecular weight (M_e) and entanglement density. More kinked structures possessed a lower M_e and more entanglements.

Introducing kinked monomers posed the question of cyclic species generation during polymerization, common in step-growth reactions. Thus, systematic incorporation of *meta*-substituted hydroxyethylresorcinol and *para*-substituted hydroxyethylhydroquinone regioisomers into PET analogues enabled the characterization of cyclic formation due to monomer regioisomers. Increased *meta* substitution produced increased amounts of cyclic species, analyzed by size exclusion chromatography (SEC).

Adding functionality to high performance polyetherimides (PEI)s is difficult due to the high temperatures required for processing. The lack of thermal stability for commonly utilized H-bonding/reactive groups limits viable moieties. Utilizing the high temperature processing, PEIs incorporating pendant carboxylic acids reacted in the melt to form branched PEIs. These branched PEIs exhibited steeper shear thinning as well as improved flame resistance, limited in thin film commercial PEIs.

Structure-Property Relationships of Polyester Regioisomers and Pendant Functionalized Polyetherimides

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GENERAL AUDIENCE ABSTRACT

My research focused on making new plastics (polymers) for use in consumer and performance markets. Typical applications utilizing these plastics include food packaging, consumer goods, automotive, aerospace, microelectronics, construction, and medical devices. Large changes such as intricate new chemicals used to make the plastics increase the difficulty in incorporating these new materials into existing synthesis and processing techniques and infrastructure. Thus, my research revolved around subtle changes to the chemical structure of the plastic, suitable for easy industrial adoption while also improving targeted properties necessary for the aforementioned applications.

Polyesters are a class of polymers commonly used for food packaging and consumer goods. Thus, improving gas barrier performance and mechanical integrity/strength is crucial when designing new polyesters. Changing the bond angles through the linear *versus* kinked nature of the polymer chain imparts processability and improved gas barrier, compared to commercial poly(ethylene terephthalate) (PET), commonly used in food packaging applications. The density of the polyesters is also increased, which improves mechanical strength. The specific structures used also increased the thermal resistivity compared to PET. This higher thermal resistivity enables use in applications where high temperature cleaning such as steam sterilization and dish-washing

could deform products or processing such as filling food packaging containers with hot foods.

Similar types of polymers which possess much higher thermal resistivity are classified as high performance polymers. One class of these include polyetherimides (PEIs). The specific chemical structures and their high thermal resistance makes them great candidates for applications in automotive, aerospace, and microelectronic applications; although, these same properties make these polymers very difficult and expensive to process into the desired parts. Thus, adding functionality to the polymer by putting specific chemical groups off of the main chain enabled easier processing and improved other polymer properties. Adding the functionality to these polymers allowed them to react and change structure at high temperatures (during processing) to achieve a different shape, thus improving desired properties, such as how easy they flow like liquids at high temperatures and processing conditions. Another benefit realized from this change during processing was the improvement of flame resistance. Due to the chemical structure of the PEIs, they inherently possess resistance to catching on fire, remaining on fire, and dripping flaming material. Although PEIs typically possess good flame resistance, thin films or small parts made from these polymers do not possess the same flame resistance and can produce flaming drips, undesirable for applications requiring flame resistance. Chemically modifying these polymers with the aforementioned functionality and processing them increased the flame resistance to eliminate flaming drips and lessen the amount of time the polymer was on fire.

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Chapter 1: Introduction

1.1 *Dissertation Overview*

This dissertation investigates the influence of regiochemistry and pendant group functionality on polymer structure-property relationships. Although changing the regiochemistry of the polymer backbone or adding a pendant group off of the polymer backbone is a subtle change, the simplicity affords easy to adopt chemistry in industrial applications while still being able to fundamentally understand the structure-property relationships. This use-inspired basic research facilitates advancement in both application driven needs as well as fundamental understanding to design new and improved polymer structures.

Chapter 2 investigates the influence of incorporating a kinked bibenzoate diester into semi-aromatic polyesters. Polyesters incorporating the linear and *para-para* linked 4,4'-bibenzoate (4,4'BB) typically produce un-processable, highly crystalline polyesters with short aliphatic or rigid amorphous diols or liquid crystalline, high performance polymers with longer aliphatic or kinked aromatic diols. Incorporating the kinked *meta-para* 3,4'-bibenzoate (3,4'BB) with the 4,4'BB in polyester with ethylene glycol (EG) as the diol disrupted the chain regularity and packing, thus affording polyesters amorphous or semi-crystalline polyesters suitable for melt processing. Incorporating the 3,4'BB increased the polymer's oxygen barrier performance 25% better than amorphous poly(ethylene terephthalate) (PET) as well as the Young's modulus and tensile yield strength to rival bisphenol-A polycarbonate (BPA-PC). One of the goals of this chapter, raising the glass transition temperature (T_g) to compete with BPA-PC (145 °C), was

partially accomplished as the polyesters T_g s ranged from 104-121 °C. In order to improve the T_g , the EG diol needed to be substituted for a bulkier compound.

Chapter 3 illustrates the change in properties of BB-based polyesters when incorporating the bulkier 1,4-cyclohexanedimethanol (CHDM) into polyesters. Compared to the EG polyesters discussed in Chapter 2, the T_g s of the BB/CHDM-based (co)polyesters improved by up to 15 °C, closer to that of BPA-PC. Melt rheology and time-temperature superposition (TTS) analysis revealed a lower molecular weight of entanglement (M_e) and entanglement density for the more kinked 3,4'-BB-based (co)polyesters. These (co)polyesters exhibited similar trends in tensile mechanical properties with the trends being related to differences in polymer density as well as entanglement. The interesting increase and trends in tensile mechanical performance prompted the exploration into more mechanical and thermomechanical properties.

Chapter 4 discusses the continued evaluation of BB-based (co)polyesters mechanical performance. Utilizing the BB-based (co)polyesters with EG as the diol, large scale reactions afforded ample sample for injection molding small dog-bone specimens and unnotched Izod bars. The dog-bone specimens confirmed the initial tensile mechanical properties and further illustrated the stress *versus* strain behavior including necking and strain hardening. Flexural testing corroborated the tensile analysis and heat deflection temperature (HDT) testing confirmed the polyesters applicable temperature window. Coefficient of thermal expansion (CTE) measurements also expanded the understanding of thermomechanical structure-property relationships. In order to confirm these trends and properties were a direct result of the regiochemistry and not the specific polyester compositions, another series of polyester regioisomers properties needed to be analyzed.

Chapter 5 reveals the structure-property relationships for another series of polyester regioisomers, specifically around dihydroxybenzene compounds, hydroxyethylresorcinol (HER) and hydroxyethylhydroquinone (HEH). Instead of (co)polyester series incorporating different ratios of the two diols, replacement of EG in PET afforded regioisomers of PET analogues. HER and HEH incorporation into PET is known to improve gas barrier performance, making these polymers interesting for both industrial applications as well as fundamental understanding the structure-property relationships. Similar analysis was performed as for the BB-based polyesters. The more kinked, *meta*-substituted HER incorporation decreased the fractional free volume at T_g (f_g), melt flow activation energy (E_a), increased the M_e , and increased the Young's modulus and tensile yield strength compared to PET and compared to HEH incorporation. One common result throughout the analysis of the polyester regioisomers (BB and HER/HEH) was the presence of cyclic species, seen in the size exclusion chromatography (SEC) analysis of molecular weight. Thus, the influence of monomer regiochemistry on cyclic formation in melt polycondensation was explored.

Chapter 6 explores the generation of cyclic species with systematic incorporation and ratios of *meta*- and *para*-substituted monomers. Utilizing the same HER and HEH diols, incorporating these two diols with terephthalate as the diester produced soluble/partially-soluble (co)polyesters suitable for low molecular weight SEC analysis. Utilizing Advanced Permeation Chromatography (APC) low molecular weight species were well resolved and the areas of each peak were used to get a relative concentration of the various cyclic sizes (dimer, trimer, tetramer, pentamer) for the different (co)polyester compositions. In general, the highest concentration of cyclics belonged to the trimer, while

the (co)polyesters incorporating higher mol % of the *meta*-substituted HER possessed higher overall concentrations of all low molecular weight cyclic species.

Chapter 7 begins investigation into high performance polymers, specifically polyetherimides (PEIs). High performance polymers typically possess high thermal stability and high mechanical properties. Although PEIs offer these desirable properties due to their highly aromatic character, difficulties in processing arise, thus requiring high temperature processing or advanced processing techniques. Improving the processability of these polymers while ideally improving other key properties through new monomers or reactive functionality is still desirable. Installing pendant carboxylic acid groups as pendant groups off of the backbone through monomer selection afforded series of PEIs with increased T_g s and a reactive handle. The imidization temperature (T_{im}) related directly to the composition and T_g . At high temperatures, common for processing PEIs, the pendant carboxylic acids decarboxylated, and formed biphenyl crosslink sites. Analyzing this decarboxylation, a linear relationship was found for initial mol % of pendant carboxylic acid functionality and IR signal of the off-gas during heating. Exploiting the reactive nature of the carboxylic acid at high temperatures, samples with low mol % of the pendant carboxylic acid branched the PEIs in the melt, thus making the shear thinning slope steeper, which is desirable for improved processability. Additionally, the sample possessed higher viscosities at low shear rates due to the growth in molecular weight due to branching as well as the change in topology. The increased viscosity imparted improved flame resistance as evident by the flame testing and lack of flaming dripping, noticed when testing the commercial sample with no pendant carboxylic acid functionality. Other pendant groups needed to be explored to further understand the pendant groups' influence on properties.

Chapter 9 reviews the current needs of polymers for stereolithographic (SLA) 3D printing of soft tissue engineering scaffolds. Most 3D printing reviews for tissue scaffolds focus on the printing methods themselves, the shapes of the printed parts, and/or the interaction of the printed parts with cells. This review first introduces the relationship between polymer structure and properties, with a focus on key properties required for both making a printable resin as well as maintaining desirable properties once fabricated into a part. The key properties for the printed scaffold include low cytotoxicity, degradation preference and mechanism, and mechanical properties replicating the desired tissue. The key properties for SLA 3D printable polymers include low viscosity, reactive functionality that are photocurable, fast curing reactions, and cross-linkable topology. Designing a polymer to possess both the properties before SLA 3D printing while obtaining the desirable properties of the scaffold after SLA 3D printing is challenging. This review intends to offer guidance in these designs. The second component of this review involves summarizing the current fabricated parts and discussing their properties with an emphasis on mechanical properties, specifically related to their comparison to real tissue. Synthetic and natural polymers are covered and future perspective wraps up the review.

Chapter 10 investigates coating of a peptide nucleic acid (PNA) onto clothing fibers to impart selective antibacterial performance. Common antibacterial chemistries remain non-selective, thus killing both healthy and harmful bacteria. PNAs utilize specific sequences to inhibit growth of harmful and drug-resistant bacteria such as MRSA, while not inhibiting healthy bacteria. A model peptide was developed and used to assess the adhesion to the fibers as well as its resistance to removal with simulated washing cycles. Pad dry cure coating adhered the peptides onto the nylon-cotton cloths (commonly used by

military and healthcare professionals). The peptide preferentially adhered to the cotton fibers, suggesting hydrogen bonding as the primary interaction. Utilizing the same coating method, PNAs coated on the fibers inhibited MRSA bacterial colonization but not growth of healthy bacteria.

Finally, Chapter 11 provides overall conclusions for the dissertation. Chapter 12 suggests future work. Future work may be in progress, while some future work is suggested to continue off of the discussed chapters.

Chapter 2: Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance

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2.1 Abstract

Melt polycondensation of bibenzoate dimethyl esters with ethylene glycol enabled the synthesis of polyesters containing linear (4,4'-bibenzoate (4,4'BB)) and kinked (3,4'-bibenzoate (3,4'BB)) repeating units. Novel 3,4'BB:4,4'BB (co)polyesters with ethylene glycol (EG) showed an onset of weight loss ($T_{d,5\%}$) above 350 °C. ¹H NMR spectroscopy confirmed 4,4'BB:3,4'BB incorporation, and size exclusion chromatography (SEC) revealed high molecular weights. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) revealed glass transition temperatures (T_g) approaching 121 °C, crystallization and melting transition temperatures (T_c and T_m), and sub- T_g β -relaxations. 4,4'BB incorporation below ~45 mol % afforded an amorphous morphology, while 4,4'BB incorporation above 45 mol % induced crystallinity. Melt rheology elucidated the effect of structure on flow behavior, and time-temperature superposition (TTS) revealed distinct flow transitions. TTS analysis also provided insight into the

structural influence of regioisomers on fractional free volume (f_g) and flow activation energies (E_a). Incorporation of the symmetrical 4,4'BB monomer negligibly affected the f_g but imparted a stiffer overall chain, resulting in higher E_a . Positron annihilation lifetime spectroscopy (PALS) of the (co)polyesters confirmed a lack of change in free volume through measuring the average free volume of a spherical hole. Determination of oxygen permeability offered fundamental understanding of the relationship of monomer symmetry with gas permeability and free volume in unoriented films; kinked 3,4'BB monomer afforded higher overall barrier in amorphous films. Finally, tensile testing elucidated Young's moduli and yield strengths, confirming (co)polyesters' mechanical similarity to BPA-polycarbonate. Moduli ≤ 2.7 GPa and yield strengths up to 74 MPa confirmed BB-based (co)polyesters enhanced properties compared to other high T_g polyesters.

2.2 Introduction

High performance engineering polymers continue to impact many emerging technologies, ranging from coatings and food packaging to high temperature electronics.¹ These applications require tailorable properties, and polycarbonates, polyesters, poly(arylene ethers) and polyimides remain key synthetic polymer platforms.² Polymers for high temperature environments such as dishwashers, autoclaves, or electronic devices demand superior thermal properties, while reactive environments that expose the material to harsh conditions, such as high temperatures or extended UV light exposure, require thermal and chemical resistance. Thus, researchers continue to search for new materials to balance properties needed for a wide range of demanding performance.

Applications that demand transparency and high temperature performance commonly employ bisphenol A polycarbonate (BPA-PC) due to high impact strength,

thermal properties, and optical clarity. BPA-PC exhibits a glass transition temperature (T_g) near 145 °C,² enabling dishwasher and autoclave cleaning or sterilization. However, the bisphenol A monomer (BPA) continues to receive scrutiny as an endocrine-disrupting chemical (EDC).³ Potential residual BPA monomer or hydrolytic degradation of BPA-PC leads to BPA leaching, which causes concern for applications involving direct human interaction or contact with consumed products.⁴⁻⁵ Thus, the search for a suitable replacement polymer for BPA-PC continues, especially for food and beverage containers.⁶⁻⁸ Our research group previously described polymeric materials suitable for BPA-PC replacement,^{4-5, 9-10} and earlier literature identified several copolyesters with thermal properties desirable for BPA-PC replacement.^{6-8, 11-18}

Mechanical integrity, tunable thermal properties, and relatively low cost make semi-aromatic polyesters common in high performance commercial applications.² Moreover, well-established, melt phase polycondensation reactions ensure potential commercial viability. Most common applications include fibers, injection molded parts, blow molded bottles, extruded films, and liquid crystalline displays. The synergy of an inexpensive manufacturing process, gas barrier properties, non-organoleptic properties, optical clarity, and superior mechanical properties upon orientation make poly(ethylene terephthalate) (PET) the most common polyester packaging material.² Amorphous cyclobutanediol-based copolyesters, a relatively new high performance amorphous polymer platform, offer enhanced T_g s compared to common commercial amorphous copolyesters and are regarded as attractive alternatives to BPA-PC for transparent food packaging applications.^{5, 11-14, 16} While cyclobutanediol-based polyesters afford the higher T_g necessary to replace BPA-PC in many packaging applications, the copolyester lacks the

performance necessary to replace BPA-PC in all applications and does not afford the same gas barrier properties as unoriented or oriented PET. Poly(ethylene furanoate) (PEF), a recently announced biobased polyester, imparts improved thermal and barrier properties compared to PET, but lacks the high T_g and thermal stability of BPA-PC.¹⁹⁻²¹ Therefore, the need to identify new polymers with improved thermal and barrier properties continues for packaging applications and BPA-PC replacement.

Dimethyl 4,4'-biphenyldicarboxylate (4,4'-bibenzoate, 4,4'BB) presents a symmetrical biphenyl linkage, which affords polyesters with superior thermal and mechanical properties compared to terephthalate based (co)polyesters.²²⁻²⁵ Various copolyester compositions of 4,4'BB and terephthalate provide mechanical and thermal properties approaching BPA-PC. This mesogenic monomer also imparts liquid crystallinity in combination with a longer, flexible alkylene spacer.²⁶⁻²⁸ A regioisomer of the 4,4'BB monomer, i.e. dimethyl 3,4'-biphenyldicarboxylate (3,4'-bibenzoate, 3,4'BB), shows a slight improvement in thermal and barrier properties as a comonomer with terephthalate.²⁴ The lack of a feasible commercial synthetic method limited the production of 3,4'BB for use in polycondensation, but recent development of a single-step synthetic route to access various bibenzoate (BB) regioisomers permitted a commercially viable pathway to 3,4'BB manufacture.²⁹ Thus, minimal literature exists on 4,4'BB/3,4'BB-based (co)polyesters other than preliminary thermal transition characterization and permeability analysis.¹⁸

This report describes the synthesis and characterization of novel BPA-free (co)polyesters containing mixtures of 4,4'BB and 3,4'BB with ethylene glycol (EG). Melt polymerization techniques, including transesterification and polycondensation, afforded tough, ductile (co)polyesters and complementary characterization revealed structure-

property relationships over a broad compositional range. Increasing 3,4'BB levels in the copolyesters resulted in a decreased melting point and level of crystallinity, leading to amorphous (co)polyester compositions that afforded desirable optical properties and easier melt processing. Various analytical techniques provided the (co)polyesters thermal, rheological, and barrier properties. 4,4'BB, 3,4'BB, and EG containing (co)polyesters with high T_g s and improved oxygen barrier properties, suggest a new polymer platform for advanced packaging.

2.3 Experimental

2.3.1 Materials. Dimethyl 4,4'-biphenyldicarboxylate (4,4'BB) (MP = 210 °C)³⁰ and dimethyl 3,4'-biphenyldicarboxylate (3,4'BB) (MP = 97-99 °C)²⁹ were supplied by ExxonMobil and used as received. Ethylene glycol (EG) (Sigma-Aldrich, ≥99%) was used as received. Titanium tetra(isopropoxide) (99%) was purchased from Sigma-Aldrich, and a 0.01 g/mL titanium solution in anhydrous 1-butanol was prepared according to previously described procedures.³¹ All solvents were obtained from Spectrum and used as received. Nitrogen gas (Praxair, 99.999%) and oxygen gas (Airgas, 100%) was used as received.

2.3.2 Analytical Methods. ¹H NMR spectroscopy was performed at 23 °C on a Varian Unity 400 at 399.87 MHz in deuterated trifluoroacetic acid (TFA-d). A Waters size exclusion chromatograph (SEC) equipped with an auto sampler, three 5 µm PLgel Mixed-C columns, and a Waters 2410 refractive index (RI) detector operating at 880 nm with a flow rate of 1 mL min⁻¹ at 35 °C in tetrahydrofuran (THF) afforded molecular weight characterization relative to polystyrene. Prior to SEC analysis, dynamic light scattering (DLS) at 35 °C analyzed all polymer solutions in THF to confirm no aggregation in the utilized SEC solvent. Differential scanning calorimetry (DSC) determined thermal

transitions using a TA instruments Q1000 DSC, calibrated using indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards, and employing a nitrogen flow of 50 mL/min at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. Glass transition temperatures were measured as the midpoint of the transition in the second heating ramp. Thermogravimetric analysis (TGA) utilizing a TA Instruments Q50 from 25 to 600 °C at a heating rate of 10 °C/min afforded thermal stability characterization. Different sample shapes resulted in varying char yields between 10 and 30 %. Dynamic mechanical analysis (DMA) on a TA Instruments Q800 Dynamic Mechanical Analyzer in oscillatory tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 μ m, and a static force of 0.01 N with a temperature ramp of 3 °C/min revealed modulus *versus* temperature behavior. Compression molding with a PHI Q-203H manual hydraulic press resulted in optically clear, free-standing films. A Systech Illinois 8001 Oxygen Permeation Analyzer at 23 °C and 0% relative humidity with an oxygen flow of 20 cc/min and a nitrogen flow of 10 cc/min measured oxygen transmission rate (OTR). A BOY XS injection molded dog bone tensile specimens at 282 °C, with a mold temperature of 13 °C. A slow screw speed was used along with 1700 psi to fill and a 1300 psi hold. ASTM 638 provided guidance for tensile property measurements and data analysis. A MTS model No. 4204 with a 1kN load cell, applied a crosshead motion rate of 10 mm/min under ambient conditions. An epsilon micro-extensometer was applicable at low strains.

Rheological analysis was conducted on a TA Instruments Discovery Hybrid Rheometer-2 using a disposable 25 mm diameter aluminum parallel-plate geometry under nitrogen. Strain sweep testing from 0.01-10% oscillatory strain at 1 Hz determined the linear viscoelastic region. Using 1.25% oscillatory strain and a frequency range of 1-100

rad/s, frequency sweeps at 10 °C intervals from 170 °C to 270 °C provided storage and loss moduli and viscosity responses. TA Instruments TRIOS software shifted resulting data to generate master curves. Determination of melt flow properties involved fitting resulting shift factors to the WLF equation in the TRIOS software.

Average molecular hole volume, $\langle V_h \rangle$, was probed by positron annihilation lifetime spectroscopy (PALS). The data, about 10^6 incidences for each sample, were collected over one hour at 23 °C and 45 % relative humidity using Ortec Positron Lifetime System (Advanced Measurement Technology Oak Ridge, TN) which employs a fast-fast coincidence scheme. Compression-molded, thin films were stacked to a total thickness of about 1 mm and a 30 μCi ^{22}Na positron source was sandwiched between two thick pieces. The sample-source assembly was placed between two photomultiplier tubes (PMT) each equipped with BaF_2 gamma radiation sensitive scintillators and tuned so one PMT can differentiate and convert into a signal the absorbed gamma quanta associated with a positron emission and another PMT with its annihilation. A multichannel analyzer compiled the coincidences resulting in determining for each positron the time difference between ‘birth’ and ‘death’ events (the lifetime) with a time resolution of 290 ps, and PATFIT-88 software analyzed the annihilation spectra assuming three components.³² The characteristic lifetime, τ_3 , of the orthopositronium (o-Ps) annihilation component acquired from PALS spectra was first related to the average spherical hole radius, $\langle R_h \rangle$, via the Tao-Eldrup equation and then to the average hole volume $\langle V_h \rangle = 4\pi(\langle R_h \rangle)^3/3$.³³⁻³⁴

2.3.3 Synthesis of poly(EG-4,4’BB-co-3,4’BB). The following example details the synthetic procedure for all (co)polyesters and the synthesis of 25:75 4,4’BB:3,4’BB is used as a representative example. Reactions were conducted in a dry 100-mL round-bottomed

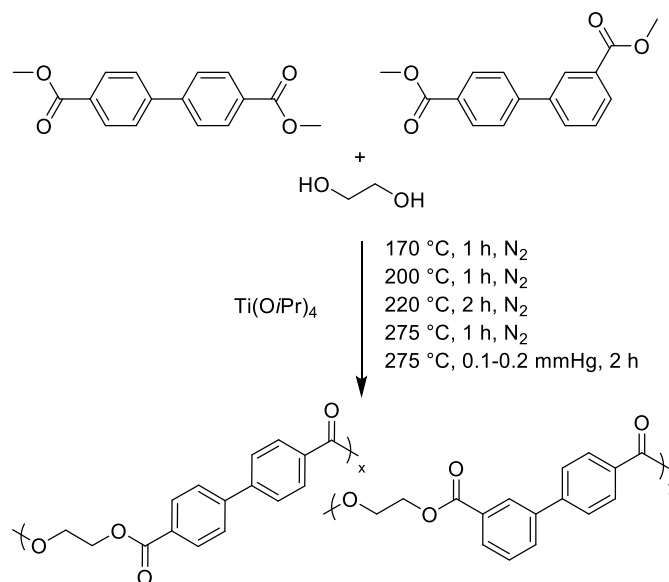
flask equipped with an overhead stirrer, nitrogen inlet, and distillation apparatus. EG (7.63 g, 1.5 mol eq.), 4,4'BB (5.54 g, 0.25 mol eq.), and 3,4'BB (16.62 g, 0.75 mol eq.) were introduced to the flask, followed by addition of titanium tetra(isopropoxide) (0.12 mL; 40 ppm; 0.01 g/mL in anhydrous 1-butanol) catalyst. Degassing with vacuum and purging with nitrogen three times allowed the reaction to proceed oxygen-free. The reaction progressed at 170 °C for 1 h, 200 °C for 1 h, 220 °C for 2 h, and 275 °C for 1 h, all while under constant stirring at 75 rpm and nitrogen purge. Methanol condensate collection in a cold round-bottomed flask ensured reaction progress. Applying vacuum produced a pressure of 0.1-0.2 mmHg and the reaction stirred at 275 °C for 1 h. Polymer was recovered by breaking the flask and retrieving the solid polymer from the stir rod without further purification.

2.3.4 Compression molding (co)polyesters. Melt pressing polymers between two stainless steel plates, layered with Kapton® films afforded ductile transparent films. Steel shims, either 3 or 16 mil thick, controlled film thickness. Rexco Partall® Power Glossy Liquid mold release agent applied to the Kapton® films ensured the polyester did not adhere during processing. Samples were heated (~3 min for amorphous; ~5 min for semi-crystalline) at 275 °C before the top stainless steel plate was added. Centering the plates and closing the press afforded no visible light between plates. After an additional 2 min of heating at 275 °C, four press-release-press cycles with the first two presses utilizing 5 tons of force and the last two presses utilizing 10 tons of force completed the film pressing procedure. Immediate submersion of the plates and film in an ice bath quench cooled the films to ensure no crystallization. Samples with >52 mol % 4,4'BB incorporation remained semi-crystalline upon quenching, introducing a complex morphological component and

prohibiting DMA or rheological analysis. A vacuum-oven dried the films at 60 °C overnight before use.

2.4 Results and Discussion

Melt transesterification using titanium tetra(isopropoxide) catalyst with subsequent polycondensation afforded (co)polyesters with a broad range of BB regioisomer incorporation, as illustrated in **Scheme 2.1**. Transesterification occurred at 170 °C, slightly below the boiling point of 3,4'BB. The titanium catalyst and excess diol facilitated transesterification, and monitoring methanol removal confirmed reaction progress.^{4, 12-14, 35} After 1 h of stirring and heating to 200 °C, a clear melt resulted, due to the 4,4'BB (T_m = 210 °C)³⁰ dissolving in the EG and 3,4'BB melt. After 1 h at 200 °C, increasing the temperature to 220 °C completed transesterification and methanol distillation within 2 h. Gradually increasing the temperature to 275 °C initiated polycondensation with the removal of EG. Polycondensation under reduced pressure reached a constant melt viscosity and ceased distillation, confirming complete excess diol removal and affording high molecular weight polyester. Polycondensation concluded within 1 h, and overall reaction times did not exceed 6 h. Pale yellow, optically clear products resulted for compositions with less than 50 mol % 4,4'BB incorporation. Above 50 mol % 4,4'BB incorporation, opaque semi-crystalline polyesters resulted.



Scheme 2.1. Synthesis of x-4,4'BB-y-3,4'BB-EG random copolyesters

SEC only confirmed the molecular weight of poly(ethylene 3,4'BB) homopolyester, and copolyesters incorporating 4,4'BB resulted in heterogeneous suspensions, eliminating SEC analysis. Although hexafluoroisopropanol is a common SEC solvent for semi-crystalline polyesters,^{14, 36} the corrosive nature prevented SEC analysis in our laboratories. As seen in **Figure 2.1**, low molecular weight cyclics, common in step-growth polymerization, led to minor tailing at higher elution times in the SEC chromatographs.³⁷ SEC determined a number-average molecular weight (M_n) of 50.6 kg/mol relative to polystyrene standards, a weight-average molecular weight (M_w) of 89.0 kg/mol and a PDI of 1.75 for poly(ethylene 3,4'BB), correlating well with similar polyesters.³⁶⁻³⁸ All samples attained comparable zero-shear viscosity confirming that all (co)polyesters were high molecular weight at similar reaction conditions.⁴ ^1H NMR spectroscopy confirmed BB incorporation using unique proton shifts on the meta-substituted 3,4'BB isomer (Figure S1). These distinct proton shifts with overlapping signals from both the 3,4'BB and 4,4'BB allowed for determination of the final

(co)polyester composition, as seen in **Table 2.1**. The final monomer incorporation agreed well with feed ratios.

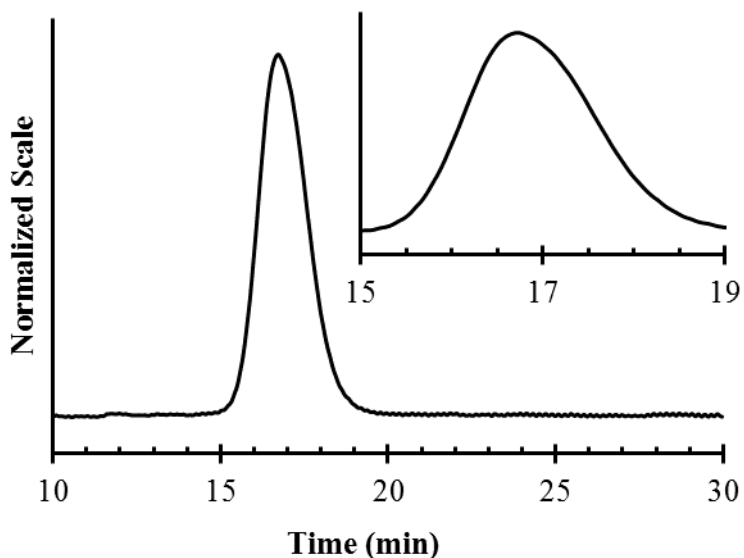


Figure 2.1. Size exclusion chromatography (SEC) analysis in THF of poly(ethylene 3,4'BB) homopolymer. Columns maintained at 35 °C and a flow rate of 1 mL/min was employed using a refractive index (RI) detector for analysis.

TGA identified a single-step weight loss profile at temperatures above 350 °C for all polyester compositions. Char yields ranged from 10-30 weight % remaining, as seen in **Figure 2.2**. DSC afforded thermal transitions, as reported in **Table 2.1**. Incorporation of the rigid, symmetric 4,4'BB increased chain stiffness, raising the T_g , consistent with previous literature.^{18, 22-24} Altering the BB regioisomer ratios resulted in T_g s ranging from 104-117 °C. As seen in **Figure 2.3**, (co)polyesters with 4,4'BB below 50 mol % resulted in amorphous copolyesters, but 4,4'BB levels above 50 mol % induced crystallization, which was evident from observed crystallization exotherms and melting endotherms (Figure S2). Earlier literature confirmed that 4,4'BB encourages highly crystalline polymers,²² but greater than 50 mol % 3,4'BB incorporation successfully disrupts crystallization during film fabrication. Previous literature utilized the Fox equation to predict a T_g of 122 °C for poly(ethylene 4,4'bibenzoate).²³ This enabled the prediction of

a Fox equation fit for the current copolyesters. The Fox equation fit well to experimental results, confirming random copolyesters. To eliminate the influence of crystallinity, further characterization focused on (co)polyester compositions quenched in the amorphous state.

Table 2.1. Summary of compositional, thermal, and thermomechanical analysis of (co)polyesters

x-4,4'BB-y-3,4'BB-EG (mol or wt. %)		T_g (°C)		T_m (°C)	T_β (°C)
Feed (x:y)	Observed (x:y)				
	$^1\text{H NMR}^a$	DSC ^b	DMA ^c	DSC ^b	DMA ^c
0:100	0:100	104	111	--	-80
10:90	10:90	105	113	--	-79
25:75	25:75	108	114	--	-75
45:55	39:61	110	117	--	-73
55:45	52:48	112	121	218	-66
70:30	66:34	117	--	272	--
75:25	68:32	--	--	310	--

^a CF₃COOD solvent, ambient conditions, 400 MHz.

^b DSC: heat/cool/heat, second heat; N₂, 10 °C/min. T_g reported as midpoint of step transition, T_m reported as peak maximum of endothermic event.

^c DMA: tension mode, 1 Hz, 3 °C/min. T_g reported as peak maximum in tan delta curve, T_{flow} reported as temperature prior to modulus approaching zero.

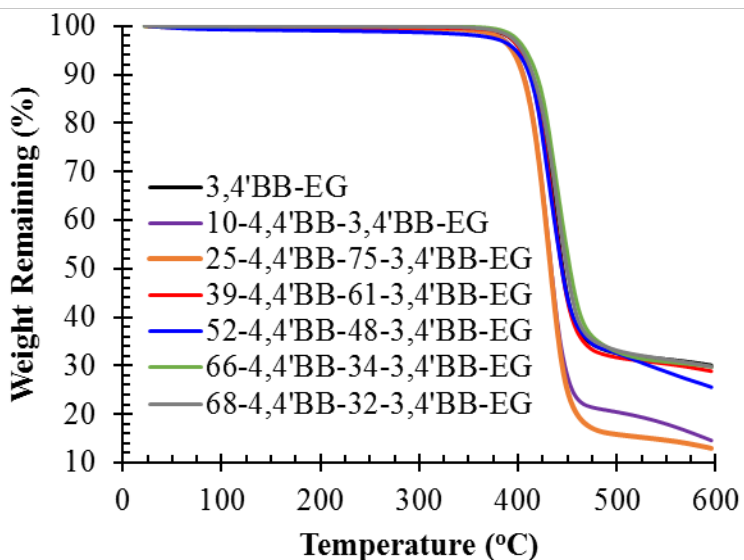


Figure 2.2. Thermogravimetric analysis (TGA) thermograms displaying single-step degradation for all x-4,4'BB-y-3,4'BB-EG (co)polyesters. TGA analysis performed at 10 °C/min under nitrogen purge.

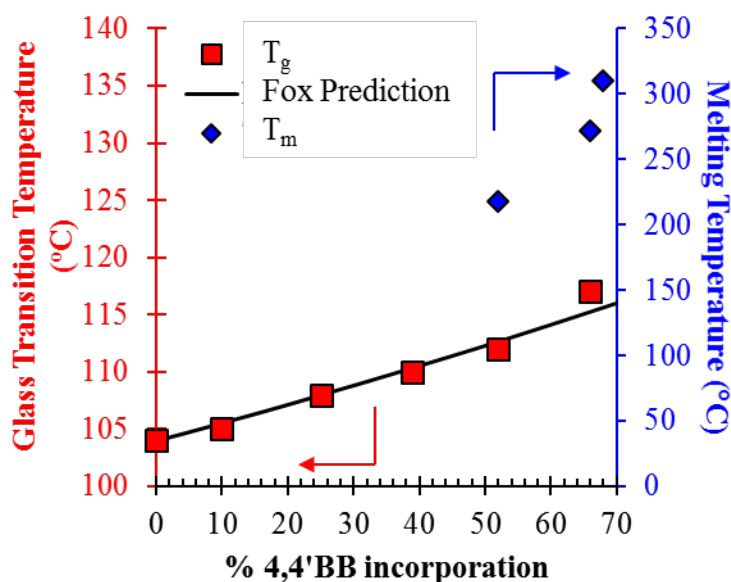


Figure 2.3. Thermal transition dependence of bibenzoate composition from DSC analysis. Mol % determined using ^1H NMR spectroscopy. Squares symbolize T_g s and diamonds symbolize T_m s.

DMA probed the thermomechanical response of the polyesters. All (co)polyesters showed a similar temperature-insensitive glassy modulus from the starting temperature (-150 °C), approaching the T_g (from DSC). All (co)polyesters exhibited sub T_g β -relaxations near -75 °C, as shown in **Figure 2.4** and reported in **Table 2.1**. The increase and broadening in the $\tan \delta$ intensity indicated complex local relaxations. The peak β -relaxation temperature minimally changed with the peak temperature ranging from -80 to -66 °C. Relaxations in this temperature range are characteristic for polyesters and are typically associated with aromatic ring-flips.^{4, 19-20, 24, 39-41} Poly(ethylene 3,4'BB) demonstrated the lowest relaxation intensity as a result of its limited ability to undergo ring-rotation at the *meta*-linkage.¹⁹⁻²⁰ The β -relaxation intensity increased with increasing 4,4'BB levels, suggesting ring-rotation as the relaxation mechanism with the increase in *para*-substituted aromatic rings affording higher energy absorption. The relative $\tan \delta$ intensities of BB (co)polyesters are lower than PET, presumably from less freely-rotating

aromatic rings. Recent literature also suggests direct correlation between gas diffusivity and ring-rotation in the polymer backbone, commonly referred to as dynamic free volume.^{19-20, 42} The broad relaxation suggests the (co)polyesters also possess comparable impact properties, commonly associated with β -relaxations.⁴³⁻⁴⁴ Probing the structural influence on sub- T_g relaxations requires further mechanical testing, which will be reported in the future.

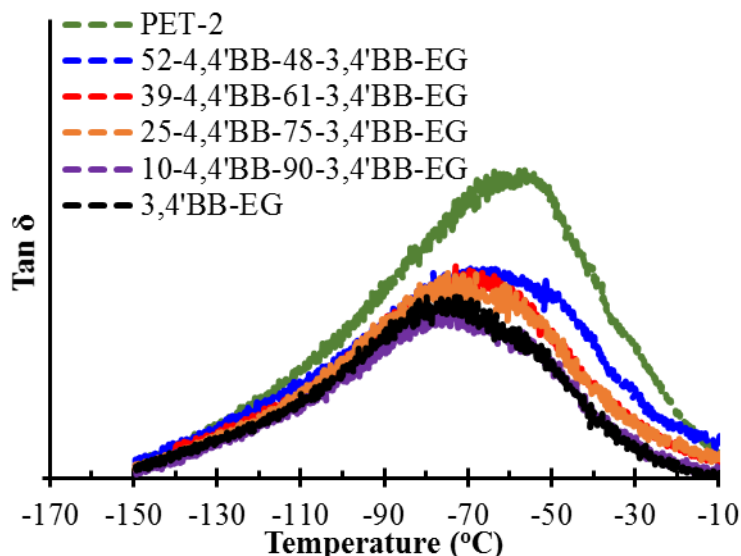


Figure 2.4. Low temperature relaxations probed using dynamic mechanical analysis (DMA). Beta relaxation temperature (T_β) determined as peak of the $\tan \delta$ curve. 1 Hz, an oscillatory amplitude of 15 μm , and a static force of 0.01 N was employed.

Melt spinning, molding, and extrusion comprise the majority of polymer processing strategies,^{4, 37, 45} which require an understanding of viscoelastic behavior. The semi-crystalline morphology of copolyesters with >50 mol % 4,4'BB prohibited in-depth rheological analysis. Melt rheology revealed the melt flow characteristics and elucidated the structural influence on chain dynamics in the melt. Well-defined time-temperature superposition (TTS) enabled analysis over a large viscoelastic window, including frequencies commonly used for processing. Shifting moduli and viscosity provided adequate overlap, allowing for determination of rheological phenomena. **Figure 2.5**

depicts a representative plot of both storage (G') and loss (G'') moduli master curves, and viscosity profiles exhibited similar behavior as shown in **Figure 2.6**. A reference temperature of 270 °C represented a comparable processing temperature that is typically employed for high performance semi-aromatic polyesters. This temperature permitted direct polyester comparison as well as an extended frequency range of up to 10^5 rad/s. A well-behaved frequency range from 1 to 10^5 rad/s revealed predictable viscoelastic behavior for various processing techniques employing high frequencies, such as thermoforming, extrusion, and blow/injection molding.⁴⁶ BB-based (co)polyesters revealed a single relaxation as viscosity restricted the lower temperature limit of the frequency sweeps, prohibiting analysis in the region approaching the onset of segmental motion. This relaxation is consistent with disentanglement and the characteristic relaxation time of reptation (τ_{rep}). τ_{rep} shifted to lower frequencies (longer times) with increasing polymer molecular weight as anticipated using relative zero-shear viscosity measurements (Figure S3). After this relaxation, long-range motions dominated, resulting in terminal flow. Slopes of 0.93-0.97 and 1.66-1.67 for G'' and G' , respectively, agreed well with the expected slopes of $G'' \sim 1.0$ and $G' \sim 2.0$ for typical polymer melts.⁴ Observation of τ_{rep} confirmed sufficient molecular weight for entanglements in BB (co)polyesters.

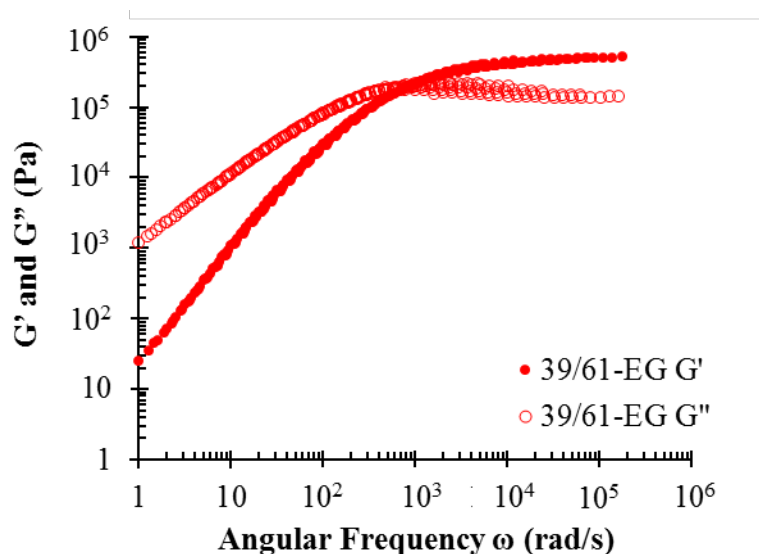


Figure 2.5. Representative storage and loss moduli master curves of 39-4,4'BB-61-3,4'BB-EG copolyesters at $T_r = 270$ °C.

Figure 2.6 shows the viscosity master curve, and all samples exhibited comparable zero-shear viscosities. SEC analysis was only possible for the soluble poly(ethylene 3,4'BB) homopolymer, however, the nearly equivalent zero-shear viscosities suggested comparable molecular weights across the compositions. Below τ_{rep} frequencies, the viscosity became frequency-independent and the polymer melt behaved as a Newtonian fluid. Higher oscillatory frequencies resulted in shear thinning as the experimental time scale exceeded the chain reptation relaxation time. The transition from Newtonian behavior to shear thinning broadened with increasing zero-shear viscosity, indicating higher dispersity (PDI),⁴⁶ or increased cyclic content. Experiments are ongoing to determine if the 3,4'BB monomer favors lower entanglement molecular weight, higher cyclic levels, and the impact of cyclic species on properties.

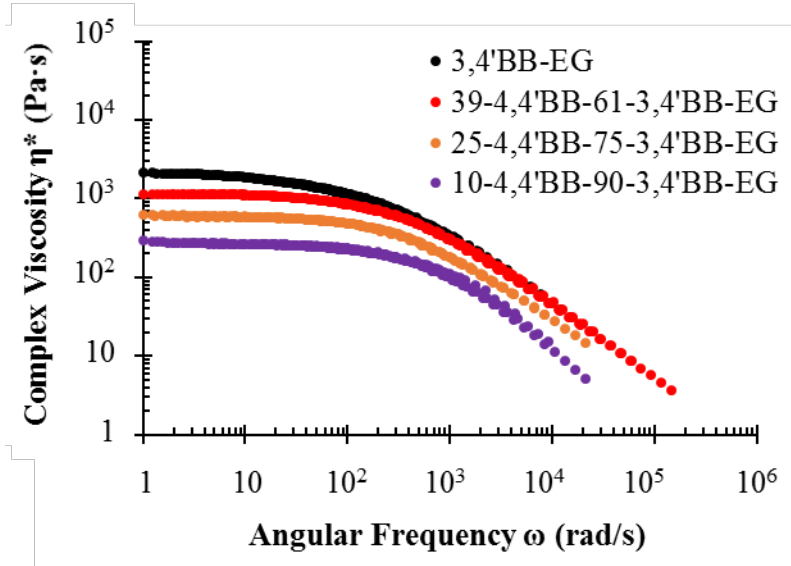


Figure 2.6. Complex viscosity master curves of x-4,4'BB-y-3,4'BB-EG (co)polyesters at $T_r = 270$ °C.

All BB-based (co)polyesters obeyed the Williams-Landel-Ferry (WLF) equation, employing shift factors, a_T , as a function of temperature, as seen in **Equation 2.1**.

$$\log(a_T) = \frac{-C_1(T-T_r)}{C_2+(T-T_r)} \quad \text{Eq. 2.1}$$

A representative WLF fit, shown in **Figure 2.7**, displayed typical behavior for a_T versus temperature. Typical processing temperatures for semi-aromatic polyesters dictated the reference temperature (T_r) and the C_1 and C_2 constants were determined by least-squares regression and were dependent on the T_r . Converting these constants to values at T_g , C_1^g and C_2^g , using **Equations 2.2** and **2.3**, enabled direct comparison to literature values.⁴⁷

$$C_1^g = \frac{C_1 C_2}{C_2 + (T_g - T_r)} \quad \text{Eq. 2.2}$$

$$C_2^g = C_2 + (T_g - T_r) \quad \text{Eq. 2.3}$$

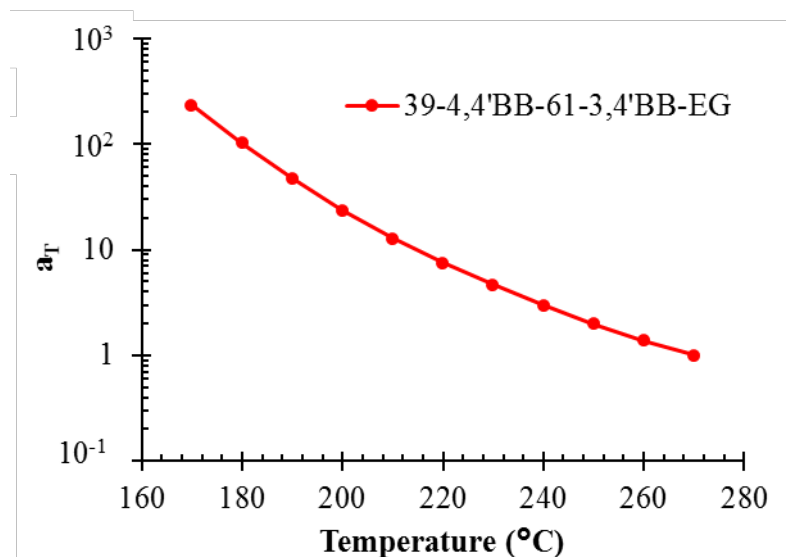


Figure 2.7. Representative WLF fitting of shift factors (a_T) *versus* temperature for 39-4,4'BB-61-3,4'BB-EG copolyesters. $T_r = 270$ °C.

As seen in **Table 2.2**, C_1^g and C_2^g values of BB-based (co)polyesters agreed well with reported values for neutral, nonassociating polymers.⁴⁷ Determining the fractional free volume at T_g (f_g), using **Equation 2.4**, and the thermal expansion coefficient of free volume (α_f), using **Equation 2.5**, provided insight into molecular arrangement and diffusion.⁴

$$f_g = \frac{B}{2.303 C_1^g} \quad \text{Eq. 2.4}$$

$$\alpha_f = \frac{B}{2.303 C_1^g C_2^g} \quad \text{Eq. 2.5}$$

No substantial change occurred for the f_g across the measured (co)polyester range. Since **Equation 2.4** determined the f_g at the polymer's T_g , normalizing the f_g to the T_g further confirmed the lack of regiochemistry influence on free volume. The kinked 3,4'BB monomer imparted minimal difference in chain packing relative to the linear, symmetric 4,4'BB, correlating well with previous specific free volume measurements of similar polymers.²⁴ Generally, higher static free volume, which is correlated to f_g , increases gas solubility in a polymer.²⁴

Table 2.2. WLF parameters, fractional free volumes, thermal expansion coefficients, and melt flow activation energies of x-4,4'BB-y-3,4'BB-EG (co)polyesters

x-4,4'BB- y-3,4'BB-EG	C_1	C_2	C_1^g	C_2^g	f_g	f_g/T_g	α_f	E_a
x:y (mol or wt. %)		K		K		$\times 10^{-3}$	$\times 10^{-4}$ K ⁻¹	kJ mol ⁻¹
0:100	2.95	231.7	10.42	65.7	0.0417	0.401	6.34	80.9
10:90	3.52	251.1	10.28	86.1	0.0422	0.402	4.91	81.8
25:75	2.82	223.5	10.25	61.5	0.0424	0.393	6.91	82.1
39:61	3.38	242.1	9.96	82.1	0.0436	0.396	5.31	83.1

Investigation of the terminal flow region using an Arrhenius relationship determined the melt flow activation energy (E_a), which refers to the energy barrier for hole formation and chain flow.⁴⁷ Increasing 4,4'BB levels resulted in a higher activation energy, as the symmetric, linear 4,4'BB segment reduced chain mobility. Furthermore, these energy barriers agreed well with similar compositions of rigid, naphthalate-based polyesters⁴⁸ and an increased activation energy relative to terephthalate-based polyesters.⁴⁹

PALS determined the (co)polyesters average molecular hole volume ($\langle v_h \rangle$). Investigation into average spherical hole size indicated insignificant change in free volume with increasing 4,4'BB content, as seen in **Figure 2.8**, corroborating the free volume findings from TTS rheological analysis.

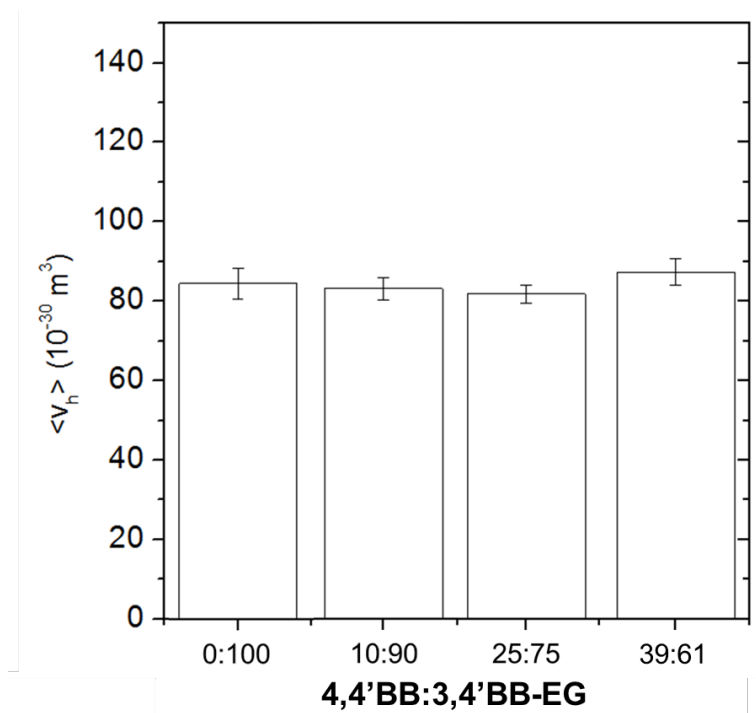


Figure 2.8. Average spherical hole size ($\langle v_h \rangle$) of x-4,4'BB-y-3,4'BB-EG (co)polyesters using positron annihilation lifetime spectroscopy (PALS)

Oxygen permeation analysis on amorphous films revealed the influence of regiochemistry on the oxygen transmission rate (OTR), depicted in **Figure 2.9**. The initial increase in OTR reflected non-steady-state diffusion.²⁴ Reaching a constant concentration gradient of a permeant across the testing film resulted in a steady-state flux (J_0). The permeant equilibrated and reached a plateau after ~ 300 min, allowing for averaging of the OTR value. Permeability calculated using **Equation 2.6**, with l the film thickness and Δp the pressure difference across the film, afforded insight into the relative permeability of the resulting (co)polyesters compared to PET.

$$P = J_0 l (\Delta p) \quad \text{Eq. 2.6}$$

The non-steady state diffusion slope increased as 4,4'BB levels increased. The increase in non-steady state diffusion slope correlates with the increased β -relaxations intensity for higher 4,4'BB level (co)polyesters. J_0 also increased with increased 4,4'BB levels. Since

the static free volume (average free volume) of the polyesters changed minimally as observed by TTS and PALS analysis, the change in J_0 most likely did not arise from a change in O_2 solubility. Instead, ring-flips likely impart an increase in dynamic free volume, which correlated with the β -relaxations and increased non-steady state diffusion slope.²⁰ As seen in **Table 2.3**, the permeability systematically increased with increased 4,4'BB levels. Relative to amorphous PET, poly(ethylene 3,4'BB) possessed a 25% lower O_2 permeability, agreeing with previous literature.²⁴ BB-based (co)polyesters also afford a significant decrease in O_2 permeability compared to cyclobutanediol-based polyesters with similar thermal properties.⁹ Future studies will probe the influence of biaxial orientation on gas permeability as a function of composition.

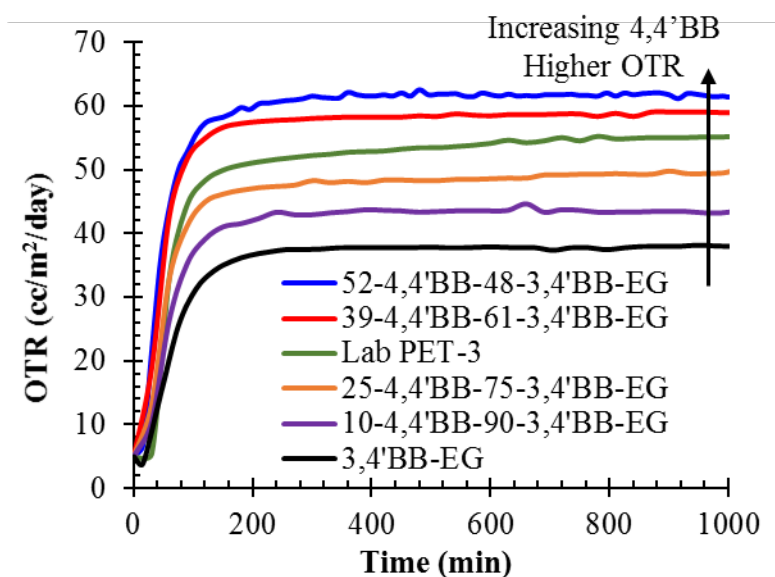


Figure 2.9. Oxygen transmission rate (OTR) analysis using an oxygen permeation analyzer. Samples were allowed to reach a steady-state equilibrium before calculating permeability.

Table 2.3. Summary of oxygen permeability data of x-4,4'BB-y-3,4'BB-EG amorphous (co)polyesters

x-4,4'BB-y-3,4'BB-EG (mol or wt. %)	Permeability (cc·cm/m ² /atm/day)	Permeability Relative to PET*	Barrer (10 ⁻¹⁰ cc·cm/cm ² /s/cmHg)
0:100	0.346 ± 0.030	0.75	0.053 ± 0.005
10:90	0.365 ± 0.011	0.79	0.056 ± 0.002
25:75	0.413 ± 0.014	0.90	0.063 ± 0.002
39:61	0.484 ± 0.008	1.03	0.074 ± 0.001
52:48	0.586	1.27	0.089
PET*	0.461 ± 0.001	1.00	0.070 ± 0.001
Poly(CHDM ₆₄ - CBDO ₃₆ -T) [#]	4.920 ± 0.150 ⁹	10.67	0.749 ± 0.023

* PET synthesized using same reaction conditions noted for BB-based (co)polyesters and quenched amorphous

Stress-strain curves for tensile analysis enabled Young's modulus, tensile strength, and elongation to break measurements. Summarized in **Table 2.4**, the Young's modulus and tensile strength decreased with higher levels of 4,4'BB. Elongation at break analysis revealed no significant variation across the compositional range studied. A large necking range (~70-80 %; Figure S5) suggested the relatively higher free volume of BB-based (co)polyesters (~2.5% average “universal” value)⁵⁰ impacted the cold drawing behavior. BB-based (co)polyesters exhibited mechanical properties similar to commercial BPA-PC and superior to cyclobutanediol-based polyesters. Mechanical structure-property relationships require further testing, which will probe the regiochemistry influence on modulus, strength, and elongation behavior.

Table 2.4. Summary of tensile mechanical testing data of x-4,4'BB-y-3,4'BB-EG amorphous (co)polyesters

x-4,4'BB-y-3,4'BB-EG (mol or wt. %)	Yield Strength (MPa)	Young's Modulus (GPa)	Elongation to Break (%)
0:100	74.4 ± 0.25	2.69 ± 0.28	163 ± 39
39:61	62.3 ± 0.66	2.36 ± 0.16	142 ± 35
52:48	60.1 ± 0.25	2.34 ± 0.03	109 ± 25
Poly(CHDM ₆₄ - CBDO ₃₆ -T)*	44.8 ± 0.20	1.45 ± 0.21	70.2 ± 9.8

* Commercial copolyester reprocessed using same injection molding procedures as detailed earlier using ground commercial container. NMR spectroscopy (Figure S6) confirmed polymer composition.

2.5 Conclusions

Melt polycondensation of isomeric BB-based dimethyl esters with ethylene glycol afforded novel melt-processable, transparent (co)polyesters with superior T_g s and barrier properties compared to PET. Thermal analysis confirmed stability above 350 °C and T_g s ranging from 104-117 °C. All BB-based (co)polyesters exhibited β -relaxations, mainly due to aromatic ring-flipping. TTS of melt rheology characterized a broad range of frequencies, resulting in a distinct relaxation related to entanglements and τ_{rep} . TTS determined flow E_a increased with higher amounts of the linear, symmetric 4,4'BB monomer, while f_g exhibited no significant change across the compositional range. PALS corroborated the free volume findings through average hole size measurements. Increasing 4,4'BB levels increased gas diffusivity through increase ring-flipping, while negligibly affecting the gas solubility, leading to an overall increase in permeability. Tensile testing confirmed Young's modulus and tensile strength values comparable to BPA-PC. With thermal and mechanical properties comparable to BPA-PC and superior barrier properties compared to PET, BB-based (co)polyesters offer a competitive platform for food packaging, consumer, medical device, and coating applications. Future studies will focus

on enhancing the T_g for high temperature applications, elucidating the bulk mechanical properties, and improving barrier performance.

Supporting Information.

^1H NMR spectra, DSC thermograms, TTS master curves of G' and G'' , WLF shift factor fittings, and tensile stress vs. strain curves. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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2.7 References

1. Lange, J.; Wyser, Y. Recent innovations in barrier technologies for plastic packaging - a review. *Packag Technol Sci* **2003**, *16* (4), 149-158.
2. Odian, G. *Principles of Polymerization*. 4th ed.; Wiley-Interscience: 2004.
3. Kunz, N.; Camm, E. J.; Somm, E.; Lodygensky, G.; Darbre, S.; Aubert, M. L.; Huppi, P. S.; Sizonenko, S. V.; Gruetter, R. Developmental and metabolic brain alterations in rats exposed to bisphenol A during gestation and lactation. *International Journal of Developmental Neuroscience* **2011**, *29* (1), 37-43.
4. Dennis, J. M.; Enokida, J. S.; Long, T. E. Synthesis and Characterization of Decahydronaphthalene-Containing Polyesters. *Macromolecules* **2015**, *48* (24), 8733-8737.
5. Nelson, A. M.; Long, T. E. A perspective on emerging polymer technologies for bisphenol-A replacement. *Polym. Int.* **2012**, *61* (10), 1485-1491.
6. Crawford, E. M.; Pecorini, T. J.; McWilliams, D. S.; Porter, D. S.; Connell, G. W. Polyester Compositions Containing Cyclobutanediol Having a Certain Combination of Inherent Viscosity and Moderate Glass Transition Temperature and Articles Made Therefrom. US2006042292 A, 2007.
7. Scott, C. E.; Morris, J. C.; Bradley, J. R. Clear polycarbonate and polyester blends. US6005059 A, 1997.
8. Scott, C. E.; Morris, J. C.; Bradley, J. R. Clear blends of polycarbonates and polyesters. US6043322 A, 1997.
9. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E. Influence of Cyclobutane Segments in Cycloaliphatic, Decahydronaphthalene-containing Copolyesters. *High Perform. Polym.* **2017**, *In Press*.
10. Dennis, J. M.; Fahs, G. B.; Moon, N. G.; Mondschein, R. J.; Moore, R. B.; Wilkes, G. L.; Long, T. E. Synthesis of Polysulfone-Containing Poly(butylene terephthalate) Segmented Block Copolymers: Influence of Segment Length on Thermomechanical Performance. *Macromolecules* **2017**.
11. Crawford, E. D.; McWilliams, D. S.; Porter, D. S.; Connell, G. W. Film(s) and/or sheet(s) comprising polyester compositions which comprise cyclobutanediol and have a certain combination of inherent viscosity and moderate glass transition temperature. US7855267 B2, 2010.
12. Beall, G. W.; Powell, C. E.; Hancock, J.; Kindinger, M.; McKenzie, H. R.; Bray, A. V.; Booth, C. J. Physical properties of CBDO based co-polyterephthalate nanocomposites. *Appl Clay Sci* **2007**, *37* (3-4), 295-306.
13. Booth, C. J.; Kindinger, M.; McKenzie, H. R.; Hancock, J.; Bray, A. V.; Beall, G. W. Copolyterephthalates containing tetramethylcyclobutane with impact and ballistic properties greater than bisphenol A polycarbonate. *Polymer* **2006**, *47* (18), 6398-6405.
14. Kelsey, D. R.; Scardino, B. M.; Grebowicz, J. S.; Chuah, H. H. High impact, amorphous terephthalate copolyesters of rigid 2,2,4,4-tetramethyl-1,3-cyclobutanediol with flexible diols. *Macromolecules* **2000**, *33* (16), 5810-5818.
15. Scott, C. E.; Stewart, M. E.; Wilmoth, D. S.; Morris, J. C.; Bradley, J. R. Polycarbonate and polyester blends. US5942585 A, 1997.

16. Barton, B. F.; Shackelford, D. B. Process for the Preparation of Copolyesters Based on 2,2,4,4-Tetramethyl-1,3-Cyclobutanediol and 1,4-Cyclohexanedimethanol. US8586701 B2, 2007.
17. Crawford, E. D.; Porter, D. S.; Connell, G. W. Polyester compositions which comprise cyclobutanediol having certain cis/trans ratios. EP20090012051, 2011.
18. Mang, M. N.; Brewbaker, J. L. Thermoplastic Polyesters Containing Biphenylene Linkages. US5138022A, 1992.
19. Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon Dioxide Sorption and Transport in Amorphous Poly(ethylene furanoate). *Macromolecules* **2015**, *48* (7), 2184-2193.
20. Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J. Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate). *Macromolecules* **2014**, *47* (4), 1383-1391.
21. Knoop, R. J. I.; Vogelzang, W.; van Haveren, J.; van Es, D. S. High molecular weight poly(ethylene-2,5-furanoate); critical aspects in synthesis and mechanical property determination. *J Polym Sci Pol Chem* **2013**, *51* (19), 4191-4199.
22. Schiraldi, D. A.; Lee, J. J.; Gould, S. A. C.; Occelli, M. L. Mechanical properties and atomic force microscopic cross sectional analysis of injection molded poly(ethylene terephthalate-co-4,4'-bibenzoate). *Journal of Industrial and Engineering Chemistry* **2001**, *7* (2), 67-71.
23. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E. Comparison of statistical and blocky copolymers of ethylene terephthalate and ethylene 4,4'-bibenzoate based on thermal behavior and oxygen transport properties. *J Polym Sci Pol Phys* **2003**, *41* (3), 289-307.
24. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E. Oxygen-barrier properties of copolymers based on ethylene terephthalate. *J Polym Sci Pol Phys* **2001**, *39* (16), 1889-1899.
25. Asrar, J., High performance polyesters based on 4,4'-biphenyl dicarboxylic acid. In *Specialty polyesters*, Shotland Business Research, Skillman, NJ: 1995.
26. Tokita, M.; Watanabe, J. Several Interesting Fields Exploited through Understanding of Polymeric Effects on Liquid Crystals of Main-Chain Polyesters. *Polymer Journal* **2006**, *38* (7), 611-638.
27. Lin, Q.; Pasatta, J.; Long, T. E. Synthesis and characterization of chiral liquid-crystalline polyesters containing sugar-based diols via melt polymerization. *J Polym Sci Pol Chem* **2003**, *41* (16), 2512-2520.
28. Krigbaum, W. R.; Asrar, J.; Toriumi, H.; Ciferri, A.; Preston, J. Aromatic Polyesters Forming Thermotropic Smectic Mesophases. *J Polym Sci Pol Lett* **1982**, *20* (2), 109-115.
29. Clary, R. S.; Lee, C. D.; Monroe Iv, W. G.; Vaughn, D. A.; Ragheb, R. T.; Erter Iii, J. W.; Brown, D. M.; Schiraldi, D. A. A Green, One-Pot Route to the Biphenyldicarboxylic Acids: Useful Intermediates in Polymer Synthesis. *International Journal of Organic Chemistry* **2013**, *03* (02), 143-147.
30. Li, X. D.; Brisse, F. X-Ray-Diffraction Study of the Structure of Poly(Ethylene 4,4'-Biphenyldicarboxylate). *Macromolecules* **1994**, *27* (8), 2276-2282.

31. Kang, H. Y.; Lin, Q.; Armentrout, R. S.; Long, T. E. Synthesis and characterization of telechelic poly(ethylene terephthalate) sodiosulfonate ionomers. *Macromolecules* **2002**, *35* (23), 8738-8744.
32. Kirkegaard, P.; Eldrup, M.; Mogensen, O. E.; Pedersen, N. J. Program System for Analyzing Positron Lifetime Spectra and Angular-Correlation Curves. *Comput Phys Commun* **1981**, *23* (3), 307-335.
33. Tao, S. J. Positronium Annihilation in Molecular Substances. *J Chem Phys* **1972**, *56* (11), 5499-&.
34. Eldrup, M.; Lightbody, D.; Sherwood, J. N. The Temperature-Dependence of Positron Lifetimes in Solid Pivalic Acid. *Chem Phys* **1981**, *63* (1-2), 51-58.
35. Zhang, M. S.; Zhang, M. Q.; Moore, R. B.; Long, T. E. Influence of charge placement on the thermal and morphological properties of sulfonated segmented copolyesters. *Polymer* **2013**, *54* (14), 3521-3528.
36. Berkowitz, S. Viscosity-Molecular Weight Relationships for Poly(ethylene Terephthalate) in Hexafluoroisopropanol-Pentafluorophenol Using SEC-LALLS. *J Appl Polym Sci* **1984**, *29*, 4353-4361.
37. Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*. John Wiley & Sons, Ltd: 2003.
38. Ki, H. C.; Park, O. O. Synthesis, characterization and biodegradability of the biodegradable aliphatic-aromatic random copolyesters. *Polymer* **2001**, *42*, 1849-1861.
39. Maxwell, A. S.; Ward, I. M.; Laupretre, F.; Monnerie, L. Secondary relaxation processes in polyethylene terephthalate-additive blends: 1. N.m.r. investigation. *Polymer* **1998**, *39* (26), 6835-6849.
40. Maxwell, A. S.; Monnerie, L.; Ward, I. M. Secondary relaxation processes in polyethylene terephthalate-additive blends: 2. Dynamic mechanical and dielectric investigations. *Polymer* **1998**, *39* (26), 6851-6859.
41. Light, R. R.; Seymour, R. W. Effect of Sub-Tg Relaxations on the Gas-Transport Properties of Polyesters. *Polym Eng Sci* **1982**, *22* (14), 857-864.
42. Sanders, D. F.; Smith, Z. P.; Ribeiro, C. P.; Guo, R. L.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. Gas permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). *Journal of Membrane Science* **2012**, *409*, 232-241.
43. Boyer, R. F. Dependence of Mechanical Properties on Molecular Motion in Polymers. *Polym Eng Sci* **1968**, *8*, 161-185.
44. Wada, Y.; Tetsuo, K. Relation Between Impact Strength and Dynamic Mechanical Properties of Plastics. *J Appl Polym Sci* **1967**, *11*, 1661-1665.
45. Pang, K. K., R.; Tonelli, A. Review of conventional and novel polymerization processes for polyesters. *Progress in Polymer Science* **2006**, *31*, 1009-1037.
46. Franck, A. *Understanding Rheology of Thermoplastic Polymers*; TA Instruments.
47. Ferry, J. D. *Viscoelastic Properties of Polymers*. John Wiley & Sons: New York: 1980.
48. Pinaud, F. Effect of Molecular Parameters on the Viscoelastic Properties of Polymer Melts. *Journal of Non-Newtonian Fluid Mechanics* **1987**, *23*, 137-149.
49. Kim, B. K.; Jeong, H. M.; Lee, Y. H. Melt Rheology of Poly(ethylene Terephthalate), Polyarylate, and Their Blends. *J Appl Polym Sci* **1990**, *40*, 1805-1818.

50. Dannhauser, W.; Child, W. C.; Ferry, J. D. Dynamic Mechanical Properties of Poly-n-octyl methacrylate. *Journal of Colloid Science* **1958**, *13*, 103-113.

2.8 Supporting Information

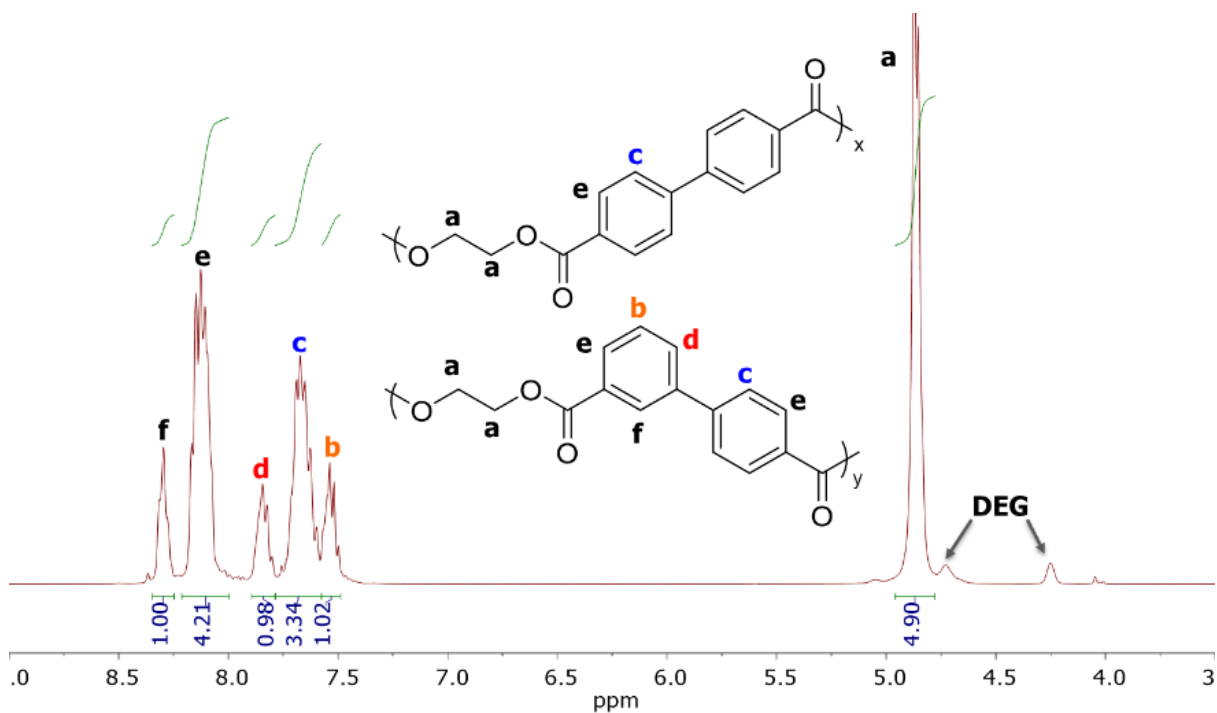


Figure S2.1. Representative ^1H NMR spectra of 25-4,4'BB-75-3,4'BB-EG with resonances assigned. Proton integrations of B, C, and D were used to determine mol % of each repeat unit. DEG content is ~4 mol %.

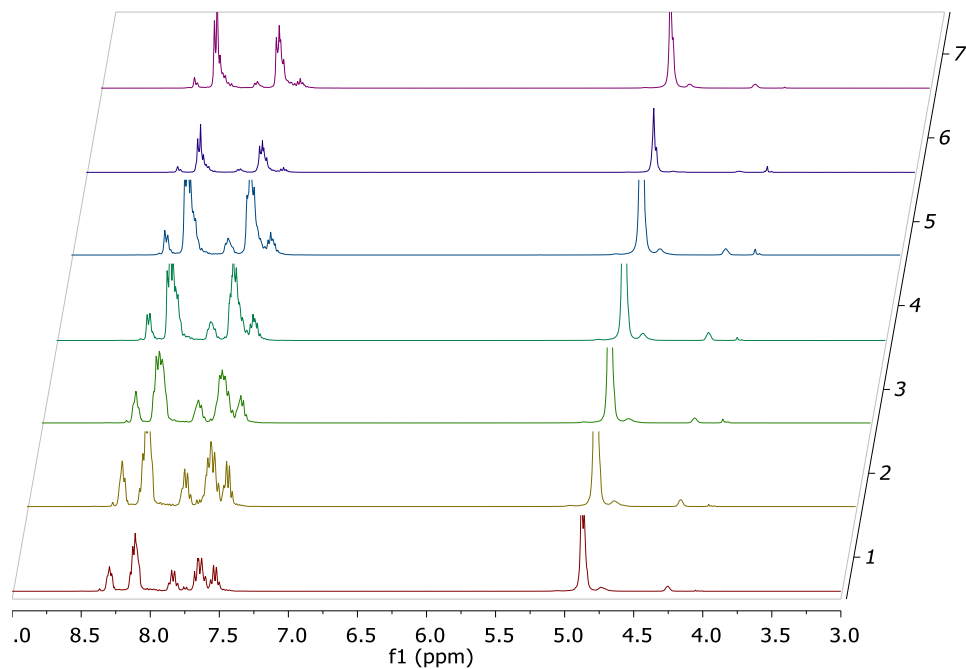


Figure S2.2. Stacked ^1H NMR spectra of 4,4'BB:3,4'BB-EG (co)polyesters. Samples increase with 4,4'BB content from 1-7.

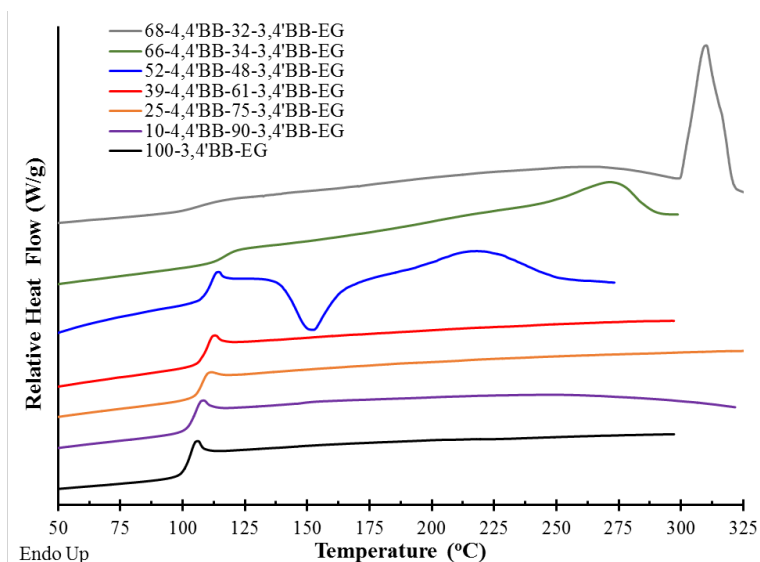


Figure S2.3. Representative DSC traces of x-4,4'BB-y-3,4'BB-EG (co)polyesters. Melting endotherms only observed above 50 % 4,4'BB incorporation. Second heat reported with a heat rate and cool rate of 10 °C/min.

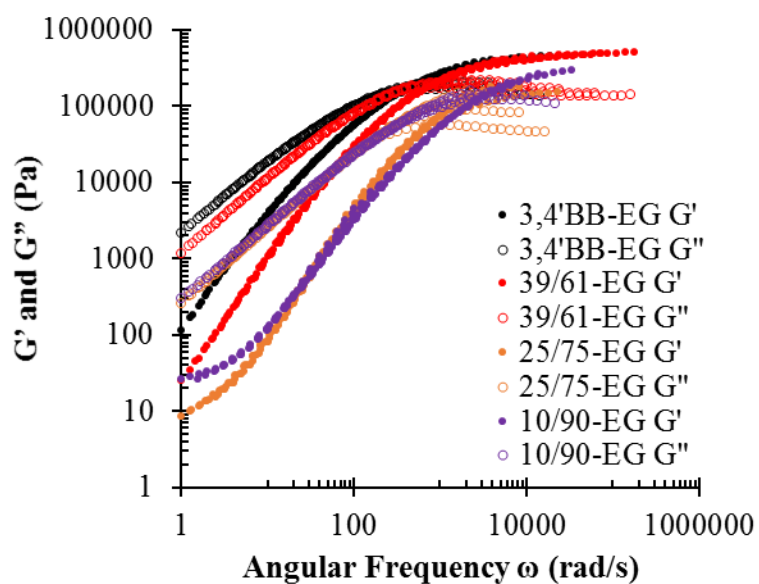


Figure S2.4. Storage and loss moduli master curves of x-4,4'BB-y-3,4'BB-EG (x/y-EG in legend) (co)polyesters at $T_r = 270$ °C.

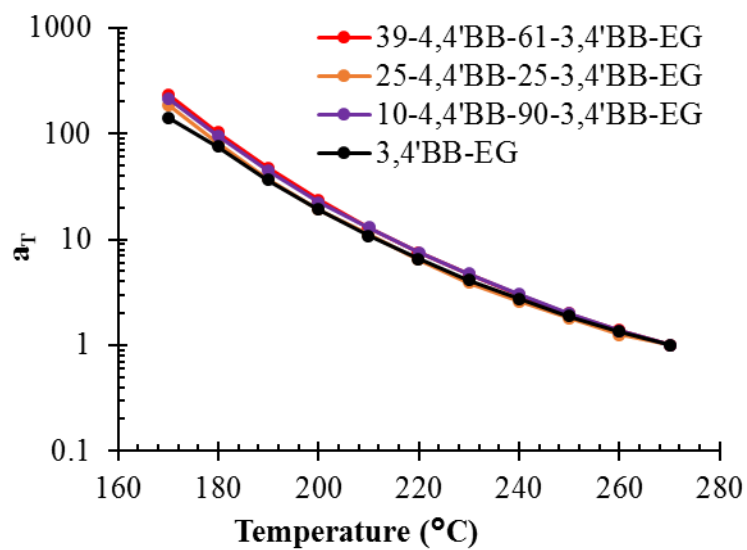


Figure S2.5. WLF fitting of shift factors *versus* temperature of x-4,4'BB-y-3,4'BB-EG. $T_r = 270$ °C.

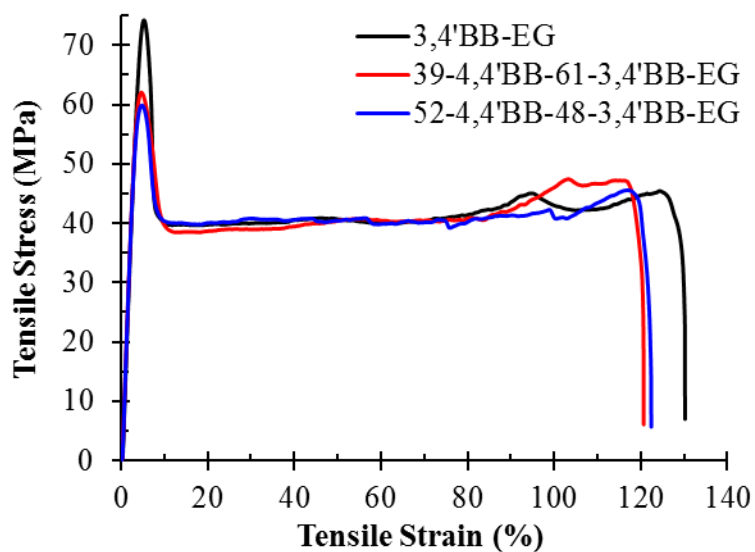
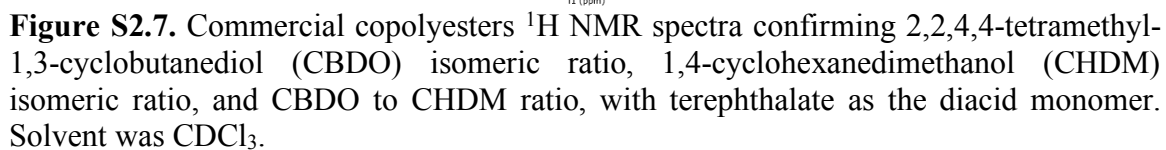


Figure S2.6. Stress *versus* strain curves for x-4,4'BB-y-3,4'BB-EG (co)polyesters.



Chapter 3: Influence of Bibenzoate Regioisomers on Cyclohexanedimethanol-based (Co)polyester Structure-Property Relationships

(Manuscript in preparation for publication)

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Keywords: Polyester, BPA replacement, cyclohexanedimethanol, Bibenzoate, Regioisomer

3.1 Abstract

Melt polymerization enabled the synthesis of semi-aromatic (co)polyesters containing 1,4-cyclohexanedimethanol (CHDM), 4,4'-bibenzoate (4,4'BB), and 3,4'-bibenzoate (3,4'BB). Proton nuclear magnetic resonance (¹H NMR) spectroscopy confirmed monomer incorporation, and size exclusion chromatography revealed molecular weights and polydispersity indices (PDIs) consistent with high conversion melt phase synthesized polyesters. All bibenzoate-based polyesters exhibited a high onset of 5% wt loss according to thermogravimetric analysis (> 350 °C), and differential scanning calorimetry provided compositionally dependent glass transition temperatures (T_g s) approaching 135 °C and crystalline melting temperatures where applicable. Dynamic mechanical analysis (DMA) probed sub- T_g β -relaxations with minimal changes in

intensity, suggesting the cyclohexyl ring relaxations dominated the low temperature energy absorption for all (co)polyester compositions. Time-temperature superposition (TTS) analysis from melt rheology revealed increasing characteristic relaxation times with increasing 4,4'BB content, which was attributed to the linear 4,4'BB stiffening the polymer chain. Increased kinked 3,4'BB content promoted chain entanglement, resulting in a lower entanglement molecular weight and a higher number of entanglements per chain (N/N_e). Similarly, increases in 3,4'BB content improved tensile yield strength and Young's modulus due to a higher polymer density and potentially due to an increase in entanglement density. Lastly, scanning electron microscopy (SEM) suggested mostly brittle failure after necking and strain hardening in tensile specimens. As a result, structure-property relationships afforded insight into regioisomer impacts on thermal, rheological, and mechanical performance for bibenzoate-based (co)polyester regioisomers.

3.2 Introduction

Bisphenol-A (BPA) containing polymers, such as BPA-polycarbonate (BPA-PC), offer excellent thermal, mechanical, impact, and optical properties required for many thermoplastic and thermoset applications.¹⁻⁵ However, despite the advantages of BPA-containing polymers, potential hydrolytic degradation of BPA-PC releases BPA, a known endocrine disruptor.³ Thus, the need for new polymeric platforms that eliminate BPA incorporation continues.^{3, 6-9} Food packaging containers and medical devices/equipment require high glass transition temperatures (T_g s), high moduli, and high gas barrier properties. Polyesters incorporating cyclobutanediol^{3, 6, 8, 10-17} and other cycloaliphatics^{6-7, 17} offer BPA-free compositions with properties that are desirable for various thermoplastic and thermoset applications. Although these polyesters are suitable in select applications,

reduced mechanical properties, melt stability concerns, high cost, low barrier properties, and decreased T_g s influence the competitiveness of this polymer platform for emerging thermoplastic applications.

Bibenzoate-based (BB) semi-aromatic polyesters possessing mechanical properties similar to BPA-PC, T_g s greater than 100 °C, oxygen barrier properties greater than poly(ethylene terephthalate) (PET), and potentially low manufacturing cost offer a novel polymer platform for improved thermoplastics.¹⁸⁻²⁶ Enhanced mechanical, gas barrier, and thermal properties offer advantages in coating, food packaging, and high temperature electronic applications. These polyesters exhibit T_g s approaching 120 °C, whereas BPA-PC T_g is ~145 °C, enabling BPA replacement in many high temperature applications. Commonly, more rigid, bulky comonomers increase T_g , such as cyclohexanedimethanol (CHDM)^{7, 17} or cyclobutanediols (CBDO),^{6, 17, 27} but high concentrations also significantly reduce mechanical properties such as tensile strength and impact resistance.^{6, 13} Raising the T_g of BB-based (co)polyesters will expand the potential applications for this family of engineering thermoplastics.

Our recent reports confirmed the influence of the 3,4'-substituted bibenzoate regioisomer on the oxygen barrier properties and tensile performance of polyesters.^{26, 28} Similarly, as seen in earlier literature, the substitution and molar ratio of regioisomers in the polymer backbone alter a variety of properties. The *meta*-regioisomer of PET, poly(ethylene isophthalate) (PEI), exhibits enhanced barrier properties but typically lowers % crystallinity and mechanical properties.^{21, 23} Similarly, altering the *meta*- versus *para*-substitution of CHDM diols in decahydronaphthalene-containing polyesters influenced low temperature relaxations, thermal properties, and viscoelastic behavior.⁷

This report describes the synthesis and characterization of bibenzoate-based (co)polyesters with varying BB isomer content and CHDM levels. Melt transesterification and subsequent polycondensation produced transparent, optically clear, ductile (co)polyesters, and physical characterization elucidated structure-property relationships. CHDM incorporation increased BB-based polyester T_g s up to 135 °C while maintaining mechanical properties necessary for thermoplastic applications. Rheological analysis suggested potentially improved energy-absorbing impact properties and predictable melt processing behavior. In-depth rheological characterization further revealed the regioisomer influence on characteristic relaxation behavior, entanglement, and chain stiffness. An increase in tensile yield strength was potentially impacted by the increase in the number of entanglements per chain (N/N_e) as determined using linear viscoelasticity. This suggested that the improvement in tensile properties could be related to polymer chain entanglements as well as chain rigidity and density.

3.3 Experimental

3.3.1 Materials. Dimethyl 3,4'-biphenyldicarboxylate (3,4'BB, melting point (MP) = 97-99 °C)²⁵ and dimethyl 4,4'-biphenyldicarboxylate (4,4'BB, MP = 210 °C)²⁹ were supplied by ExxonMobil and used as received. 1,4-cyclohexanedimethanol (CHDM) (Sigma-Aldrich, mixture of cis and trans, 99%) was used as received. Titanium tetra(isopropoxide) (99%) was purchased from Sigma-Aldrich and used as a 0.01 g/mL solution in anhydrous 1-butanol.³⁰ All solvents were obtained from Spectrum Chemical and used as received. All samples were dried overnight at 60 °C in vacuum prior to processing and analysis.

3.3.2 Analytical Methods. ¹H NMR spectroscopy at 23 °C on a Varian Unity 400 at 399.87 MHz utilized deuterated trifluoroacetic acid (TFA-d) as a solvent. A Waters size exclusion

chromatograph (SEC) with an auto sampler, three 5 μm PLgel Mixed-C columns, and a Waters 2410 refractive index (RI) detector operating at 880 nm with a flow rate of 1 mL min^{-1} at 35 $^{\circ}\text{C}$ in chloroform (CHCl_3) afforded characterization of molecular weight relative to polystyrene standards. Dynamic light scattering (DLS) of polymer solutions in CHCl_3 at 35 $^{\circ}\text{C}$ confirmed the lack of solution aggregation behavior prior to SEC analysis. Differential scanning calorimetry (DSC) probed thermal transitions using a TA instruments Q1000 DSC, calibrated using indium (MP = 156.60 $^{\circ}\text{C}$), and utilizing a N_2 gas flow of 50 mL/min with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and a cooling rate of 10 $^{\circ}\text{C}/\text{min}$. Glass transition temperatures (T_g s) were measured at the midpoint of the transition in the second heating cycle. Thermogravimetric analysis (TGA) employed a TA Instruments Q50 from 25 to 600 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Dynamic mechanical analysis (DMA) utilizing a TA Instruments Q800 Dynamic Mechanical Analyzer in oscillatory tension mode with a 1 Hz frequency, 15 μm oscillatory amplitude, 0.01 N static force, and 3 $^{\circ}\text{C}/\text{min}$ heating rate determined modulus *versus* temperature characterization. Compression molding using a PHI Q-203H manual hydraulic press and aluminum shims for film thickness control produced optically clear, ductile, and free-standing films. Tensile property measurements and coinciding analysis was guided using ASTM D638. A D-638-V die (Pioneer-Dietecs) was utilized with compression molded thin films to prepare dogbone specimens. An Instron model No. 4411 using a 1kN load cell applied a 10 mm/min crosshead motion rate in ambient conditions. An average of 6-8 runs per composition was tested. A NEO Scope JCM 5000 scanning electron microscope (SEM) at 10 kV and under high vacuum imaged fracture surfaces of tensile dog-bones utilized in tensile mechanical testing. No sputter-coating was required.

Rheological analysis performed on a TA Instruments Discovery Hybrid Rheometer (DHR)-2 utilized an 8 mm diameter disposable aluminum parallel-plate geometry under N₂ atmosphere. Oscillatory strain sweeps from 0.01-10% at a frequency of 1 Hz determined the linear viscoelastic region. Using a frequency range of 1-100 rad/s and constant 1.25% strain amplitude, frequency sweeps in 10 °C increments from 130 °C to 270 °C determined storage/loss moduli and viscosity as functions of frequency. TRIOS software from TA Instruments generated master curves by horizontally shifting resulting data and characterized characteristic relaxation times. Melt flow property analysis involved fitting master curve shift factors to the Williams-Landel-Ferry (WLF) equation.

Positron annihilation lifetime spectroscopy (PALS) probed average molecular hole volume, $\langle V_h \rangle$. Approximately 10⁶ incidences of data for each sample were collected at 45 % relative humidity and 23 °C over one hour utilizing an Ortec Positron Lifetime System (Advanced Measurement Technology Oak Ridge, TN), which uses a fast-fast coincidence scheme. Compression-molded thin films, stacked approximately 1 mm thick had a 30 µCi ²²Na positron source sandwiched between two pieces. The sample-source assembly was placed between two photomultiplier tubes (PMT) each equipped with BaF₂ gamma radiation sensitive scintillators and tuned so one PMT differentiates and converts into a signal the absorbed gamma quanta associated with a positron emission, and the second PMT correlates with its annihilation. Compiling the coincidences, a multichannel analyzer determined each positron time difference between ‘birth’ and ‘death’ events (the lifetime) with a 290 ps time resolution. Assuming three components, PATFIT-88 software analyzed the annihilation spectra.³¹ The characteristic lifetime, τ_3 , of the orthopositronium (o-Ps) annihilation component acquired from PALS spectra was first related to the average

spherical hole radius, $\langle R_h \rangle$, via the Tao-Eldrup equation and then to the average hole volume $\langle V_h \rangle = 4\pi(\langle R_h \rangle)^3/3$.³²⁻³³

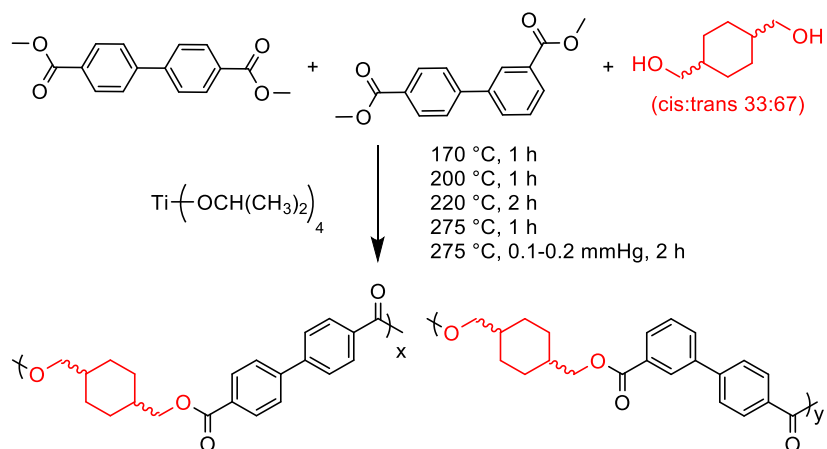
3.3.3 Synthesis of poly(4,4'BB-co-3,4'BB CHDM). The synthesis of 50:50 4,4'BB:3,4'BB with CHDM follows as an example for all (co)polyesters. Reactions were performed in dry 100-mL round-bottomed flasks utilizing an overhead stirrer, nitrogen inlet, and distillation apparatus. CHDM (9.05 g, 1.1 mol equiv), 4,4'BB (7.72 g, 0.50 mol equiv), 3,4'BB (7.72 g, 0.50 mol equiv), and titanium tetra(isopropoxide) (0.1 mL; 40 ppm; 0.01 g/mL in anhydrous 1-butanol) catalyst were introduced to a flask, and subsequent degassing with vacuum and purging with N₂ gas (3x) produced oxygen-free reaction conditions. The reaction progressed at 170 °C for 1 h, 200 °C for 1 h, 220 °C for 2 h, and 275 °C for 1 h at a constant stirring rate of 75 rpm and N₂ gas purge. Methanol condensate collection in a dry-ice cooled round-bottomed flask promoted reaction progress. A reduced pressure of 0.1-0.2 mmHg was achieved utilizing a vacuum, promoting the removal of excess diol, and the reaction continued stirring at 275 °C for an additional 1 h. Product was retrieved by breaking the round-bottomed flask and collecting the solid polymer off of the stir rod. All copolyesters were used without further purification.

3.3.4 Compression molding (co)polyesters. (Co)polyester samples were dried at 75 °C overnight before use due to their similar hydrophilicity compared to PET (Table S2). Compression molding utilized two aluminum plates layered with Kapton® films to produce transparent and ductile films. 16 mil thick steel shims controlled film thickness. Rexco Partall® Power Glossy Liquid mold release agent coated on the Kapton® films ensured easy removal post-processing. Samples were heated (~3 min for amorphous; ~5 min for semi-crystalline) at 275 °C before placing a stainless steel plate on top. The plates

were centered and the press was closed to afford no visible light between plates. After 2 min of heating at 275 °C, four press-release-press cycles with 5 tons of force for the first two cycles and 10 tons of force for the last two cycles completed the film pressing procedure. Immediate film and plate submersion in an ice bath quench cooled the films, in an effort to prevent crystallization. The films were dried in a vacuum oven at 75 °C overnight before characterization. Compositions containing > 60 mol % 4,4'-BB, including the 100-4,4'-BB-CHDM homopolyester, were too brittle to produce free-standing, ductile films for DMA and tensile analysis.

3.4 Results and Discussion

Polymerization of aromatic BB-based diesters and CHDM afforded a series of BB-based semi-aromatic (co)polyesters according to earlier procedures.^{6-7, 26, 28} Briefly, melt transesterification utilizing titanium tetra(isopropoxide) as a catalyst and polycondensation under reduced pressure produced (co)polyesters with varying 4,4'BB and 3,4'BB isomer incorporation. As seen in **Scheme 3.1**, transesterification began with stirring at 170 °C under N₂ and methanol condensation confirmed reaction progress. Once visible methanol production ceased, heating to 200 °C for 1 h, 220 °C for 2 h, and 275 °C for 1 h completed transesterification and enabled polycondensation, with partial removal of excess CHDM. Applying vacuum to attain at least 0.1-0.2 mmHg pressure in the reaction flask facilitated CHDM removal and produced polyesters with visibly high melt viscosity, whereby the polyesters wrapped the metal mechanical stirring rod. CHDM removal stopped after 1 h at reduced pressure, suggesting polycondensation afforded high molecular weight polyesters. Colorless, optically clear polyesters resulted for all compositions up to 56 mol % 4,4'BB.



Scheme 3.1. Synthesis of poly(X-4,4'BB-Y-3,4'BB-CHDM) random copolyesters

SEC confirmed relative molecular weights of all (co)polyesters up to 47 mol % 4,4'BB (Table S3.1). Compositions containing greater than 47 mol % 4,4'BB produced heterogeneous suspensions, which were unsuitable for SEC characterization. Furthermore, any compositions containing greater than 60 mol % 4,4'-BB, including the 100-4,4'-BB-CHDM homopolyester were too brittle to fully characterize. All polyesters attained high molecular weight as well as molecular weight distributions (PDI) near 2.00, as expected for strictly linear polycondensation. As seen in **Figure 2.1**, SEC chromatograms revealed uniform and monomodal peaks, suggesting linear polyesters with minimal cyclic formation. The absence of branching, as evident from a lack of a high molecular weight tail in the chromatogram, allowed in-depth rheological analysis utilizing previously derived relationships for linear polymers. ^1H NMR spectroscopy determined 4,4'BB:3,4'BB mol ratios, as well as *cis:trans* isomer ratios of CHDM. Monomer feed ratios agreed well with the final polymer composition, as seen in **Table 3.1**. CHDM monomer possessed a *cis:trans* ratio of 33:67 and maintained this molar ratio after polymerization.

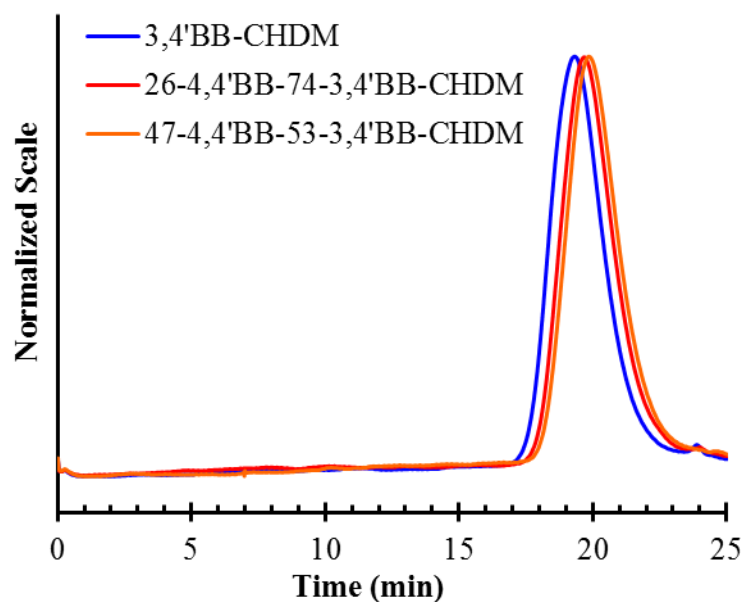


Figure 3.1. Size exclusion chromatography (SEC) analysis in CHCl_3 of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters with refractive index detection.

Table 3.1. Summary of compositional and thermal analysis of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters

x-4,4'BB-y-3,4'BB (%)		$T_d, 5\%$ (°C)	T_g (°C)		T_m (°C)	T_β (°C)
Feed (x, y)	^1H NMR	TGA ^a	DSC ^b	DMA ^c	DSC ^b	DMA ^c
0:100	0:100	393	121	117	ND	-71
25:75	26:74	392	123	121	ND	-67
50:50	47:53	394	128	125	ND	-65
60:40	56:44	393	134	132	237*	-65

^a TGA: 10 °C/min heat, N_2

^b DSC: heat/cool/heat, second heat; N_2 , 10 °C/min. T_g reported as inflection point of step transition, T_m reported as peak maximum of endothermic event. ND = not detected

^c DMA: tension mode, 1 Hz, 3 °C/min. T_g reported as peak maximum in tan delta curve, T_{flow} reported as temperature prior to modulus approaching zero.

* T_m determined from first heat

TGA indicated a single-step weight loss profile (Figure S3.2) for all compositions with $T_{d,5\%}$ around 390 °C for all polyesters, and TGA also confirmed a high onset of weight loss temperature, as seen in **Table 3.1**. DSC determined T_g s for all (co)polyesters, and an endothermic melting transition (T_m), only observed in the first heat of poly(56-4,4'BB-44-3,4'BB-CHDM), suggested a semi-crystalline morphology with relatively slow crystallization rates for samples with > 56 mol % 4,4'BB. Increasing the incorporation of

the more linear 4,4'BB repeating unit resulted in higher T_g s (Figure S3.3), consistent with previous literature.^{18, 21, 26, 28} For example, altering the molar ratio of 4,4'BB to 3,4'BB increased the T_g to 134 °C for 56 % 4,4'BB, imparting sufficient thermal properties and maintaining amorphous morphology with proper processing for BPA-PC replacement in applications that demand elevated temperature performance. Incorporation of CHDM raised the T_g of the BB (co)polyesters approximately 17 °C compared to ethylene glycol (EG) containing BB (co)polyesters,^{18, 21, 26} similar to the increase observed from poly(ethylene terephthalate) (PET) to poly(cyclohexanedimethylene terephthalate) (PCT) and poly(cyclohexanedimethylene terephthalate-co-isophthalate) copolyesters.³⁴⁻³⁵

DMA corroborated DSC T_g values and offered insight into thermomechanical polymer properties. Sub-ambient temperature DMA elucidated short chain segmental relaxations. Tan δ analysis revealed similar intensities near the starting temperature (-150 °C), but revealed slight increases in maximum β -relaxation peak intensity when incorporating more 4,4'BB, as seen in **Figure 3.2**. Increased intensity and broader β -relaxation peaks likely resulted from increased ring-rotations as well as differences in chain packing. Higher levels of the 3,4'BB monomer presumably hindered ring rotation due to the *meta*-linkage, thus slightly decreasing β -relaxation peak intensity.^{21, 26, 35-37} Similarly, decreased chain packing of compositions with higher 4,4'BB levels afforded samples with greater ability to dampen, thus a higher β -relaxation peak intensity.³⁸ Total peak intensity of BB-based (co)polyester β -relaxations compared favorably with BPA-PC, suggesting high-energy absorption and impact-resistant properties.^{6, 39-42} The conformational changes of the cyclohexane ring and ring-rotation of the BB unit occurred over similar temperature ranges, as seen with uniform and monomodal relaxation peaks. It is likely that the CHDM

relaxations and energy absorption dominated the majority of the β -relaxation peak, as previous literature indicated a larger change in peak intensity, peak breadth, and peak temperature (T_β) when changing 4,4'BB:3,4'BB molar ratios.^{21, 26} The peak intensity shifted to higher temperatures as 4,4'BB incorporation increased, suggesting slightly longer relaxation times for conformational changes.⁶

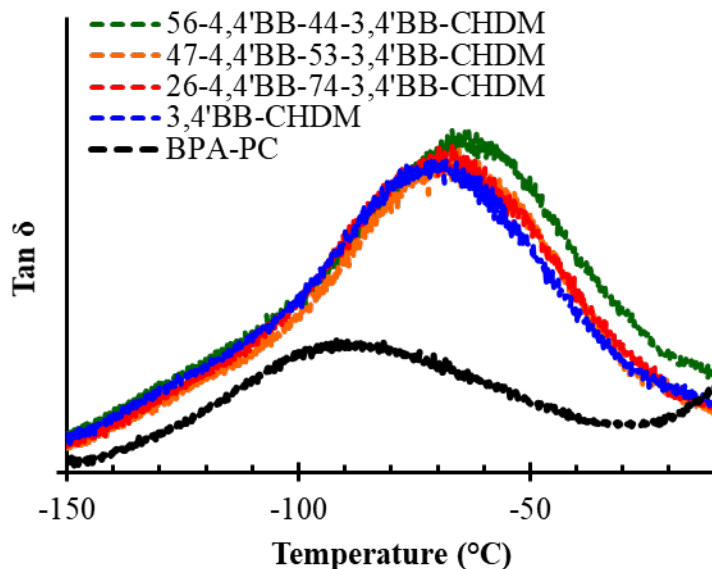


Figure 3.2. Low temperature relaxations from dynamic mechanical analysis (DMA). β -relaxation temperature (T_β) determined as peak of the $\tan \delta$ curve. Increasing 4,4'BB content shifts the T_β to higher temperatures, but minimally affects the overall intensity. 1 Hz, an oscillatory amplitude of 15 μm , and a static force of 0.01 N were employed.

Further analysis into polyester chain dynamics and relaxation times required melt rheology. Shifting complex viscosity (η^*) provided suitable curve overlap and generated η^* master curves over a large frequency range, as seen in **Figure 3.3**. A 270 $^\circ\text{C}$ reference temperature (T_r) represented typical processing temperatures for semi-aromatic polyesters and enabled prediction of processing behavior at frequencies required for common techniques such as extrusion and blow/injection molding.⁴³ All (co)polyesters exhibited zero-shear viscosities above 1000 Pa $\cdot$ s at 270 $^\circ\text{C}$, indicating high molecular weights compared to similar amorphous polyesters and corroborating SEC analysis. Higher

frequencies resulted in shear thinning behavior (slope = -0.903), similar to the behavior observed for EG-based BB polyesters.²⁶ All η^* curves converged to a similar slope and overlapped at high frequencies, suggesting that BB regiochemistry had a negligible effect on shear thinning behavior with aliphatic diols.

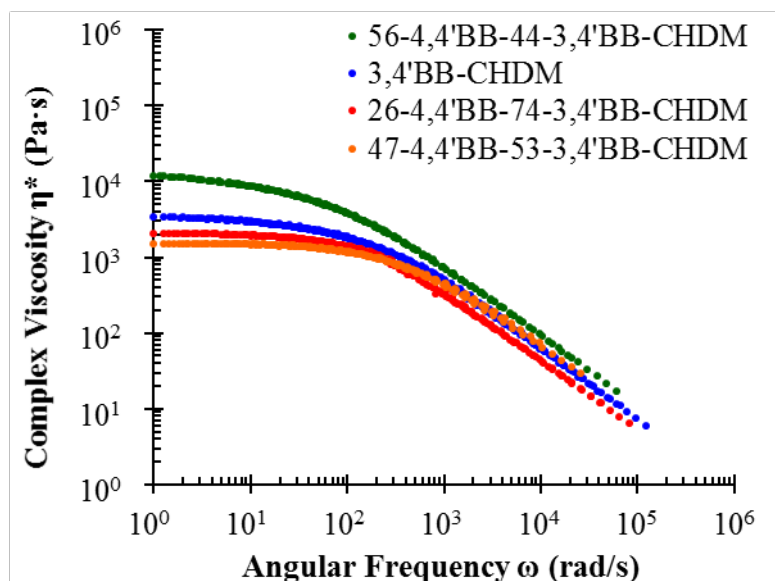


Figure 3.3. Complex viscosity master curves of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters at $T_r = 270$ °C.

Overlaying frequency sweeps from multiple temperatures generated storage moduli (G') and loss moduli (G'') master curves. Using a common T_r of 130 °C, time-temperature superposition (TTS) revealed characteristic melt flow properties. As seen in **Figure 3.4**, the master curve for poly(47-4,4'BB-53-3,4'BB-CHDM) exhibited characteristic relaxation times across all length scales. Systematic changes in relaxation times were observed when changing the regioisomer (4,4'BB:3,4'BB) molar ratios, identified as the G' , G'' crossover points in the master curves (Figures S3.5-3.6). The crystallizability of poly(56-4,4'BB-44-3,4'BB-CHDM), (**Table 3.1**) determined from DSC, prohibited rheological analysis at low temperature (high frequencies in master curves). At the lower temperatures required for the TTS master curve shifting to high frequencies, (co)polyesters

with higher 4,4'BB content crystallize; thus the rheological and relaxation behavior becomes more complex due to the semi-crystalline morphology and is not suitable for comparison to the fully amorphous samples with < 56 mol % 4,4'BB. At frequencies higher than the cooperative segmental motion crossover ($1/\tau_0$), the polymer acted as a rigid glass. Frequencies lower than both $1/\tau_0$ and the crossover related to the time of an entanglement strand ($1/\tau_e$) resulted in elastic behavior with viscous flow phenomena occurring at frequencies less than the crossover related to reptation of entangled chains ($1/\tau_{rep}$). **Figure 3.5** illustrates the influence of the backbone regiochemistry on τ_{rep} , the Rouse time of an entangled chain (τ_R), τ_e , and τ_0 . The rigid, linear 4,4'BB repeating unit strongly influenced and hindered the mobility of the various chain segments, increasing all characteristic relaxation times. Relaxation times increased up to two-orders-of-magnitude upon increasing from 0 to 47 mol % 4,4'BB incorporation, similar to decahydronaphthalene-based polyesters with altering ratios of CHDM and highly rigid 2,2,4,4-tetramethylcyclobutane-1,3-diol (CBDO).⁶ The change in relaxation behavior suggested that alteration of regiochemistry greatly influenced the polymer chain dynamics with a similar effect to adding a highly rigid comonomer.

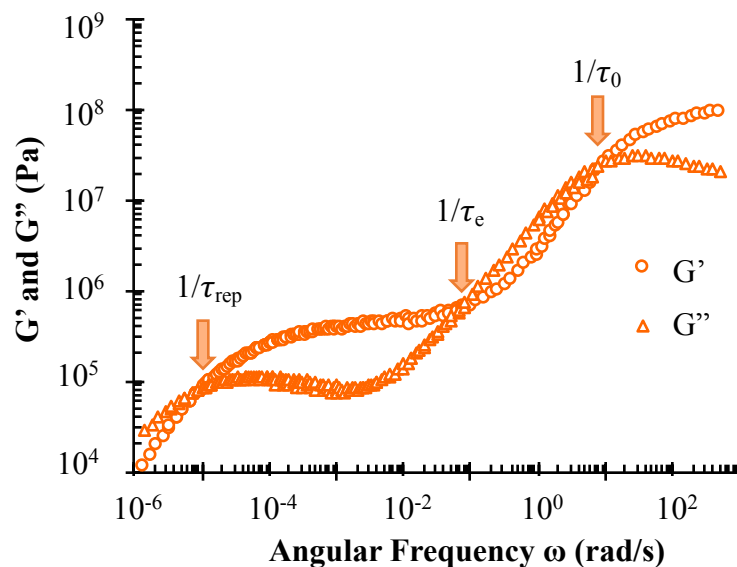


Figure 3.4. Storage and loss moduli master curve of poly(47-4,4'BB-53-3,4'BB-CHDM) at $T_r = 130$ °C. Reciprocal of relaxation time scales taken at G'/G'' crossovers, noted with arrows.

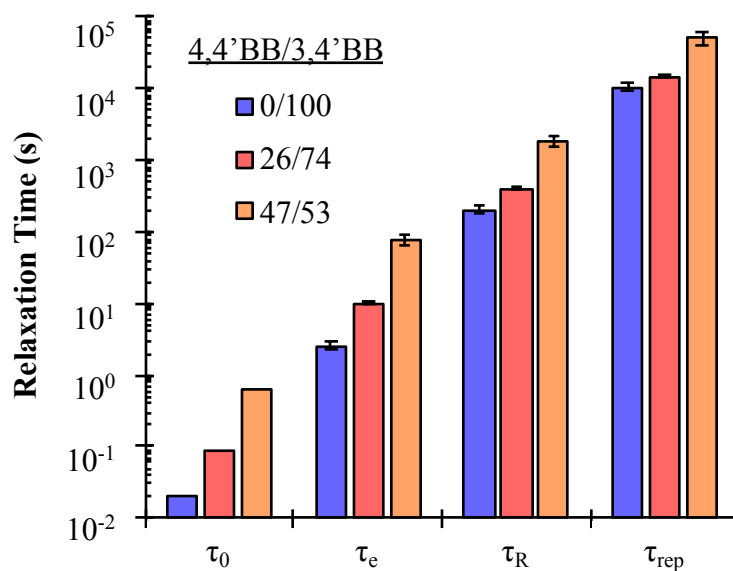


Figure 3.5. Characteristic relaxation times of (co)polyesters as determined using TTS at $T_r = 130$ °C, where τ_0 , τ_e , τ_R , and τ_{rep} are the cooperative segmental, entanglement strand, Rouse entanglement chain, and reptation relaxation times, respectively.

Further analysis of relaxation times enabled the determination of BB-based polymer entanglement and rigidity. Relationships between various relaxation times (eq 3.1) afforded the number of entanglements per chain (N/N_e). Similarly, determining the Kuhn monomer volume (v_0) (eq 3.2) offered insight into chain rigidity.

$$\frac{N}{N_e} = \left(\frac{\tau_{rep}}{6\tau_e} \right)^{1/3} \quad \text{Eq. 3.1}$$

$$v_0 = \frac{k_B T}{N_e G_N^0} \quad \text{Eq. 3.2}$$

As seen in **Figure 3.6A**, as the incorporation of 4,4'BB increases, N/N_e systematically decreases. Alternatively, v_0 increases as 4,4'BB incorporation increases, suggesting the linear 4,4'BB monomer increases backbone rigidity compared to the kinked, *meta* 3,4'BB. These results corroborate previous literature with more rigid monomer incorporation increasing molecular weight of entanglement (M_e).⁶ The linear, non-associating nature of the (co)polyesters enabled the determination of the M_e from the plateau modulus (G_N^0) obtained at $1/\tau_e$ on the moduli master curves (eq 3).⁴⁴ As seen in **Figure 3.6B**, M_e increases as 4,4'BB incorporation increases, resulting in a lower plateau modulus in the master curves, a shorter plateau width between $1/\tau_{rep}$ and $1/\tau_e$, and lower N/N_e .

$$M_e = \frac{nRT}{G_N^0} \quad \text{Eq. 3.3}$$

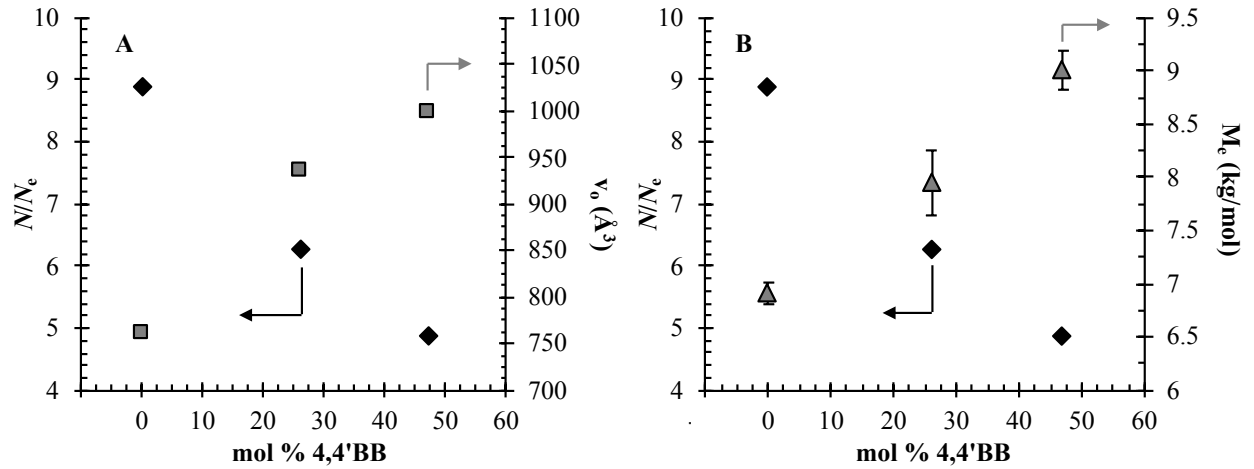


Figure 3.6. Number of entanglements per chain (N/N_e) (black diamonds) determined using characteristic relaxation times (eq 1). Number of entanglements per chain compared to (A) Kuhn monomer volume (v_0) (grey squares) (equation 2; $\tau_r = 130^\circ\text{C}$) and (B) molecular weight of entanglement (M_e) (grey triangles) using G' at τ_e (equation 3; $\tau_r = 130^\circ\text{C}$)

Characterization of TTS shift factors, a_T , using the Williams-Landel-Ferry (WLF) and Arrhenius equation revealed fractional free volumes and melt flow activation energies (Figure S3.6). The C_1 and C_2 constants determined by least-squares regression at the T_r enabled the calculation of these constants at T_g (eq 3.4 and eq 3.5), C_1^g and C_2^g . This allowed for direct comparison to literature values and the determination of the fractional free volume at T_g (f_g) (eq 3.6). These constants agreed well with other nonassociating, neutral polymers.^{6-7, 26, 45}

$$C_1^g = \frac{C_1 C_2}{C_2 + (T_g - T_r)} \quad \text{Eq. 3.4}$$

$$C_2^g = C_2 + (T_g - T_r) \quad \text{Eq. 3.5}$$

$$f_g = \frac{B}{2.303 C_1^g} \quad \text{Eq. 3.6}$$

As seen in **Table 3.2**, f_g remained constant when altering the 4,4'BB:3,4'BB molar ratio, consistent with previous literature.^{21, 26} Interestingly, f_g did not change for these

chemically similar (co)polyesters despite the noticeable change in chain rigidity. BB-based (co)polyesters with CHDM exhibited between 5 and 10 % larger f_g compared to similar 4,4'BB:3,4'BB polyesters with EG as the diol. The bulkier cyclohexyl ring in the backbone restricts chain packing compared to an ethylene unit, thus a higher f_g . PALS corroborated the findings through average molecular hole volume $\langle v_h \rangle$ measurements at RT. A significant change in $\langle v_h \rangle$ was not observed, although the 3,4'BB-CHDM homopolymer possessed the lowest T_g as well as the lowest $\langle v_h \rangle$. A smaller $\langle v_h \rangle$ is the result of smaller free-volume elements forming as the more flexible, lower T_g sample packs better upon cooling through the glass transition. The melt flow activation energy (E_a) increased with higher incorporation of the rigid and bulkier 4,4'BB repeating unit, supporting the increase in v_0 and longer relaxation times at the same T_r . The CHDM-based BB (co)polyesters exhibited higher overall E_a compared to EG analogs due to the bulkier CHDM diol hindering chain mobility.²⁶

Table 3.2. WLF parameters, fractional free volume, average hole volume at RT, thermal expansion coefficients of free volume, and melt flow activation energies of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters

x-4,4'BB-y-3,4'BB	C_1^*	C_2^*	C_1^g	C_2^g	f_g	$\langle v_h \rangle$	E_a
x:y (%)		K		K		$\times 10^{-30} \text{ m}^3$	kJ mol^{-1}
0:100	4.7	283.0	9.9	134.0	0.044	92.9 ± 2.3	91.7
26:74	4.3	261.3	9.8	114.3	0.044	94.4 ± 5.3	91.9
47:53	3.7	230.3	9.7	88.3	0.045	95.9 ± 3.8	93.5
56:44	4.2	241.3	9.4	106.3	0.046	94.9 ± 2.7	95.4

*Based on reference temperature $T_r = 130 \text{ }^\circ\text{C}$.

As seen in **Figure 3.7**, engineering stress-strain curves elucidated the influence of BB regioisomers on tensile properties for thin films. Increasing 4,4'BB levels reduced the Young's modulus as seen in **Table 3.3**. A reduction in chain packing and thus density²¹ in

the glassy state for higher 4,4'BB levels lowered Young's modulus, consistent with previous tensile analysis utilizing EG as the diol.²⁶ Similar results were observed when comparing amorphous PET and poly(ethylene isophthalate) (PEI).^{21, 28} PEI possesses a higher amorphous density compared to PET and similarly a higher Young's modulus, although a lower tensile yield strength. CHDM-based (co)polyesters' yield strength decreased as 4,4'BB levels increased, and all yield points occurred between 4.5-5% strain. Thus, the yield strength follows a similar trend as the Young's modulus, due to homogeneous deformation prior to yielding. Elongation at break analysis was consistent across the (co)polyester series. Analysis of injection molded tensile samples, rather than die punched dogbone specimens, is required to produce more consistent elongation to break data. More consistent elongation data will allow for further analysis of the structure-property relationships with respect to tensile properties.

Changes in M_e also potentially influences the yield strength. Amorphous PET exhibits a higher yield strength compared to PEI even though PEI has a higher amorphous density and Young's modulus.^{21, 28} PEI packs better than PET but PEI's M_e is 2-4 times higher than PET's M_e .⁴⁶⁻⁴⁸ Illustrated in **Figure 3.8**, CHDM-based BB (co)polyesters exhibited reduced yield strengths as entanglement density decreased, with higher 3,4'BB levels increasing the number of entanglements, potentially aiding in increasing yield strength. Further testing including scattering to probe chain conformation and spacing while undergoing deformations at low strain % is required to fully understand the influence of the chain parameters on the yield strength.

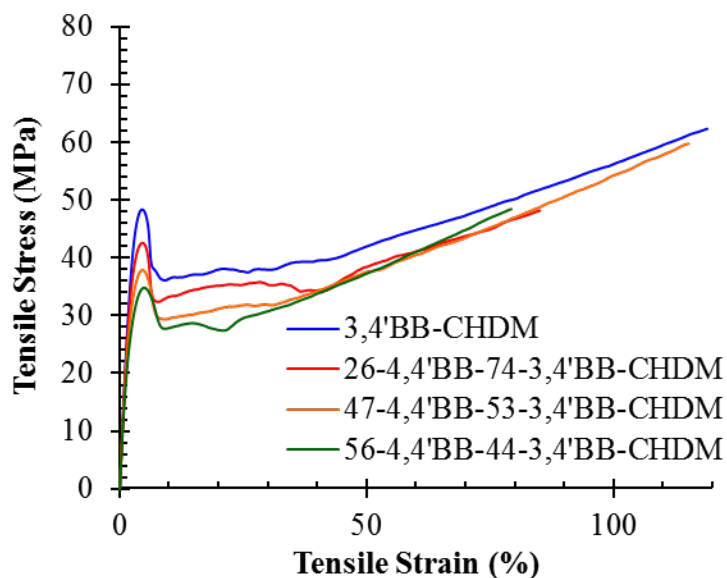


Figure 3.7. Tensile mechanical testing. Young's modulus, tensile strength, and elongation to break was analyzed. A 10 mm/min extension rate was employed. Onset of strain hardening occurs at lower % strain with increasing 4,4'BB content. Curves represent selective samples to guide interpretation of results.

Table 3.3. Summary of tensile mechanical properties of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters

x-4,4'BB-y-3,4'BB	Young's Modulus	Yield Strength	Elongation to Break
x:y (%)	GPa	MPa	%
0:100	2.08 ± 0.06	47.2 ± 1.0	120. ± 21
26:74	2.00 ± 0.03	45.1 ± 0.4	86.2 ± 18
47:53	1.92 ± 0.04	40.3 ± 1.2	104 ± 16
56:44	1.78 ± 0.01	36.2 ± 0.5	79.4 ± 5.2

*Compression molded films (~400 μm thick) used to punch out (D-638-V Pioneer-Dietecs die) dogbone specimens

*Reported data is average of 6-8 runs per composition

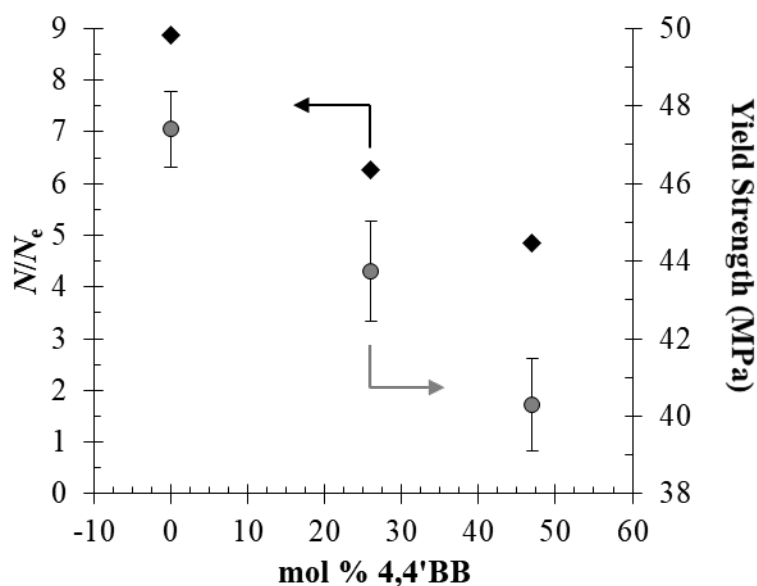


Figure 3.8. Number of entanglements per chain (N/N_e) (black diamonds) versus tensile Yield Strength (grey circles).

Increasing (co)polyesters' 4,4'BB levels resulted in more rigid chain segments and less coiled, initial conformations between entanglements. Thus, these chains possess less extensibility under uniaxial deformation. As seen in **Figure 3.7**, the onset of strain hardening decreased as the 4,4'BB content increased. Earlier neck stabilization suggests a lower draw ratio and a higher propensity to strain harden. Once the chains reach their extensible limit, strain hardening begins, with a slight increase in strain hardening slope for samples incorporating higher levels of 4,4'BB. The higher rigidity imparted from the linear 4,4'BB unit hinders the conformation changes needed for further elongation, thus varying the stress required to continue elongation. Structure-morphology-property relationships require further mechanical testing and chain conformation analysis during necking and strain hardening, which will probe chain packing and alignment during tensile analysis. Other bulk mechanical testing is also necessary to further understand the mechanical properties of BB-based (co)polyesters and will be included in future work.

SEM analysis of dogbone fracture surfaces explored the origin of tensile mechanical failure. Lines, protruding from the ultimate break location, known as conchoidal lines,⁴⁹ are indicative of brittle fracture when the sample undergoes stretching above necking. As depicted in **Figure 3.9**, more ductile fracture is observed in the 3,4'BB homopolymer. These results corroborated the rheological analysis, which determined increasing the 4,4'BB levels increased polymer chain rigidity and thus a higher likelihood of brittle failure after necking.

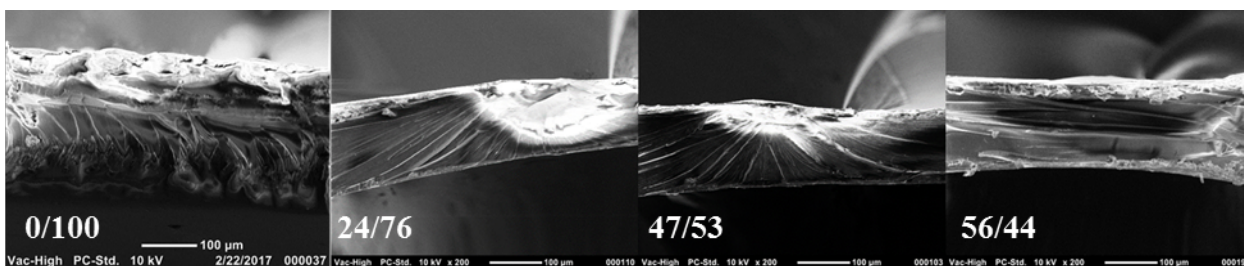


Figure 3.9. SEM analysis of tensile dog bone fractures suggests brittle fracture above necking as primary failure mechanism.

3.5 Conclusions

Altering backbone regiochemistry offers a unique way to tune polymer properties, with the potential to greatly enhance desired properties. This study confirmed that backbone regiochemistry of bibenzoates greatly influenced thermal, rheological, and tensile properties. Free volume and strain hardening are slightly affected by changes in backbone bibenzoate regiochemistry. These results also confirm the ability of CHDM-based BB polyesters to compete with current commercial thermoplastics, such as BPA-PC, due to T_g s approaching 135 °C, which permits use in sterilizable and dish-washable packaging, automotive components, and consumer goods.

Melt transesterification followed by polycondensation afforded semi-aromatic polyesters with repeat units comprised of CHDM and targeted BB-regioisomer ratios (4,4'BB and 3,4'BB). Thermal analysis revealed T_g s up to 135 °C, approaching BPA-PC (~145 °C). The cyclohexyl ring in the backbone from CHDM influenced the β -relaxation intensity as observed by DMA, while comparison to BPA-PC suggested CHDM-based BB-copolyesters potentially possess desirable impact resistant properties. Melt rheology analyzed η^* and shear thinning behavior, which were both minimally affected by BB regiochemistry. As determined with TTS analysis, higher 4,4'BB levels restricted chain mobility and resulted in longer τ_{rep} , τ_R , τ_e , and τ_0 relaxation times. (Co)polyesters with more 4,4'BB mol % possessed a larger v_0 , suggesting increased chain stiffness, thus increasing M_e , decreasing N/N_e , and lowering entanglement density. Through WLF analysis of shift factors, f_g did not change with altering the backbone regioisomers suggesting that at T_g these chemically similar (co)polyesters maintained similar free volume even though the chain rigidity is noticeably changed. PALS determined higher 3,4'BB levels resulted in smaller $\langle v_h \rangle$ at RT, although there was not a significant trend when changing composition. Arrhenius analysis confirmed that (co)polyesters with higher 4,4'BB levels required more energy to activate melt flow. Young's modulus decreased with increasing 4,4'BB due to less molecular packing and thus a less dense glassy state. The yield strength also decreased with increasing 4,4'BB levels, due to less molecular packing and potentially from a decrease in entanglement density. Further characterization of chain alignment, disentanglement stresses, and morphology analysis requires X-ray scattering techniques during tensile deformation. Altering the regioisomers also impacted the onset of strain hardening. High 4,4'BB incorporation resulted in more rigid chains and a less coiled

conformation between entanglements resulting in an earlier onset of strain hardening due to a shorter extensible limit of the polymer chains. SEM confirmed brittle fracture after necking and strain hardening as the primary failure mechanism, with more ductile-type fracture noticed in the 3,4'-BB homopolymer.

Supporting Information.

¹H NMR spectra, DSC & TGA thermograms, water contact angle measurements, TTS master curves of G' and G'', WLF shift factor fittings, and PALS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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3.7 References:

1. Scott, C. E.; Morris, J. C.; Bradley, J. R. Clear polycarbonate and polyester blends. US6005059 A, 1997.
2. Scott, C. E.; Morris, J. C.; Bradley, J. R. Clear blends of polycarbonates and polyesters. US6037424 A, 1997.
3. Nelson, A. M.; Long, T. E., A perspective on emerging polymer technologies for bisphenol-A replacement. *Polym. Int.* **2012**, *61* (10), 1485-1491.
4. Wyzgoski, M. G.; Yeh, G. S. Y., Origin of Impact Strength in Polycarbonate: II. Effect of Thermal Treatments. *Int. J. Polymer. Mater.* **1974**, *3* (2), 149-163.
5. Wyzgoski, M. G.; Yeh, G. S. Y., Origin of Impact Strength in Polycarbonate: I. Effect of Crystallization and Residual Solvent. *Int. J. Polymer. Mater.* **1974**, *3* (2), 133-148.
6. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E., Influence of cyclobutane segments in cycloaliphatic decahydronaphthalene-containing copolyesters. *High Perform. Polym.* **2017**, *29* (6), 750-756.
7. Dennis, J. M.; Enokida, J. S.; Long, T. E., Synthesis and Characterization of Decahydronaphthalene-Containing Polyesters. *Macromolecules* **2015**, *48* (24), 8733-8737.
8. Crawford, E. M.; Pecorini, T. J.; McWilliams, D. S.; Porter, D. S.; Connell, G. W. Polyester Compositions Containing Cyclobutanediol Having a Certain Combination of Inherent Viscosity and Moderate Glass Transition Temperature and Articles Made Therefrom. US2006042292 A, 2007.
9. Dennis, J. M.; Fahs, G. B.; Moon, N. G.; Mondschein, R. J.; Moore, R. B.; Wilkes, G. L.; Long, T. E., Synthesis of Polysulfone-Containing Poly(butylene terephthalate) Segmented Block Copolymers: Influence of Segment Length on Thermomechanical Performance. *Macromolecules* **2017**, *50* (13), 5107-5113.
10. Crawford, E. D.; Porter, D. S.; Connell, G. W. Polyester compositions which comprise cyclobutanediol having certain cis/trans ratios. EP20090012051, 2011.
11. Booth, C. J.; Kindinger, M.; McKenzie, H. R.; Handcock, J.; Bray, A. V.; Beall, G. W., Copolyterephthalates containing tetramethylcyclobutane with impact and ballistic properties greater than bisphenol A polycarbonate. *Polymer* **2006**, *47* (18), 6398-6405.
12. Beall, G. W.; Powell, C. E.; Hancock, J.; Kindinger, M.; McKenzie, H. R.; Bray, A. V.; Booth, C. J., Physical properties of CBDO based co-polyterephthalate nanocomposites. *Applied Clay Science* **2007**, *37* (3-4), 295-306.
13. Kelsey, D. R.; Scardino, B. M.; Grebowicz, J. S.; Chuah, H. H., High impact, amorphous terephthalate copolyesters of rigid 2,2,4,4-tetramethyl-1,3-cyclobutanediol with flexible diols. *Macromolecules* **2000**, *33* (16), 5810-5818.
14. Crawford, E. D.; McWilliams, D. S.; Porter, D. S.; Connell, G. W. Film(s) and/or sheet(s) comprising polyester compositions which comprise cyclobutanediol and have a certain combination of inherent viscosity and moderate glass transition temperature. US7855267 B2, 2010.
15. Burke, D. J.; Kawauchi, T.; Kade, M. J.; Leibfarth, F. A.; McDearmon, B.; Wolffs, M.; Kierstead, P. H.; Moon, B.; Hawker, C. J., Ketene-Based Route to rigid

Cyclobutanediol Monomers for the Replacement of BPA in High Performance Polyesters. *ACS Macro Letters* **2012**, *1* (11), 1228-1232.

16. Zhang, M. S.; Moore, R. B.; Long, T. E., Melt transesterification and characterization of segmented block copolyesters containing 2,2,4,4-tetramethyl-1,3-cyclobutanediol. *J Polym Sci Pol Chem* **2012**, *50* (18), 3710-3718.
17. Iyer, K. A., Chain mobility, secondary relaxation, and oxygen transport in terephthalate copolyesters with rigid and flexible cyclic diols. *Polymer* **2017**, *129*, 117-126.
18. Mang, M. N.; Brewbaker, J. L. Thermoplastic Polyesters Containing Biphenylene Linkages. US5138022A, 1992.
19. Asrar, J., High performance polyesters based on 4,4'-biphenyl dicarboxylic acid. In *Specialty polyesters*, Shotland Business Research, Skillman, NJ: 1995.
20. Schiraldi, D. A.; Lee, J. J.; Gould, S. A. C.; Occelli, M. L., Mechanical properties and atomic force microscopic cross sectional analysis of injection molded poly(ethylene terephthalate-co-4,4'-bibenzoate). *Journal of Industrial and Engineering Chemistry* **2001**, *7* (2), 67-71.
21. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of copolymers based on ethylene terephthalate. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (16), 1889-1899.
22. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Comparison of statistical and blocky copolymers of ethylene terephthalate and ethylene 4,4'-bibenzoate based on thermal behavior and oxygen transport properties. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41* (3), 289-307.
23. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Improving oxygen barrier properties of poly(ethylene terephthalate) by incorporating isophthalate. I. Effect of orientation. *J. Appl. Polym. Sci.* **2005**, *98* (4), 1615-1628.
24. Ma, H.; Hibbs, M.; Collard, D. M.; Kumar, S.; Schiraldi, D. A., Fiber Spinning, Structure, and Properties of Poly(ethylene terephthalate-co-4,4'-bibenzoate) Copolyesters. *Macromolecules* **2002**, *35* (13), 5123-5130.
25. Clary, R. S.; Lee, C. D.; Monroe Iv, W. G.; Vaughn, D. A.; Ragheb, R. T.; Erter Iii, J. W.; Brown, D. M.; Schiraldi, D. A., A Green, One-Pot Route to the Biphenyldicarboxylic Acids: Useful Intermediates in Polymer Synthesis. *International Journal of Organic Chemistry* **2013**, *03* (02), 143-147.
26. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R. K.; Nazarenko, S.; Turner, S. R.; Long, T. E., Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance. *Macromolecules* **2017**, *50* (19), 7603-7610.
27. Hasek, R. H.; Elam, E. U. Preparation of 2,2,4,4-tetraalkylcyclobutane-1,3-diols. 2,936,324, 1960.
28. Edling, H. E.; Liu, H.; Sun, H.; Mondschein, R. J.; Schiraldi, D. A.; Long, T. E.; Turner, S. R., Copolyesters based on bibenzoic acids. *Polymer* **2018**, *135*, 120-130.
29. Li, X.; Brisse, F., X-ray Diffraction Study of the Structure of Poly(ethylene 4,4'-biphenyldicarboxylate). *Macromolecules* **1994**, *27* (8), 2276-2282.

30. Kang, H. Y.; Lin, Q.; Armentrout, R. S.; Long, T. E., Synthesis and characterization of telechelic poly(ethylene terephthalate) sodiosulfonate ionomers. *Macromolecules* **2002**, *35* (23), 8738-8744.
31. Kirkegaard, P.; Eldrup, M.; Mogensen, O. E.; Pedersen, N. J., Program system for analysing positron lifetime spectra and angular correlation curves. *Comput. Phys. Commun.* **1981**, *23* (3), 307-335.
32. Tao, S. J., Positronium Annihilation in Molecular Substances. *The Journal of Chemical Physics* **1972**, *56* (11), 5499-5510.
33. Eldrup, M.; Lightbody, D.; Sherwood, J. N., The temperature dependence of positron lifetimes in solid pivalic acid. *Chem. Phys.* **1981**, *63* (1-2), 51-58.
34. Turner, S. R.; Seymour, R. W.; Dombroski, J. R., Amorphous and Crystalline Polyesters based on 1,4-Cyclohexanedimethanol. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Scheirs, J.; Long, T. E., Eds. John Wiley & Sons, Ltd: 2003.
35. Light, R. R.; Seymour, R. W., Effect of sub-T_g relaxations on the gas transport properties of polyesters. *Polym. Eng. Sci.* **1982**, *22* (14), 857-864.
36. Burgess, S. K.; Kriegel, R. M.; Koros, W. J., Carbon Dioxide Sorption and Transport in Amorphous Poly(ethylene furanoate). *Macromolecules* **2015**, *48* (7), 2184-2193.
37. Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J., Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate). *Macromolecules* **2014**, *47* (4), 1383-1391.
38. Knowles, K. R. Effect of Chain Rigidity on Network Architecture and Deformation Behavior of Glassy Polymer Networks. The University of Southern Mississippi, Hattiesburg, MS, 2017.
39. Wada, Y.; Tetsuo, K., Relation Between Impact Strength and Dynamic Mechanical Properties of Plastics. *J. Appl. Polym. Sci.* **1967**, *11*, 1661-1665.
40. Maxwell, A. S.; Monnerie, L.; Ward, I. M., Secondary relaxation processes in polyethylene terephthalate-additive blends: 2. Dynamic mechanical and dielectric investigations. *Polymer* **1998**, *39* (26), 6851-6859.
41. Maxwell, A. S.; Ward, I. M.; Lauprêtre, F.; Monnerie, L., Secondary relaxation processes in polyethylene terephthalate-additive blends: 1. N.m.r. investigation. *Polymer* **1998**, *39* (26), 6835-6849.
42. Boyer, R. F., Dependence of Mechanical Properties on Molecular Motion in Polymers. *Polym. Eng. Sci.* **1968**, *8*, 161-185.
43. Franck, A. *Understanding Rheology of Thermoplastic Polymers*; TA Instruments.
44. Herrmannschönherr, O.; Schneller, A.; Seifert, A. M.; Soliman, M.; Wendorff, J. H., Chain Dimensions, Entanglement Molecular-Weights and Molecular-Weight Distributions of Poly(Aryl Ethers) - a Combined Rheological and Mndo Analysis. *Makromol Chem* **1992**, *193* (8), 1955-1974.
45. Ferry, J. D., *Viscoelastic Properties of Polymers*. John Wiley & Sons: New York: 1980.
46. Wu, S., Predicting chain conformation and entanglement of polymers from chemical structure. *Polym. Eng. Sci.* **1992**, *32* (12), 823-830.

47. Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A., Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* **1994**, 27 (17), 4639-4647.
48. Aharoni, S. M., Unperturbed Dimensions and Critical Molecular-Weight for Entanglement of Poly(Ethylene-Terephthalate) and Poly(Ethylene Isophthalate). *Makromol Chem* **1978**, 179 (7), 1867-1871.
49. Baca, A. C.; Thornton, J. I.; Tulleners, F. A., Determination of Fracture Patterns in Glass and Glassy Polymers. *J Forensic Sci* **2016**, 61 Suppl 1, S92-S101.

3.8 Supporting Information

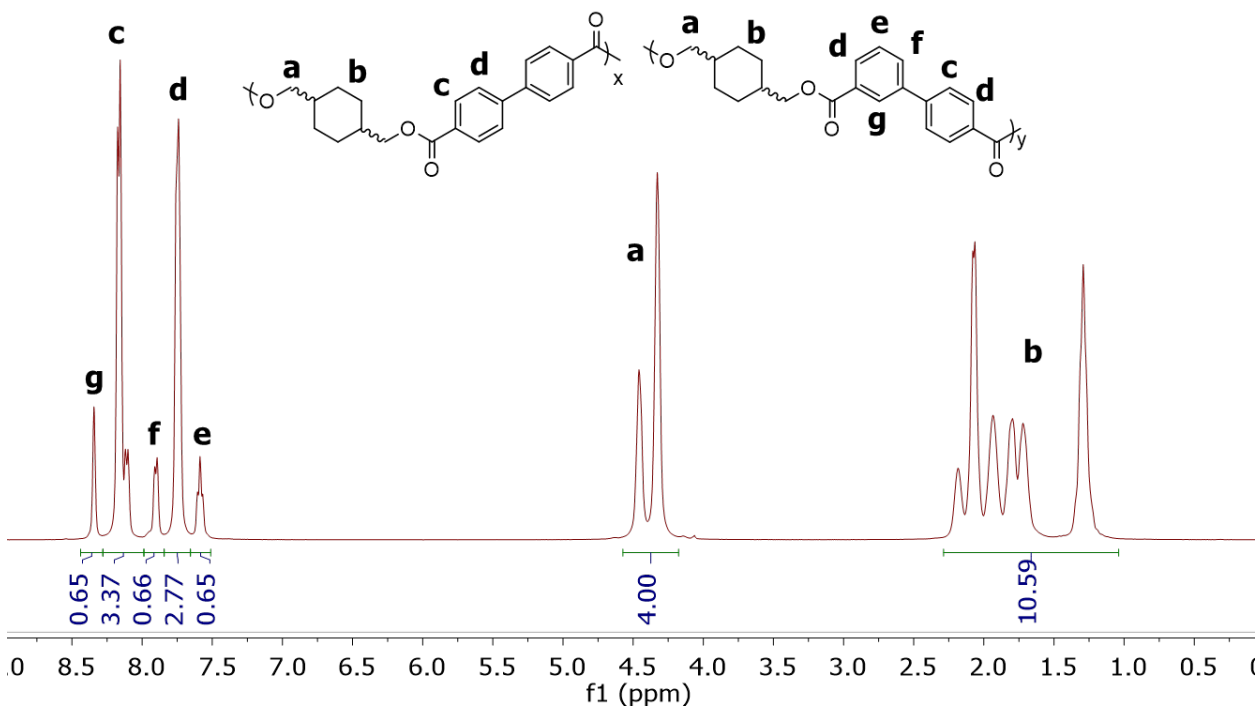


Figure S3.1. Representative ^1H NMR spectra of poly(X-4,4'BB-Y-3,4'BB-CHDM) with resonances assigned. Proton integrations of C, E, and F were used to determine mol % of each repeat unit. *Cis/trans* ratios of CHDM were determined using proton shift A. CHDM was determined to be 33% *cis* and 67% *trans*.

Table S3.1. Summary of molecular weight analysis of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters

x-4,4'BB-y-3,4'BB (%)		M _n (kg/mol)	M _w (kg/mol)	PDI	M _e (g/mol)
Feed (x:y)	Observed (x:y)				
	¹ H NMR ^a	SEC ^b			Rheology ^c
0:100	0:100	41.0	81.1	1.97	6900 ± 100
25:75	26:74	30.4	59.0	1.94	8000 ± 300
50:50	47:53	25.0	49.7	1.98	9000 ± 180
60:40	56:44	ND*	ND*	ND*	ND

^a CF_3COOD solvent, ambient conditions, 400 MHz; All compositions possessed a CHDM *cis:trans* ratio of 33:67

^b SEC: 1 mg/mL concentration, 1 mL/min flow rate in CHCl_3 , relative to polystyrene standards

^c Rheometer torque limits prohibited G' values necessary to calculate M_e for 60:40 polyester

*60:40 polyester limited solubility prohibited SEC analysis

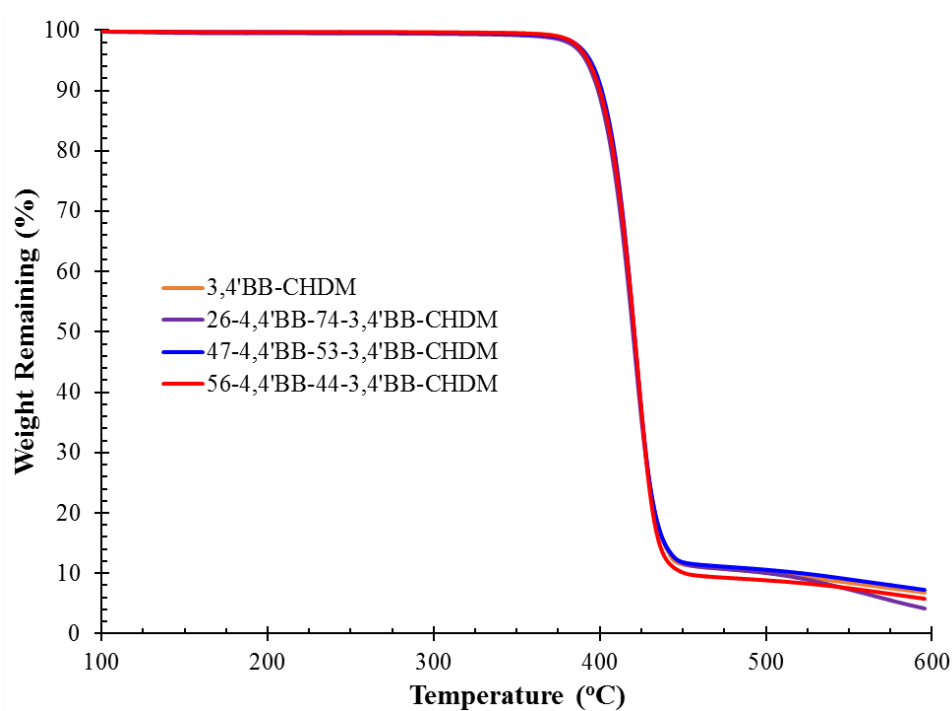


Figure S3.2. Thermogravimetric analysis (TGA) thermograms displaying similar temperature, single-step degradation for all poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters. TGA analysis performed at 10 °C/min under nitrogen purge.

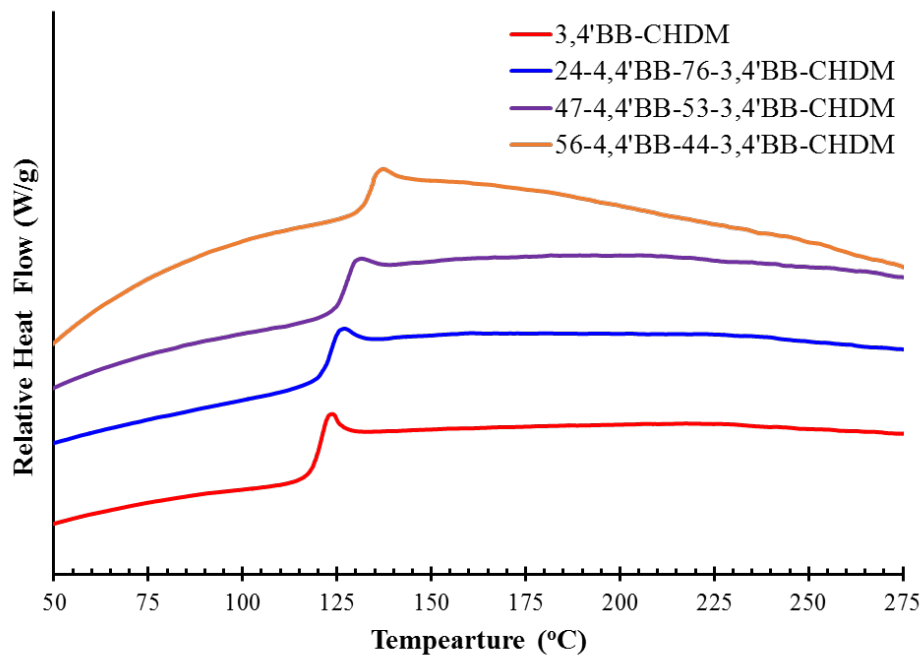


Figure S3.3. Representative DSC traces of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters. Second heat reported with a heat rate and cool rate of 10 °C/min.

Table S3.2. Summary of water contact angle analysis of poly(X-4,4'BB-Y-3,4'BB-CHDM) (co)polyesters.

x-4,4'BB-y-3,4'BB	$\theta_{\text{advancing}}$	θ_{receding}
x:y (%)	Degrees (°)	
0:100	88.0 ± 2.1	61.3 ± 4.0
26:74	77.2 ± 0.6	29.4 ± 3.5
47:53	81.7 ± 1.9	36.5 ± 2.9
56:44	78.8 ± 4.7	37.8 ± 6.4
PET	72.5	

Contact angle goniometry was performed with deionized water on a Ramé-Hart Model 590 F4 series goniometer with equipped automatic water dispensing unit and DROPimage Advanced V2.5 software package recording at 30 frames per second. Advancing (θ_A) and receding contact angles (θ_R) were determined with a needle-in-sessile-drop method adapted from literature.¹ Briefly, θ_A and θ_R values were determined when "inflating" or "deflating" droplets with water, and obtained while contact line length was increasing (θ_A) or decreasing (θ_R) and the measured contact angle was value. Contact angles were similar to PET.²⁻³

¹ Korhonen, J. T.; Huhtamaki, T.; Ikkala, O.; Ras, R. H. A. Reliable Measurement of the Receding Contact Angle. *Langmuir*, **2013**, 29 (12), 3858-3863.

² Donelli, I.; Taddei, P.; Smet, P. F.; Poelman, D.; Nierstrasz, V. A.; Freddi, G. Enzymatic Surface Modification and Functionalization of PET: A Water Contact Angle, FTIR, and Fluorescence Spectroscopy Study. *Biotechnol. Bioeng.* **2009**, 103 (5), 845-856.

³ Teshima, K.; Sugimura, H.; Inoue, Y.; Takai, O.; Takano, A. Transparent ultra water-repellent poly(ethylene terephthalate) substrates fabricated by oxygen plasma treatment and subsequent hydrophobic coating. *Appl. Surf. Sci.* **2005**, 244 (1-4), 619-622.

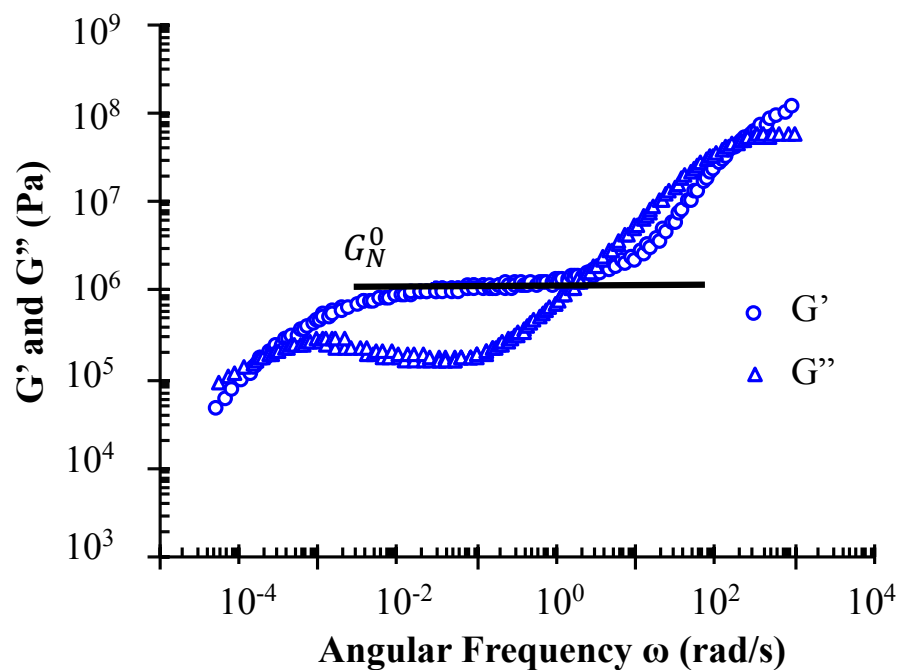


Figure S3.4. Storage and loss moduli master curve of poly(50-4,4'BB-50-3,4'BB-CHDM) polyesters at $T_r = 130$ °C.

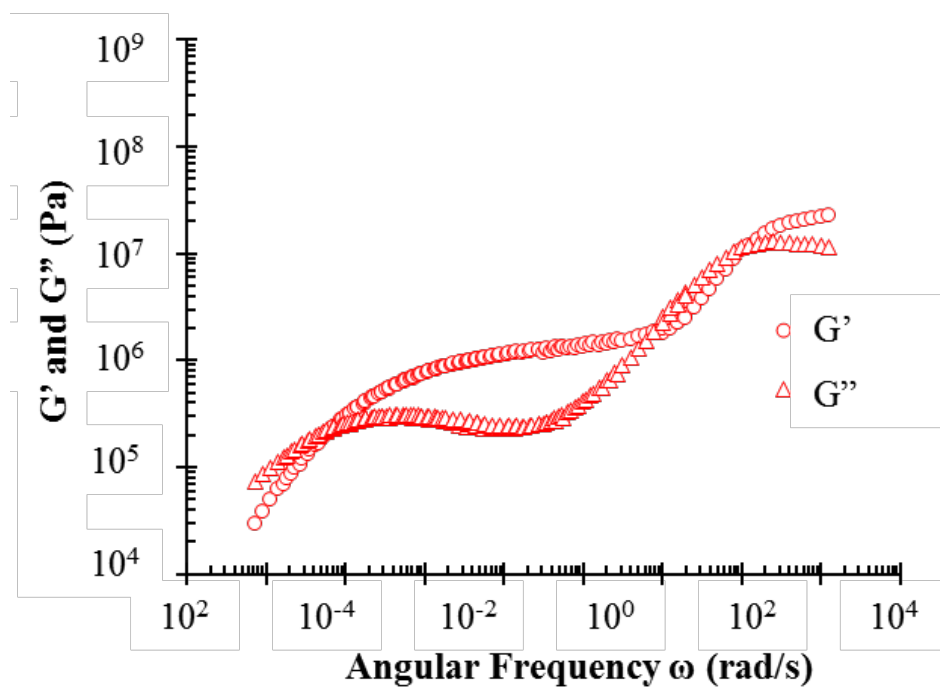


Figure S3.5. Storage and loss moduli master curve of poly(25-4,4'BB-75-3,4'BB-CHDM) polyesters at $T_r = 130$ °C.

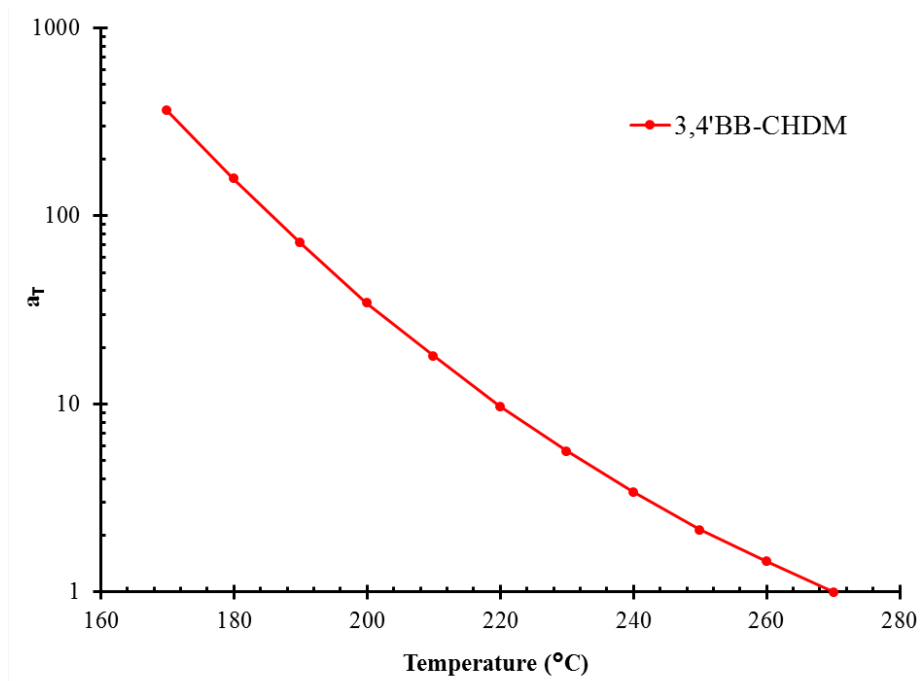


Figure S3.6. Representative WLF fitting of shift factors (a_T) versus temperature for the poly(100-3,4'BB-CHDM) homopolyester. $T_r = 270$ °C.

Chapter 4: Mechanical and Thermomechanical Properties of Kinked Amorphous Bibenzoate (Co)polyester Regioisomers

(Manuscript in preparation for publication)

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Keywords: Polyester, Bibenzoate, Mechanical Properties, Regioisomers

4.1 Abstract

Melt transesterification and polycondensation afforded bibenzoate (BB)-based (co)polyesters at 150 g scales, producing enough quantity for injection molded specimens for bulk mechanical testing. Size exclusion chromatography (SEC) confirmed high molecular weights and Advanced Permeation Chromatography (APC) resolved low molecular weight species, presumably cyclics. Water uptake analysis including sorption analysis and water contact angle measurements demonstrated the (co)polyesters propensity to uptake water, and thus need for sufficient drying pre-processing. Melt rheology probed melt stability under processing conditions, with minimal decrease in complex viscosity (η^*) measured over common processing times. Tensile and flexural mechanical testing revealed moduli and strength values greater than other high T_g amorphous thermoplastic polymers. Heat deflection temperature (HDT) analysis determined applicability of these polyesters to perform as rigid thermoplastic at elevated temperatures.

4.2 Introduction

Bibenzoate (BB)-based (co)polyesters continue to gain interest in industrial applications ranging from thermoplastics to high performance polymers due to their thermal properties, mechanical performance, and tunable morphology. Although dimethyl 4,4'-biphenyldicarboxylate (4,4'-bibenzoate, 4,4'BB) is commonly utilized in highly crystalline and liquid crystalline polyesters,¹⁻⁹ few examples illustrate the performance of (co)polyesters with dimethyl 3,4'-biphenyldicarboxylate (3,4'-bibenzoate, 3,4'BB). Although previously difficult to produce commercially, a simple and efficient synthesis to produce bibenzoates with tunable regiochemistry enabled monomer production.¹⁰ Recent examples of (co)polyesters incorporating the kinked, asymmetric 3,4'BB demonstrate their potential as a polymer platform to compete with standard industrial thermoplastics such as poly(ethylene terephthalate) (PET) and Bisphenol A Polycarbonate (BPA PC).^{3, 7, 11-14}

Incorporation of 3,4'BB into (co)polyesters with PET produced (co)polyesters with glass transition temperatures (T_g) approaching ~ 100 °C, lower oxygen permeability, and improved Young's modulus and yield strength.^{7, 13} Similarly, addition of 3,4'BB into (co)polyesters possessing 4,4'BB and ethylene glycol (EG) disrupted crystallinity, a common detriment to processing poly(4,4'BB-EG). These (co)polyesters maintained T_g s between 104-120 °C and melting point depression allowing for processable bibenzoate (co)polyesters incorporating 4,4'BB. Initial mechanical property testing revealed high Young's modulus and yield strength, approximately 1.5-2 times greater than PET and comparable with BPA-PC. Replacing EG with 1,4-cyclohexane dimethanol (CHDM) increased glass transitions up to 135 °C and β -relaxation intensities greater than BPA PC.¹² Analysis of chain dynamics through melt rheology revealed polyesters with higher levels

of 3,4'BB possessed a higher entanglement density due to a lower molecular weight of entanglement. Although BB-based (co)polyesters exhibit desirable thermal, barrier, and tensile properties for a variety of thermoplastic applications,^{7, 11, 13} further bulk mechanical property analysis is required to fill out structure-property relationships.

This report describes further compositional, mechanical, thermomechanical, and surface properties of BB-based (co)polyesters utilizing EG as the diol. Size exclusion chromatography analyzed molecular weight distributions and isolated multiple low molecular weight peaks, suggesting high amounts of cyclics produced during synthesis. Water contact angle measurements and water sorption analysis determined (co)polyesters propensity to absorb/adsorb water. Melt stability tests utilizing rheological analysis confirmed viability of melt processing techniques such as injection molding. Heat deflection temperature (HDT; deflection temperature under load, DTUL), flexural testing, and tensile testing of injection molded specimens confirmed BB-based (co)polyesters applicability in thermoplastic applications demanding robust mechanical integrity and thermal resistivity.

4.3 Experimental

4.3.1 Materials. All BB-based (co)polyester samples were synthesized at 150 g, following a previously published procedure scaled to the desired quantity.¹¹ Lab-made poly(ethylene terephthalate) (PET) was synthesized following a similar procedure as the BB-based (co)polyesters. PET #138 was obtained from Scientific Polymer Products, Inc. and used as received. All solvents were obtained from Spectrum Chemical and used as received. All samples were dried overnight at 80 °C in vacuum prior to processing and analysis.

4.3.2 Analytical Methods. ^1H NMR spectroscopy was performed at 23 °C on a Varian Unity 400 at 399.87 MHz utilizing the solvent deuterated trifluoroacetic acid (TFA-d). A Waters size exclusion chromatograph (SEC) equipped with three 5 μm PLgel Mixed-C columns, and a Waters 2410 refractive index (RI) detector analyzing at 880 nm used a flow rate of 1 mL min⁻¹ at 35 °C in tetrahydrofuran (THF) to characterize molecular weight relative to polystyrene standards. A Waters ACQUITY Advanced Permeation Chromatograph (APC) equipped with three 45 Å 150 mm XT columns and a Waters ACQUITY RI detector used a 0.8 mL min⁻¹ flow rate at 40 °C in THF to resolve low molecular weight species.

Compression molding utilized a PHI Q-203H manual hydraulic press and steel shims for film thickness control afforded optically clear, free-standing, and ductile films. Tensile property analysis and coinciding characterization was conducted in accordance with ASTM 638. A model No. 4411 Instron employing a 1kN load cell applied a 10 mm/min crosshead motion rate in ambient conditions. A micro injection molding machine (BOY XS) with 11-ton clamp and a 12 mm diameter screw was utilized to produce tensile dogbone specimens (ISO 37 Type 3) and un-notched Izod bars using a melt temperature of 282°C and a mold temperature of 13°C. A slow injection speed was utilized with a 1700 psi injection pressure setting and a 1300 psi holding pressure. ASTM D638 guided tensile measurements and tensile data analysis. A MTS model No. 4204 with a 1kN load cell, applied a crosshead motion rate of 10 mm/min under ambient conditions. An epsilon micro-extensometer was applied to accurately characterize low strains. Flexural testing utilized a crosshead motion rate of 1.2-1.4 mm/min was employed in accordance with ASTM D790 specifications. Flexural strength was determined at 5 % strain (0.05 strain).

Melt stability analysis performed on a TA Instruments Discovery Hybrid Rheometer (DHR)-2 utilized 25 mm diameter disposable aluminum parallel-plate geometry in N₂ atmosphere. Time sweeps were performed over 60 min at 275 °C under ambient atmosphere utilizing an oscillatory strain of 1.25% and a oscillatory shear of 1 Hz. Heat distortion temperature (HDT) used a TA Instruments Q800 dynamic mechanical analyzer (DMA) in 3-point bend mode. Displacement temperatures were determined at a heating rate of 2 °C min⁻¹ under a stress of 1.82 or 0.455 MPa stress in accordance with ASTM D648. Coefficient of thermal expansion (CTE) was characterized on a TA Instruments Q400 thermomechanical analyzer (TMA) in film mode (16 or 24 mm length). Samples were heated at 3 °C min⁻¹ while applying a 0.05 N static force. Linear analysis of the displacement versus temperature with respect to the length of the sample being measured determined CTE values.

Contact angle goniometry was performed with deionized water on a Ramé-Hart Model 590 F4 series goniometer with equipped automatic water dispensing unit and DROPImage Advanced V2.5 software package recording at 30 frames per second. Advancing (θ_A) and receding contact angles (θ_R) were determined with a needle-in-sessile-drop method adapted from literature.¹⁵ Briefly, θ_A and θ_R values were determined when "inflating" or "deflating" droplets with water, and obtained while contact line length was increasing (θ_A) or decreasing (θ_R) and the measured contact angle was value. Water absorption/adsorption analysis and hysteresis testing utilized a TA instruments Q5000 SA dynamic vapor sorption analyzer. Samples were subjected to 15% intervals of relative humidity ranging from 0-75% at 23 °C and allowed to equilibrate before measuring weight change. Hysteresis analysis utilized a cycle

between 0 and 95% relative humidity at 23 °C with % humidity changing once the weight change was less than 0.01%.

4.3.3 Compression molding (co)polyesters. Compression molding followed a previously published procedure.^{11, 16}

4.4 Results and Discussion

Synthesis of BB-based (co)polyesters with EG as the diol followed a previously published procedure as seen in Scheme S1.¹¹ Previous synthesis targeted 20 g of product, but processing into dogbones/bars suitable for bulk mechanical and thermomechanical processing required larger yields of product. Although similar compositions were targeted, scaling up the reaction volume required subtle changes in the reaction conditions to produce high molecular weight (co)polyesters. A dry 500 mL round bottomed flask was utilized to adequately fit the desired monomers and afford a melt volume that could be adequately mixed with the overhead stirrer. Initial transesterification temperatures and times remained unchanged. Polycondensation under vacuum required longer times to sufficiently remove all excess diol and condensate, due to the larger volumes restricting diffusion of condensate through the melt and out of the reaction vessel. Polycondensation steps under vacuum required approximately 3 h from when the reaction system reached 0.2 mmHg. Once the melt became visibly viscous, increasing the final temperature from 275 to 285 °C ensured the entire reaction melt reached appropriate temperatures to complete polycondensation through removal of the excess diol. Optically clear products resulted from the reactions and no further purification was necessary.

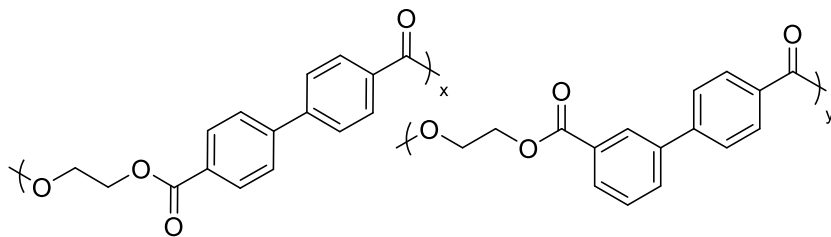


Figure 4.1: Structure of BB-based (co)polyesters

Three (co)polyester compositions were targeted due to their compositional-morphological relationship. The three compositions included the fully amorphous homopolymer poly(ethylene 3,4'BB) and copolyester poly(ethylene 4,4'BB₄₀/3,4'BB₆₀) along with the semi-crystalline poly(ethylene 4,4'BB₅₅/3,4'BB₄₅). 60 mol % 3,4'BB produced an amorphous copolyester with the maximum amount of 4,4'BB incorporated before obtaining a semi-crystalline morphology while 45 mol % 3,4'BB produced a copolyester which exhibited semi-crystalline morphology. In order to develop clear structure-property relationships, all further analysis is performed with amorphous morphologies. ¹H NMR spectroscopy confirmed compositions utilizing previously assigned peaks (Figure S4.1).¹¹ All (co)polyesters obtained compositions within error of targeted ratios.

Size exclusion chromatography (SEC) confirmed high molecular weights for poly(ethylene 3,4'BB). A relative number average molecular weight (M_n) of 49.5 kg/mol and a relative weight average molecular weight (M_w) of 86.7 kg/mol resulted in a dispersity (PDI) of 1.75, consistent with previous molecular weight and dispersity values for the smaller scale reaction.¹¹ The homopolymer dissolved readily in THF, while compositions incorporating 4,4'BB repeat units resulted in heterogenous solutions, unsuitable for SEC analysis with the non-corrosive solvents used for our SEC systems. Although molecular weights could not be determined for compositions incorporating 4,4'BB, rheological

analysis of zero-shear viscosity suggested similar molecular weights of all (co)polyesters. As seen in **Figure 4.2**, a monomodal peak with slight tailing at high retention times confirmed the expected molecular weight distribution of a step-growth polymer as well as potential cyclic species, known to results from step-growth reactions. To confirm the small molecule species, chromatography analysis continued on a Waters Advanced Permeation Chromatograph (APC), as seen in **Figure 4.3**. Utilizing three of the smallest pore-sized columns (45 Å x 150 mm), low molecular weight species, presumably cyclics, eluted at high retention times (4.25-5.5 min), completely resolved of the parent molecular weight distribution. A lack of a high molecular weight tail in the main APC parent peak confirmed the peaks at high retention times overlaid with the broad peak in the SEC. Further characterization is needed to characterize the amount of cyclics, size of cyclics (molecular weight/repeat units), and influence of starting monomer regiochemistry/shape on these results.

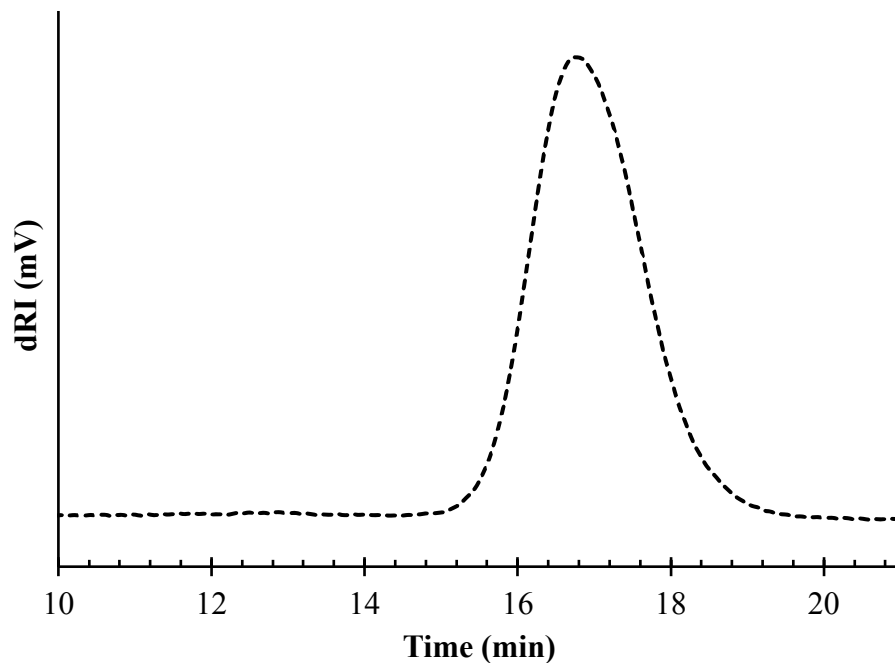


Figure 4.2. Size exclusion chromatography (SEC) analysis in THF of 100-3,4'BB-EG. Columns maintained a 35 °C temperature and a flow rate of 1 mL/min was used.

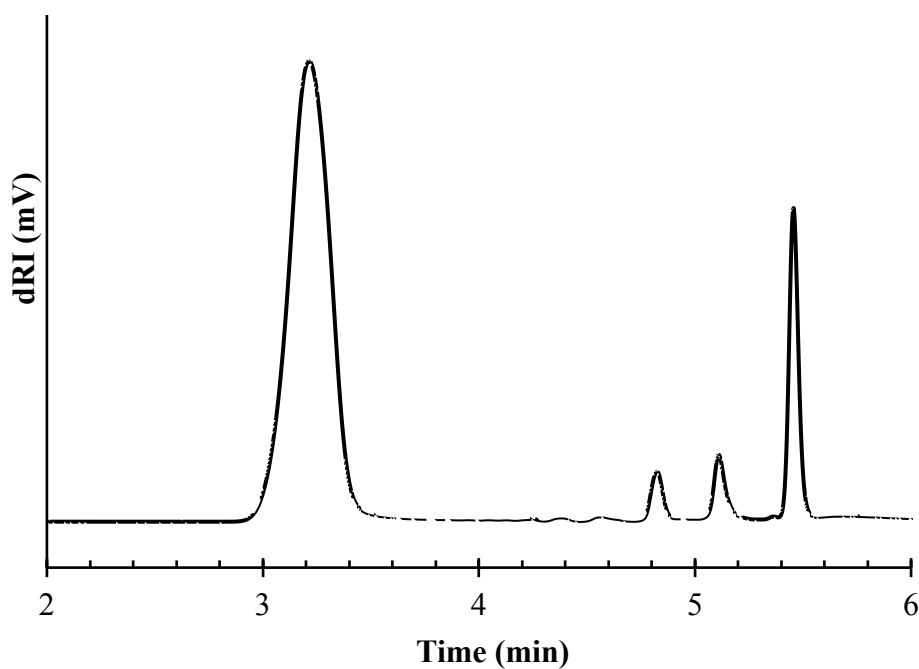


Figure 4.3. Advanced permeation chromatography analysis of 3,4'BB-EG polyester. Peaks highlighted at higher retention times (4.5-5.5 min) are assumed to be cyclic species formed during polymerization.

An undesirable PET property is its water uptake in ambient conditions. Too much water uptake before melt processing leads to hydrolytic cleavage and a reduction in molecular weight and properties, as well as bubbles and defects in the processed part, thus a rigorous drying step before melt processing is required. Terephthalate-based polyesters containing CHDM as the diol do not require as extensive drying before processing, due to the more hydrophobic nature of the polymer.¹⁷ To further understand the pre-processing needs of BB-based (co)polyesters, water uptake, hysteresis, and advancing and receding contact angle measurements are required.

As seen in **Figure 4.4**, amorphous PET (aPET) increases by ~0.2 weight % at 75% relative humidity and 23 °C. Poly(ethylene 3,4'BB) exhibits similar water uptake as aPET, but upon incorporation of 4,4'BB, water uptake increases up to ~0.6 weight % at 75% relative humidity and 23 °C. Water uptake trends are consistent with water absorption of PET and PEI. Poly(ethylene isophthalate) (PEI) absorbed less water compared to PET.¹⁸⁻¹⁹ One potential explanation for this includes the changes in density. PEI possesses a higher amorphous density compared to PET;^{7,20} thus less propensity to absorb/adsorb water.²¹ To understand the nature of the weight % increase, a water uptake hysteresis test was utilized to confirm adsorption, absorption, or both. As seen in **Figure 4.5**, samples were exposed to 0 or 95% relative humidity at 23 °C in cyclic fashion. Once the weight % changed by less than 0.01% over 1 min, the next step began. The weight % reached approximately 100.6% when equilibrated at 95% relative humidity but rapidly and repeatedly returned to 100 weight % after equilibrating at 0% relative humidity. This quick return suggests adsorption as the major mode of water uptake. Water contact angle analysis corroborated the hydrophilic/hydrophobic nature of the polymers. As seen in **Table 4.1**, (co)polyesters

with higher levels of 4,4'BB exhibited lower advancing and receding contact angles. BB-based (co)polyesters tendency to uptake more water than aPET demonstrated the need for sufficient drying before melt processing. Thus, polymer samples were dried at 80 °C overnight under high vacuum before melt rheology or melt processing.

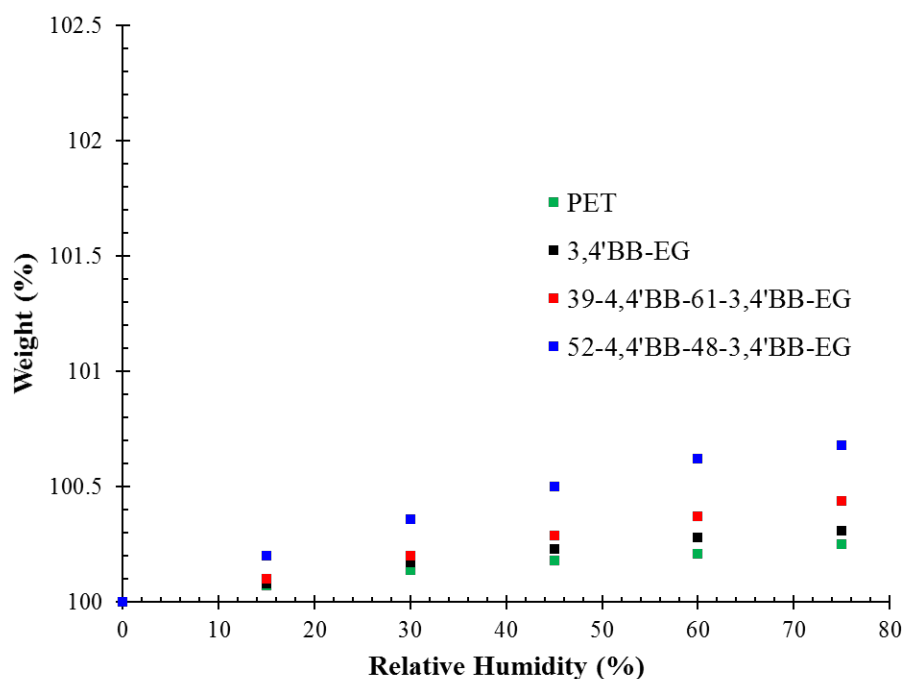


Figure 4.4. Water uptake test of amorphous x-4,4'BB-y-3,4'BB-EG (co)polyesters with lab synthesized amorphous PET as a standard. Samples were allowed to equilibrate at various percent relative humidity and the percent weight change was determined.

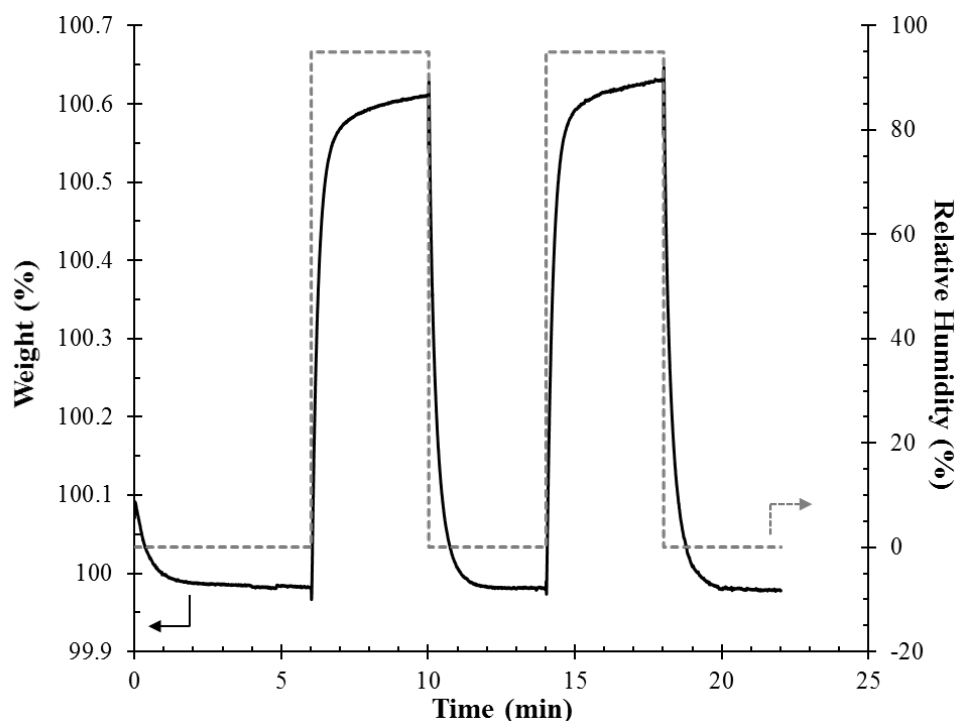


Figure 4.5. Water adsorption hysteresis test of 39-4,4'BB-61-3,4'BB-EG. Weight percent (solid) was allowed to equilibrate at 0 or 95 % relative humidity (dashed) until percent weight change decreased below 0.01 %. Typical adsorption profiles are observed.

Table 4.1. Advancing and receding water contact angle measurements for x-4,4'BB-y-3,4'BB-EG (co)polyesters. Lab synthesized PET used as a standard.

x-4,4'BB-y-3,4'BB-EG	$\theta_{\text{advancing}}$	θ_{receding}
x:y (%)	Degrees (°)	
0:100	74.3 ± 0.8	39.0 ± 2.8
39:61	72.9 ± 3.9	28.6 ± 5.4
52:48	70.2 ± 1.2	28.1 ± 4.4
Lab PET	78.1 ± 1.1	34.0 ± 6.7

Melt rheological time sweeps under simulated processing conditions confirmed BB-based (co)polyesters melt stability. The environment was set at 275 °C and put under air atmosphere to best simulate polyester processing conditions. Polyester samples endured a time sweep of 60 min at a constant 1.25% strain and constant oscillatory shear of 1 Hz, while monitoring complex viscosity (η^*). As seen in **Figure 4.6**, all (co)polyesters showed

minimal drop in η^* over 60 min. All BB-based (co)polyesters started at similar η^* and dropped by less than 10% over 10 min, representing a common maximum time the sample will be in the melt during processing. Commercial PET started at a lower η^* due to its lower molecular weight, but maintained a similar drop in η^* over the first 10 min. Similar trends confirmed no drastic difference between samples after 60 min. After determining pre-processing conditionings and confirming melt stability, injection molding produced dogbones for tensile analysis and bars for both flexural testing and heat deflection temperature (HDT) determination.

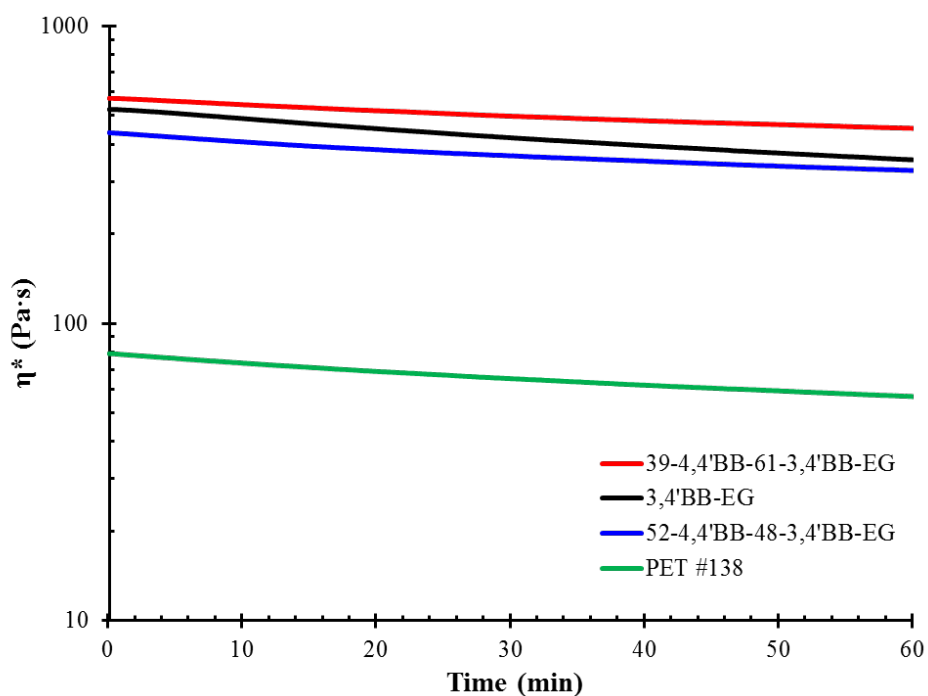


Figure 4.6. Melt stability of x-4,4'BB-y-3,4'BB-EG (co)polyesters with commercial PET #138 as a standard. A constant 1 Hz shear and constant nominal strain of 1.25 % was applied for 60 min at 275 °C under air.

Table 4.2. Melt stability complex viscosity loss profile as a function of time relative to complex viscosity at time 0.

x-4,4'BB-y-3,4'BB-EG	η_0^*	$\frac{\eta_{10}^*}{\eta_0^*}$	$\frac{\eta_{60}^*}{\eta_0^*}$
x:y (%)	Pa·s		
0:100	524	0.93	0.68
39:61	571	0.95	0.79
52:48	438	0.93	0.74
PET #138	79	0.93	0.72

Tensile stress versus strain curves from tensile testing enabled the determination of yield strength, Young's modulus, and elongation to break, summarized in **Table 4.3**. More precise analysis required an extensometer to accurately measure short strains, although the extensometer extension limit prohibited yield strength determinations, as seen in Figure S4.3. Yield strength and elongation behavior was characterized without an extensometer, as seen in **Figure 4.7**. Testing followed ASTM D638.

Young's modulus and yield strength increased with higher levels of 3,4'BB, consistent with previous results.¹¹⁻¹² The increase in Young's modulus is attributed to the higher amorphous density imparted by the kinked 3,4'BB repeat unit.⁷ All polyesters yield around 4% tensile strain. As a result, yield strength values follow a similar trend to the Young's modulus with higher 3,4'BB levels possessing increased yield strengths. Another potential influence on the yield strength is the increased entanglement density the (co)polyesters with higher 3,4'BB possess, as previously reported.¹² After yield, all samples underwent necking and cold-draw. Necking lasted 70-80% strain until strain hardening begins, followed by tensile failure around 130-140% strain. BB-based (co)polyesters exhibit Young's moduli and yield strengths superior to PET and cyclobutanediol-based polyesters, while similar to commercial BPA-PC.

(Co)polyesters incorporating more 3,4'BB repeat units exhibited an earlier onset of strain hardening. Strain hardening typically begins when chains no longer possess the ability to undergo gauche to trans conformation changes. PET possess more *trans* conformations than its *meta*-regioisomer poly(ethylene isophthalate) (PEI),^{20, 22} suggesting the *meta*-substituted 3,4'BB-based (co)polyesters with EG possess less *trans* conformations than (co)polyesters incorporating higher levels of 4,4'BB. Thus, 3,4'BB-based (co)polyesters with EG exhibit a shorter necking length, lower draw ratio, and higher propensity to strain harden. Interestingly, the opposite trend is observed when BB-based (co)polyesters incorporated 1,4-cyclohexanedimethanol (CHDM) as the diol.¹² This suggests the diol significantly contributes to the chain conformations as well as the diacid regiochemistry.

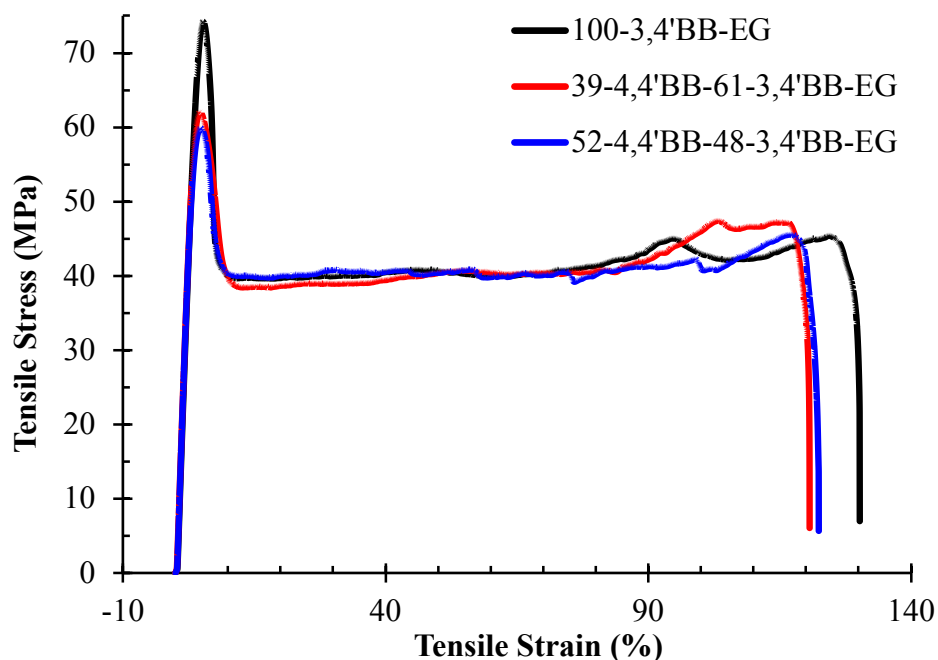


Figure 4.7. Tensile mechanical testing utilizing a 10 mm/min extension rate. Curves shown are representative of the average of 3-5 runs.

Similar to tensile analysis, flexural testing further confirmed BB-based (co)polyesters' robust mechanical integrity. Testing followed ASTM D790 and the results are summarized in **Table 4.3**. Flexural stress versus flexural strain revealed higher flexural modulus for (co)polyesters with higher levels of 3,4'BB, as seen in **Figure 4.8**. Since no clear yield point resulted during the testing, the flexural strength value corresponds to the flexural stress at 5% flexural strain. Flexural testing corresponded well with tensile testing as the flexural modulus and Young's modulus are approximately the same, while flexural strength is approximately 1.5 times greater than the tensile yield strength, expected for linear polymers.

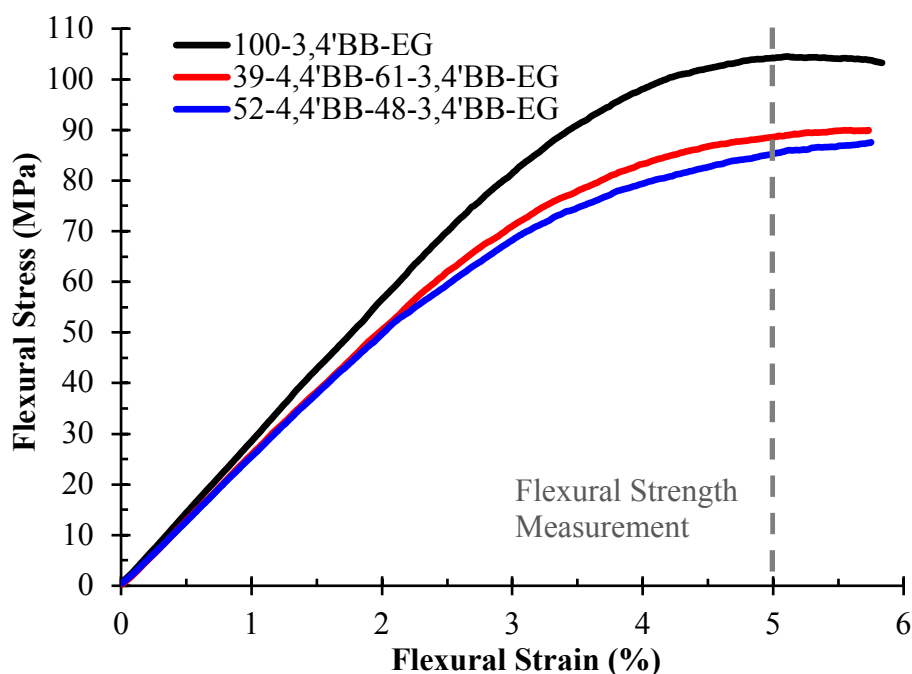


Figure 4.8. Flexural mechanical testing of x-4,4'BB-y-3,4'BB-EG (co)polyesters. Flexural modulus determined from the slope of the linear portion of the stress vs. strain plot. The flexural strength was determined at 5 % strain (0.05 strain). A crosshead motion rate of 1.2-1.4 mm/min was employed in accordance with ASTM D790 specifications.

Although BB-based (co)polyesters exhibit desirable tensile and flexural properties at RT, which is common for many thermoplastic applications, the thermomechanical

performance and resistivity to displacement at elevated temperatures is important for applications in above ambient conditions. The T_g indicates the onset of long-range segmental motion but is a static test, which does not consider stresses applied to the sample at elevated temperatures. Thus, the heat deflection temperature (HDT) is a more common measurement to determine when the polymer begins to lose shape and fidelity and limits the highest temperature where a thermoplastic polymer maintains its rigid character.²³⁻²⁴ HDT measurements followed ASTM D648, although were scaled down to 50 mm bars to accommodate size and instrument restrictions.

Based on sample bar dimensions, HDT values were determined to correspond to ~240-260 μm displacement.²⁴ After applying either 0.455 or 1.82 MPa to the sample in a 3-point bend mode, the samples were heated at 2 $^{\circ}\text{C min}^{-1}$ until displacement values reached the desired length. The temperature at the corresponding displacement value is reported as the HDT, as seen in **Table 4.3**. As seen in **Figure 4.9**, initial displacement went negative due to thermal expansion of the samples before deformation occurred. Once the sample began to soften and bend, the displacement quickly became positive and increased rapidly through the HDT. Due to the amorphous morphology of the sample bars tested, HDT trends followed T_g trends closely, with poly(ethylene 3,4'BB) possessing the lowest HDT value at both 0.455 and 1.82 MPa. The resulting HDT value is approximately 15-20 $^{\circ}\text{C}$ below the T_g as expected. Increasing the 4,4'BB levels in the (co)polyester resulted in higher HDT measurements, consistent with T_g trends. Although the 52 mol % 4,4'BB is crystallizable, no apparent crystallization was noticed during the experiments. Introducing crystallinity would hinder the displacement thus causing a change in the shape of the curve, not seen around the crystallization temperatures in **Figure 4.9**.

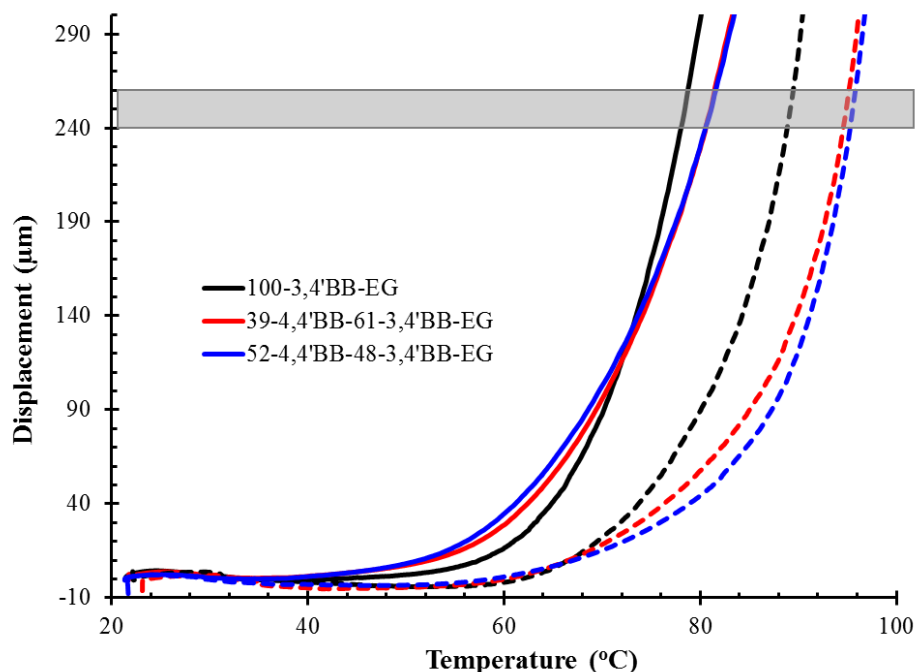


Figure 4.9. Heat distortion temperature (HDT) analysis of x-4,4'BB-y-3,4'BB-EG (co)polyesters using a dynamic mechanical analyzer (DMA) in 3-point bend mode. Temperatures were determined under a stress of 1.82 MPa (solid) or 0.455 MPa (dashed) in accordance with ASTM D648. Grey box outlines common displacement value range.

Table 4.3. Summary of flexural and tensile mechanical properties of x-4,4'BB-y-3,4'BB-EG (co)polyesters as well as measured heat distortion temperatures

x:y (%)	Flexural Modulus ^b GPa	Flexural Strength ^b MPa	Young's Modulus ^c GPa	Yield Strength ^d MPa	Elongation to Break ^d %	Heat Distortion Temperature ^e °C	
						0.455 MPa	1.82 MPa
0:100	2.89 ± 0.07	104.2 ± 0.1	2.69 ± 0.28	74.4 ± 0.3	163 ± 39	89	79
39:61	2.64 ± 0.04	88.8 ± 0.4	2.36 ± 0.16	62.3 ± 0.7	142 ± 35	95	81
52:48	2.50 ± 0.07	84.7 ± 0.8	2.34 ± 0.03	60.1 ± 0.3	109 ± 25	95	81

^aCF₃COOD solvent, ambient conditions, 400 MHz.

^bFlexural testing: 1kN load cell, 1.2-1.4 mm/min crosshead motion rate. Flexural strength was determined at 5% flexural strain.

^cTensile testing with extensometer: miniature extensometer used during first 5% strain to eliminate grip slippage

^dTensile testing without extensometer: initial grip separation 25.4 ± 2.0 mm, 10 mm/min crosshead motion rate

^eDMA: static force mode, 3-point bending, 2 °C/min.

Further thermomechanical analysis probed the (co)polyesters' coefficient of thermal expansion (CTE). As seen in **Figure 4.10**, the CTE increases upon higher incorporation of the linear 4,4'BB repeat unit. Imparting the linear and rigid repeat unit slightly increases free volume and β -relaxation intensities,^{7, 11-13} and lowers the amorphous density.⁷ Thus, compositions with higher 4,4'BB levels impart a greater ability to thermally expand during heating.²⁵ All samples exhibited a CTE lower than PET.²⁶⁻²⁷ Incorporation of the kinked 3,4'BB repeat unit offers advantages in applications needing minimal shrinkage over a broad range of temperatures, while higher 4,4'BB compositions offers advantages in applications which utilize shrinking upon cooling.

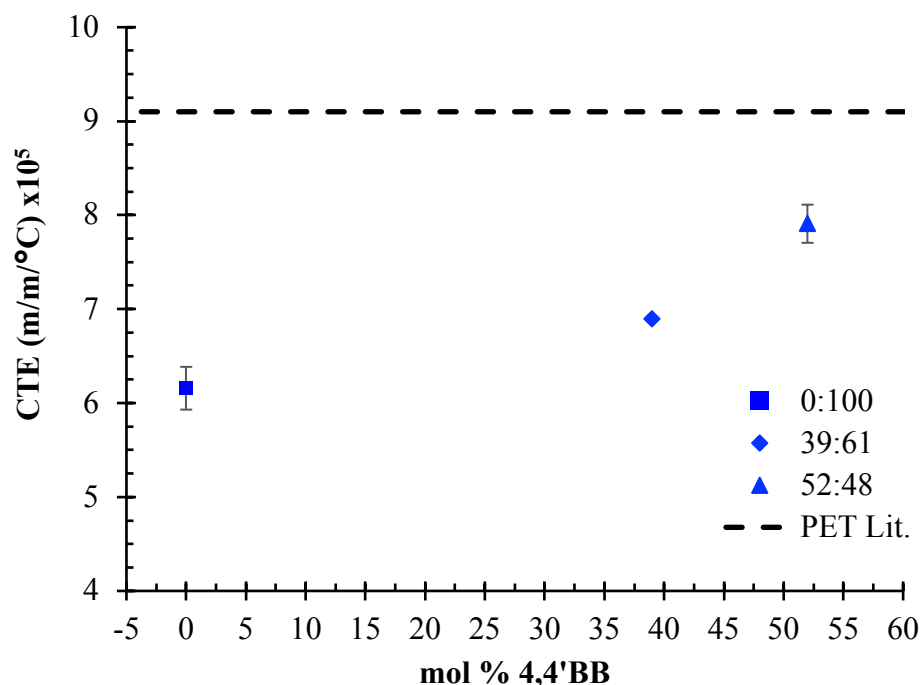


Figure 4.10. Coefficient of thermal expansion (CTE) versus mol % 4,4'BB. BB-based samples possess lower CTE values compared to PET literature (dashed line).

4.5 Conclusions

Most examples of high T_g thermoplastic and amorphous polyesters possess a tradeoff between thermal properties and mechanical properties. The rigid alicyclic monomers utilized to produce higher T_g s limits the high amorphous density and entanglement necessary to impart robust mechanical properties. Alternatively, highly rigid and symmetric aromatic monomers tend to produce highly crystalline polyesters with melting points approaching or exceeding degradation temperatures. Thus, altering the regiochemistry of rigid, aromatic monomers to exploit the asymmetric nature allows for polyesters which possess desired thermal, mechanical, and processing properties.

Bibenzoate (BB)-based (co)polyesters continue to gain interest due to their combination of thermal, barrier, and mechanical properties in comparison to commonly used thermoplastics PET and BPA PC. BB-based (co)polyester possess improved barrier properties compared to PET, improved thermal properties compared to PET and approaching BPA PC, and tensile properties out-performing BPA PC and other high T_g amorphous polyesters. Further surface, mechanical, and thermomechanical testing verified BB-based (co)polyesters performance and applicability in competing with common thermoplastic across a wide range of applications and temperature ranges.

A slightly modified transesterification and polycondensation afforded BB-based (co)polyesters at 150 g scaled, with targeted comonomer incorporations. SEC confirmed molecular weights were consistent with previous smaller scale reactions. APC analysis confirmed relatively high amounts of low molecular weight species, presumably cyclics. The larger reaction quantity allowed for injection molding of dogbone and bar specimens for tensile, flexural, and thermomechanical testing. Prior to processing, water uptake

determined all polyesters required ample drying before processing. Poly(ethylene 3,4'BB) exhibited similar weight % gain as PET at 75% relative humidity and 23 °C. As the 4,4'BB level increased, the weight % increased similarly under the same conditions. Water contact angles corroborated the water uptake analysis with the higher 4,4'BB (co)polyesters possessing a lower water contact angle. All BB-based (co)polyesters possessed water contact angles lower than PET, thus requiring a sufficient drying step before processing. Water uptake hysteresis tests suggested water adsorption as the main weight gain mechanism due to the quick equilibration at the high and lower % relative humidity steps. Melt rheological time sweeps confirmed the melt stability of all BB-based (co)polyesters with less than 10% decrease in η^* at processing conditions.

Tensile stress versus strain curves elucidated the BB-based (co)polyesters' mechanical properties. All samples yielded around 4% tensile strain, with Young's modulus and yield strength increasing with higher levels of 3,4'BB. Flexural stress versus strain analysis corroborated the mechanical properties with similar flexural modulus and flexural strengths approximately 1.5 times greater than tensile yield strengths. HDT measurements confirmed applicability at elevated temperatures and the polyesters ability to perform as a rigid thermoplastic approaching 100 °C. Further thermomechanical analysis probed thermal expansion with higher 3,4'BB levels decreasing the CTE.

Supporting Information.

Synthetic scheme, ^1H NMR spectra, representative water contact image, and stress-strain tensile analysis utilizing an extensometer.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

4.6 Acknowledgements

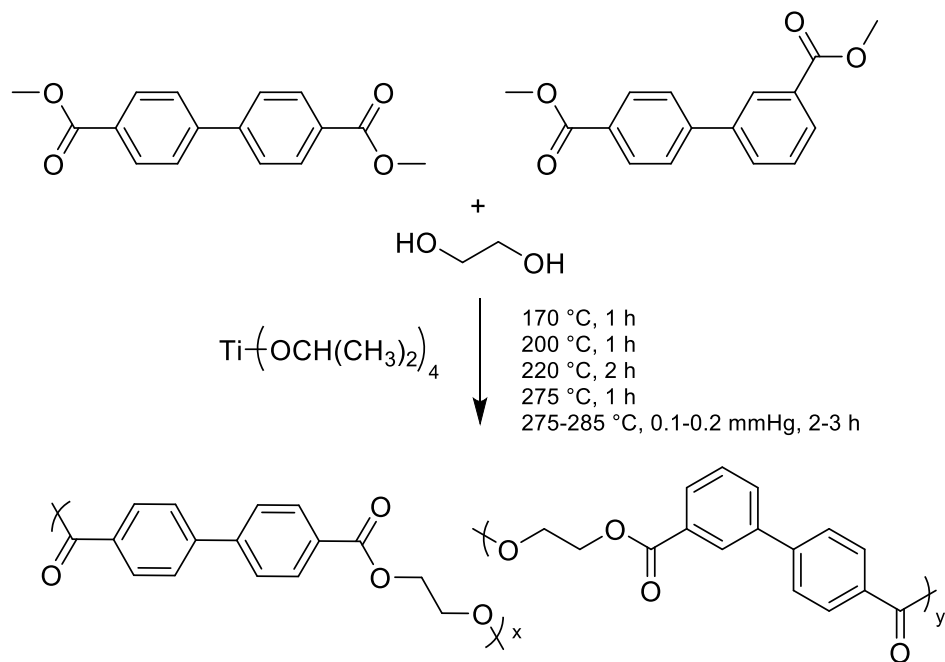
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4.7 References

1. Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of cold-drawn polyesters. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40* (9), 862-877.
2. Hu, Y. S.; Liu, R. Y. F.; Rogunova, M.; Schiraldi, D. A.; Nazarenko, S.; Hiltner, A.; Baer, E., Oxygen-barrier properties of cold-crystallized and melt-crystallized poly(ethylene terephthalate-co-4,4'-bibenzoate). *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40* (22), 2489-2503.
3. Mang, M. N.; Brewbaker, J. L. Thermoplastic Polyesters Containing Biphenylene Linkages. US5138022A, 1992.
4. Asrar, J., High performance polyesters based on 4,4'-biphenyl dicarboxylic acid. In *Specialty polyesters*, Shotland Business Research, Skillman, NJ: 1995.
5. Krigbaum, W. R.; Asrar, J.; Toriumi, H.; Ciferri, A.; Preston, J., Aromatic polyesters forming thermotropic smectic mesophases. *Journal of Polymer Science: Polymer Letters Edition* **1982**, *20* (2), 109-115.
6. Schiraldi, D. A.; Lee, J. J.; Gould, S. A. C.; Occelli, M. L., Mechanical properties and atomic force microscopic cross sectional analysis of injection molded poly(ethylene terephthalate-co-4,4'-bibenzoate). *Journal of Industrial and Engineering Chemistry* **2001**, *7* (2), 67-71.
7. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen - barrier properties of copolymers based on ethylene terephthalate. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (16), 1889-1899.
8. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Comparison of statistical and blocky copolymers of ethylene terephthalate and ethylene 4,4'-bibenzoate based on thermal behavior and oxygen transport properties. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41* (3), 289-307.
9. Nelson, A. M.; Fahs, G. B.; Moore, R. B.; Long, T. E., High-Performance Segmented Liquid Crystalline Copolyesters. *Macromol. Chem. Phys.* **2015**, *216* (16), 1754-1763.
10. Clary, R. S.; Lee, C. D.; Monroe Iv, W. G.; Vaughn, D. A.; Ragheb, R. T.; Erter Iii, J. W.; Brown, D. M.; Schiraldi, D. A., A Green, One-Pot Route to the Biphenyldicarboxylic Acids: Useful Intermediates in Polymer Synthesis. *International Journal of Organic Chemistry* **2013**, *03* (02), 143-147.
11. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R. K.; Nazarenko, S.; Turner, S. R.; Long, T. E., Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance. *Macromolecules* **2017**, *50* (19), 7603-7610.
12. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R.; Sirrine, J. M.; Weiseman, T. F.; Nazarenko, S.; Colby, R. H.; Turner, S. R.; Long, T. E., Influence of Bibenzoate Regioisomers on Cyclohexanedimethanol-based (Co)polyester Structure-Property Relationships. *Macromolecules* **2018**, *In Press*.
13. Edling, H. E.; Liu, H.; Sun, H.; Mondschein, R. J.; Schiraldi, D. A.; Long, T. E.; Turner, S. R., Copolyesters based on bibenzoic acids. *Polymer* **2018**, *135*, 120-130.
14. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E., Influence of cyclobutane segments in cycloaliphatic

- decahydronaphthalene-containing copolyesters. *High Perform. Polym.* **2017**, 29 (6), 750-756.
15. Korhonen, J. T.; Huhtamaki, T.; Ikkala, O.; Ras, R. H., Reliable measurement of the receding contact angle. *Langmuir* **2013**, 29 (12), 3858-63.
 16. Dennis, J. M.; Fahs, G. B.; Moon, N. G.; Mondschein, R. J.; Moore, R. B.; Wilkes, G. L.; Long, T. E., Synthesis of Polysulfone-Containing Poly(butylene terephthalate) Segmented Block Copolymers: Influence of Segment Length on Thermomechanical Performance. *Macromolecules* **2017**, 50 (13), 5107-5113.
 17. Turner, S. R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *J Polym Sci Pol Chem* **2004**, 42 (23), 5847-5852.
 18. Quintana, R.; de Ilarduya, A. M.; Rude, E.; Kint, D. P. R.; Alla, A.; Galbis, J. A.; Munoz-Guerra, S., Poly(ethylene isophthalate)s: effect of the tert-butyl substituent on structure and properties. *Polymer* **2004**, 45 (15), 5005-5012.
 19. Merdas, I.; Thominet, F.; Tcharkhtchi, A.; Verdu, J., Factors governing water absorption by composite matrices. *Compos. Sci. Technol.* **2002**, 62 (4), 487-492.
 20. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Improving oxygen barrier properties of poly(ethylene terephthalate) by incorporating isophthalate. I. Effect of orientation. *J. Appl. Polym. Sci.* **2005**, 98 (4), 1615-1628.
 21. Tang, P.; Brouwers, H. J. H., Integral recycling of municipal solid waste incineration (MSWI) bottom ash fines (0-2 mm) and industrial powder wastes by cold-bonding pelletization. *Waste Manage. (Oxford)* **2017**, 62, 125-138.
 22. Karayiannis, N. C.; Mavrantzas, V. G.; Theodorou, D. N., Detailed atomistic simulation of the segmental dynamics and barrier properties of amorphous poly(ethylene terephthalate) and poly(ethylene isophthalate). *Macromolecules* **2004**, 37 (8), 2978-2995.
 23. Nielsen, L. E.; Landel, R. F., *Mechanical Properties of Polymers and Composites*. 2nd ed.; Marcel Dekker, Inc.: New York, 1994.
 24. Wadud, S. E. B.; Ullbrich, R. R. *Using the DMA Q800 for ASTM International D 648 Deflection Temperature Under Load*; tainsruments.com.
 25. Knowles, K. R. Effect of Chain Rigidity on Network Architecture and Deformation Behavior of Glassy Polymer Networks. The University of Southern Mississippi, Hattiesburg, MS, 2017.
 26. *Hand Book of Plastics Materials and Technology, Rubin II, Ed.* John Wiley and Sons, Inc.: New York, 1990.
 27. Brozenick, N. J., *Modern Plastics Encyclopedia*. McGraw-Hill, Inc.: New York, 1986-1987.

4.8 Supporting Information



Scheme S4.1 Synthesis of x-4,4'BB-y-3,4'BB-EG co(polyesters).

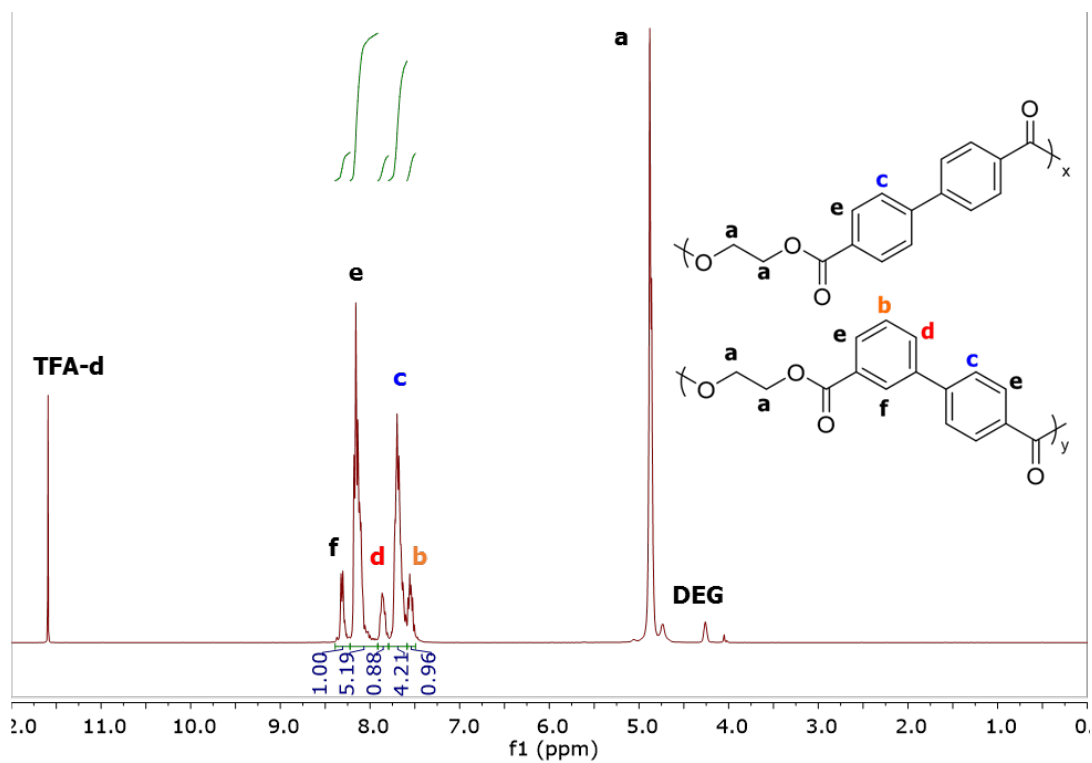


Figure S4.1 Representative ^1H NMR spectra of 39-4,4'BB-61-3,4'BB-EG. DEG content is $\sim 4\%$.

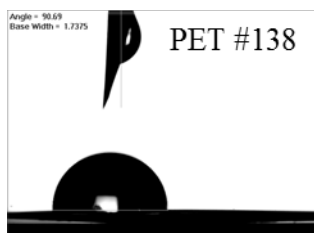


Figure S4.2 Representative water contact angle measurements of lab synthesized PET.

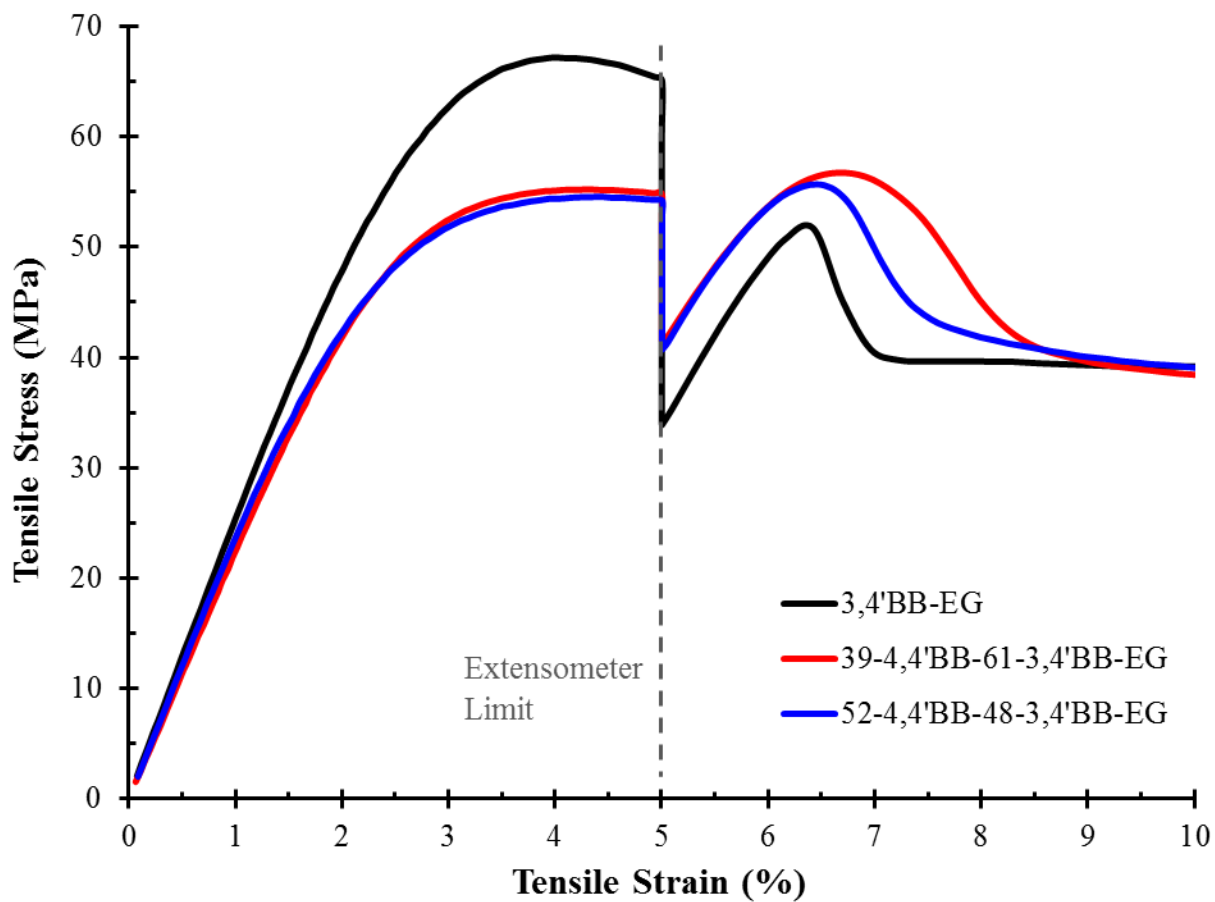


Figure S4.3. Tensile mechanical testing using an extensometer. Young's modulus determined from the slope of the linear portion of the stress vs. strain plot. Due to the limit of the extensometer extension, only the Young's modulus was determined from these tensile experiments. A 10 mm/min extension rate was employed.

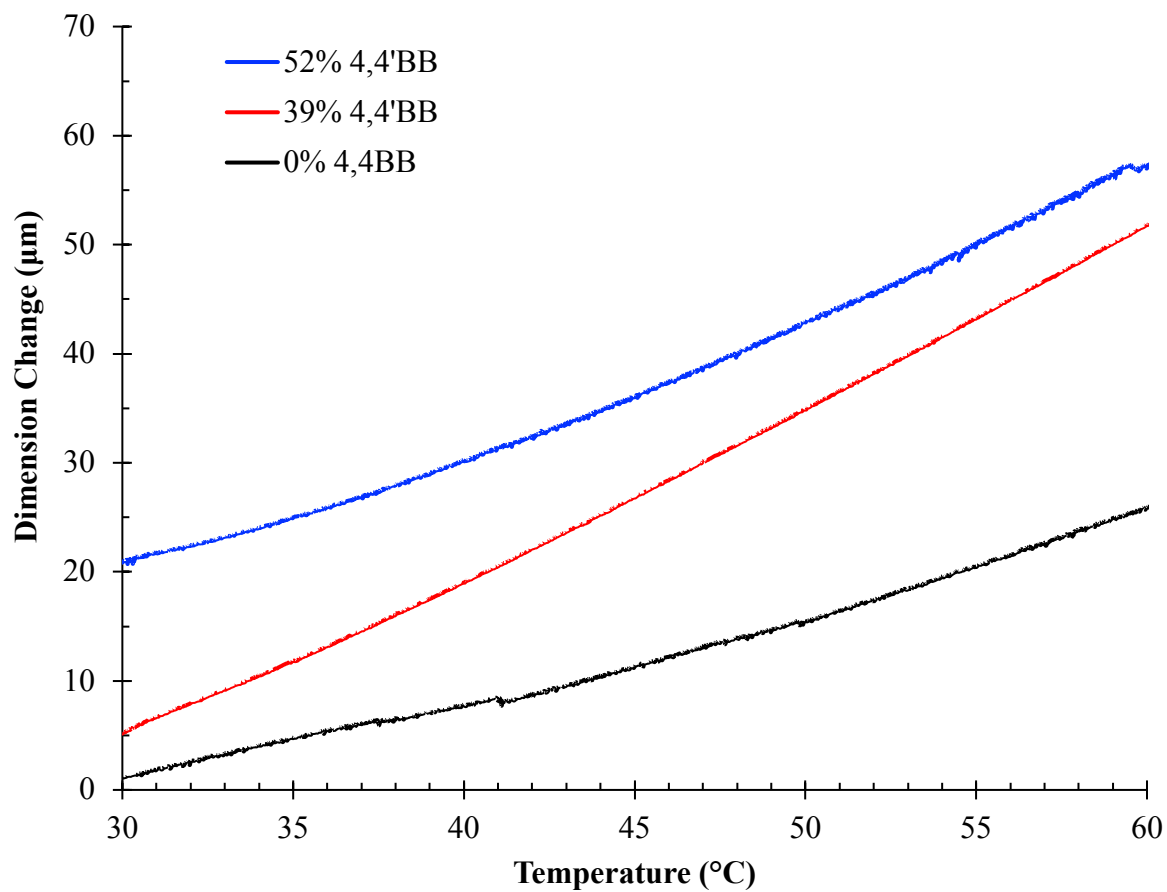


Figure S4.4. Thermomechanical analysis (TMA) of BB-based (co)polyesters below T_g . Dimension change *versus* Temperature enabled analysis of coefficient of thermal expansion (CTE) analysis. 39 mol % 4,4'BB exhibits a higher slope because of its longer starting length.

Chapter 5: Synthesis and Characterization of PET-based (Co)polyester Regioisomers Incorporating Hydroxyethylresorcinol (HER) or Hydroxyethylhydroquinone (HEH)

(Manuscript in preparation for publication)

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5.1 Abstract

Melt transesterification and polycondensation incorporating *meta*-substituted hydroxyethylresorcinol (HER) or *para*-substituted hydroxyethylhydroquinone (HEH) regioisomers enabled the synthesis of poly(ethylene terephthalate) (PET)-based (co)polyesters with targeted comonomer mol %. Incorporation of either HER or HEH lowered the glass transition temperature (T_g) relative to PET, but did not change the 5% weight loss temperature ($T_{d,5\%}$). Similarly, amorphous/semi-crystalline morphology depended on monomer selection and mol % comonomer. Sub T_g relaxation analysis confirmed decreasing beta-relaxation intensities for both HER and HEH incorporation, while HER impacted beta-relaxation intensity more at similar mol %. HER incorporation also shifted the beta-relaxation temperature (T_β) to lower temperatures considerably more than HEH. Time-temperature-superposition (TTS) shifts and Williams-Landel-Ferry (WLF) analysis of melt rheology probed physical polymer characteristics including melt flow activation energy (E_a), fractional free volume at T_g (f_g), and molecular weight of

entanglement (M_e). HER-based (co)polyesters exhibited lower E_a compared to HEH. Likewise, HER incorporation lowered f_g while HEH incorporation increased f_g . HER-based (co)polyesters possessed higher M_e compared to HEH-based (co)polyesters, although both resulted in higher M_e compared to PET. Tensile testing determined HER/HEH-based (co)polyesters mechanical integrity compared to amorphous PET. Both HER and HEH incorporation increased Young's modulus and yield strengths, although comonomer incorporation above 25-30 mol % yielded minimal change. As a result, structure-property relationships provided insight into different regioisomers and comonomer incorporations impact on thermal, rheological, and mechanical performance for PET-based (co)polyesters.

5.2 Introduction

Typical methods to enhance bulk properties in common thermoplastics, such as poly(ethylene terephthalate) (PET), include incorporating comonomers,¹⁻¹⁴ tuning morphology,^{4, 15-19} and utilizing additives.¹⁸⁻²¹ Synthesizing (co)polyesters through comonomer incorporation offers the greatest ability to widely impact desired properties. Common comonomers for PET include rigid aromatic bibenzoates,^{3-4, 11-12, 14, 22-24} phthalate regioisomers,^{1, 5-7, 13, 22, 25-27} ether/alicyclic diols,^{2, 8, 28-30} and aromatic ether diols.^{10, 31-34} One particular diol of interest is 1,3-bis(2-hydroxyethyl)resorcinol (HER) due to the large reduction in O_2 permeability when incorporated as a comonomer into PET.^{10, 31, 33} Although limited investigation offers insight into the increased barrier of HER incorporation, hypothesis include the reduction in short-range segmental relaxations limiting gas diffusion³²⁻³³ as well as a lower free volume reducing gas solubility.³³ As a result of improved barrier properties, polyesters incorporating HER remain attractive candidates for

food packaging applications. Although poly(ethylene-co-HER terephthalate) (poly(E-co-HER T)) (co)polyesters exhibit desirable barrier performance, there is a lack of thermomechanical, rheological, and mechanical characterization. Thus, further evaluation of these (co)polyesters as candidates for a variety of thermoplastic applications requires bulk property analysis to fully understand the influence of HER incorporation.

Recent literature also highlights the influence backbone regiochemistry imparts on rheological, mechanical, and barrier properties.^{14, 35-38} Bibenzoate (co)polyester-regioisomers exhibited tunable glass transition temperatures (T_g), melting temperatures (T_m), and mechanical properties including tensile and flexural modulus/strength.^{35, 37} Incorporating these regioisomeric monomers into copolymers with PET afforded increased T_g s, mechanical properties, and barrier performance.¹⁴ Thus, the *para* regioisomer of HER, 1,4-bis(2-hydroxyethyl)hydroquinone (HEH), is intriguing to analyze in concert with HER, as limited literature has reviewed the incorporation of HEH into PET (poly(E-co-HEH)).³⁹ Systematic studies of thermal, rheological, and mechanical properties helps to further understand the influence of regiochemistry and kinked versus linear polymers on various properties.

This report highlights the synthesis and characterization of poly(E-co-HER T) and poly(E-co-HEH T) (co)polyesters. Melt transesterification and melt polycondensation afforded series of PET (co)polymers with targeted incorporation of HER and HEH up to 100 mol %. Analytical polymer characterization probed compositional, thermal, rheological, and mechanical properties. Incorporation of both HER and HEH afforded tunable thermal properties and amorphous/semi-crystalline morphology based on monomer selection and mol % comonomer incorporation. Melt rheological analysis in

conjunction with time-temperature-superposition (TTS) and Williams-Landel-Ferry (WLF) analysis determined physical polymer characteristics. Tensile testing also characterized HER/HEH-based (co)polyesters mechanical integrity. Through systematic analysis, structure-property relationships developed between different regioisomers and comonomer incorporations allowed for determination of these (co)polyesters applicability in a broad range of thermoplastic applications such as food packaging.

5.3 Experimental

5.3.1 Materials. 1,3-bis(2-hydroxyethyl)resorcinol (HER) (>98.0%) was supplied by TCI America and 1,4-bis(2-hydroxyethyl)hydroquinone (HEH) (98%) and dimethyl terephthalate (DMT) (ReagentPlus $\geq 99\%$) was supplied by MilliporeSigma and used as received. Ethylene glycol (EG) (Sigma-Aldrich, $\geq 99\%$) was used as received. Titanium tetra(isopropoxide) (99%) was purchased from Sigma-Aldrich, and a 0.01 g/mL titanium solution (anhydrous 1-butanol) was prepared according to previously detailed procedures.¹⁵ All solvents were obtained from Spectrum and used as received. Nitrogen gas (Praxair, 99.999%) was used as received.

5.3.2 Analytical Methods. ^1H NMR spectroscopy was performed at 23 °C and at 400 MHz on a Varian Unity 400 in deuterated chloroform (CDCl_3). A Waters size exclusion chromatograph (SEC) utilizing an auto sampler, three 5 μm PLgel Mixed-C columns, and connected to a Waters 2410 refractive index (RI) detector with a flow rate of 1 mL min^{-1} at 35 °C in chloroform (CHCl_3) afforded molecular weight determination relative to polystyrene standards. Dynamic light scattering (DLS) at 35 °C analyzed all polymer solutions in CHCl_3 , prior to SEC analysis, to confirm no aggregation in the utilized SEC solvent. Differential scanning calorimetry (DSC) characterized thermal transitions using a

TA instruments Q1000 DSC, calibrated utilizing indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards, and using a nitrogen flow of 50 mL/min at a 10 °C min⁻¹ heating rate and a 10 °C min⁻¹ cooling rate. Utilizing the second heating ramp, glass transition temperatures (T_g) were determined at the midpoint of the transition and melting temperatures (T_m) were determined at the maximum of the endothermic peak. Thermogravimetric analysis (TGA) using a TA Instruments Q50 from 25 to 600 °C at a 10 °C min⁻¹ heating rate probed weight loss versus temperature. Dynamic mechanical analysis (DMA) utilizing a TA Instruments Q800 Dynamic Mechanical Analyzer in oscillatory tension mode at a 1 Hz frequency, a 15 µm oscillatory amplitude, and a 0.01 N static force with a 3 °C min⁻¹ temperature ramp revealed modulus *versus* temperature behavior. Compression molding films was performed with PHI Q-203H manual hydraulic press. Tensile property measurements and data analysis followed guidance from ASTM D638. An Instron model No. 4411 using a 1kN load cell applied a 10 mm min⁻¹ crosshead motion rate in ambient conditions.

Rheological analysis was performed on a TA Instruments Discovery Hybrid Rheometer (DHR)-2 using a disposable 8 mm diameter aluminum parallel-plate geometry under N₂ atmosphere. Strain sweep testing from 0.01-10% oscillatory strain at 1 Hz probed the linear viscoelastic region (LVR). Utilizing 1.25% oscillatory strain and an oscillatory frequency range of 1-100 rad s⁻¹, frequency sweeps at 10 °C intervals from 170 °C to 270 °C provided viscosity as well as storage and loss moduli. TA Instruments software (TRIOS) generated master curves by shifted resulting data. Melt flow property determination involved fitting shift factors resulting from master curve generation to the WLF equation utilizing the TRIOS software.

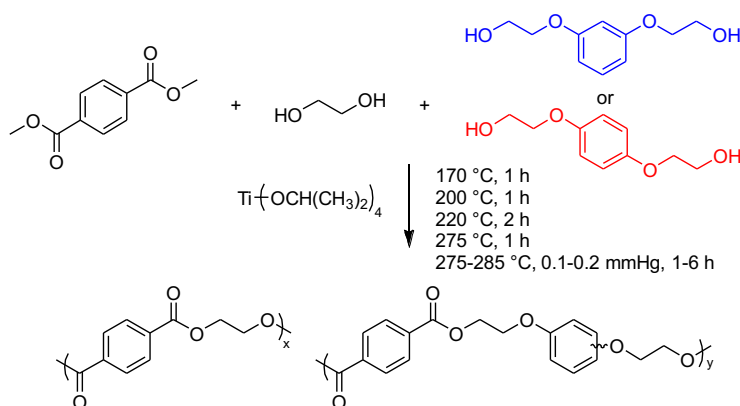
5.3.3 Synthesis of poly(E-co-(HER/HEH) T). The following example details the synthetic procedure for all (co)polyesters and the synthesis of 50:50 E:HER is used as a representative example. Reactions were performed in a dry 100-mL round-bottomed flask equipped with a nitrogen inlet, overhead stirrer, and distillation apparatus. EG (7.16 g, 1.0 mol equiv), HER (11.43 g, 0.5 mol equiv), and DMT (22.39 g, 1.0 mol equiv) were introduced to the flask. Titanium tetra(isopropoxide) (0.16 mL; 40 ppm; 0.01 g/mL in anhydrous 1-butanol) catalyst was then added to the monomers. Vacuum degassing and purging with nitrogen 3x allowed the reaction to proceed free of oxygen. The reaction progressed at 170 °C for 1 h, 200 °C for 1 h, 220 °C for 2 h, and 275 °C for 1 h, all under constant 75-100 rpm stirring and N₂ purge. Methanol condensate was collected in a cold round-bottomed flask to ensure reaction progress. Applying vacuum resulted in a system pressure of 0.1-0.2 mmHg and the reaction continued by stirring at 275 °C for 1-6 h. Polymer was isolated by breaking the flask and collecting the solid polymer from the stir rod. No further purification was necessary.

5.3.4 Compression molding. Compression molding followed previously published procedures.^{37, 40}

5.4 Results and Discussion

Melt polymerization of regioisomeric HER or HEH with EG and DMT utilized titanium tetra(isopropoxide) as a catalyst and produced two series of PET-based (co)polyesters adapted from previously reported procedures.^{14, 36-38} Charged amounts of HER or HEH matched desired incorporation as minimal loss of HER or HEH occurred during polycondensation due to the higher boiling points of these diols compared to EG. Excess charged EG ensured enough diol remained in the reaction throughout transesterification and subsequent polycondensation. Two equiv of desired EG

incorporation was charged to the flask to ensure EG endured the polymerization when EG targets were > 50 mol %. At least 0.5 mol equiv excess EG was charged to the reaction for EG targets < 50 mol % to ensure adequate excess EG during polymerization. Briefly, transesterification in the melt enabled subsequent polycondensation under reduced pressure to afford (co)polyesters with targeted HER or HEH regioisomer incorporation, as seen in **Scheme 5.1**. Transesterification started at 170 °C with stirring under N₂ and condensation of methanol ensured reaction progress. Once condensate production ceased, transesterification continued with heating to 200 °C for 1 h, 220 °C for 2 h, and 275 °C for 1 h. Polycondensation ensued through application of vacuum to attain 0.1-0.2 mmHg pressure in the reaction flask to facilitate removal of excess EG. Once the melt achieved visibly high viscosity, indicated by the polyester melt wrapping the metal mechanical stirring rod, the reaction finished. EG removal stopped between 1 and 6 h at reduced pressure, suggesting polymerization produced high molecular weight (co)polyesters. Optically clear (co)polyesters resulted for all compositions with > 20 mol % HER or HEH incorporation.



Scheme 5.1. Synthesis of poly[ethylene(E)-co-hydroxyethyl(resorcinol(HER)/hydroquinone(HEH)) terephthalate(T)] (co)polyesters utilizing DMT, EG, and hydroxyethylresorcinol (blue) or hydroxyethylhydroquinone (red).

Size exclusion chromatography (SEC) confirmed molecular weight consistent with bottle grade PET for all compositions soluble in solvents suitable for our SEC setups (Figure S5.1.). A low molecular weight tail suggests cyclic formation, common for step growth polymerization and PET synthesis,⁴¹⁻⁴⁷ but a lack of a high molecular weight tail suggested linear polymers with no branching. Most (co)polyesters produced heterogeneous solutions in common, non-hazardous SEC solvents, thus unsuitable for analysis. Viscosity comparisons confirmed similar molecular weights for all compositions. ¹H NMR spectroscopy subsequently confirmed incorporation of targeted (co)polyesters' compositions (Figure S5.2.-S5.3.). Final compositions agreed well with charged monomer targets (± 2 mol %), suggesting limited removal of the HER or HEH monomer upon complete polycondensation.

Thermogravimetric analysis (TGA) (Figure S.4. & S.5.) and differential scanning calorimetry (DSC) (Figure S.6. & S.7.) identified thermal properties for all PET-based (co)polyesters. TGA revealed a single-step weight loss occurring around 400 °C for all compositions, consistent with expected weight loss for semi-aromatic (co)polyesters.³⁷ Glass transition temperatures (T_g) decreased upon incorporation of HEH or HER and only one T_g was observed for each composition. As seen in **Figure 5.1** and summarized in **Table 5.1**, *meta*-substituted HER decreased the T_g more than *para*-substituted HEH at similar mol % compositions, consistent with previous polyester regioisomers.^{14, 22, 35, 37} Both HER- and HEH-based (co)polyesters' T_g s matched the Fox eq. fit over the entire composition range, suggesting random repeat unit sequences resulting from polymerization at high temperatures. Thus, these (co)polyesters possess predictable T_g s.

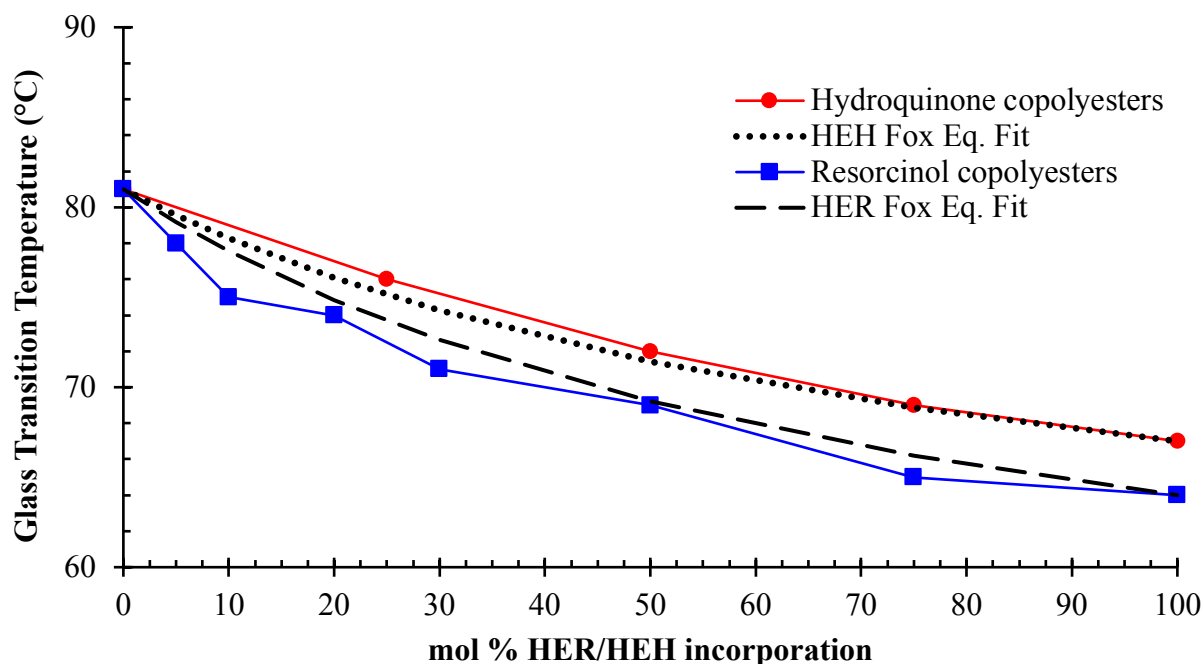


Figure 5.1. Glass transition temperature (T_g) versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

Both HER- and HEH-based (co)polyesters exhibited an endothermic melting peak for compositions ≤ 25 mol % HER/HEH due to the semi-crystalline nature of PET, (Figure S5.6. & S5.7.) and the associated T_m s are plotted in **Figure 5.2** and summarized in **Table 5.1**. Upon incorporation of > 25 mol % HER, (co)polyesters remained amorphous due to the *meta*-substitution disrupting chain-regularity. HEH-based (co)polyesters possessed an amorphous morphology between 25 and 75 mol % HEH incorporation, due to random comonomer incorporation limiting crystallizability at these conditions. Once HEH levels reached 75 mol %, (co)polyesters once again possessed crystallinity due to the regularity and high wt % of the *para*-substituted HEH. HEH-based (co)polyesters displayed eutectic behavior with a melting point depression as a result upon incorporation of EG.

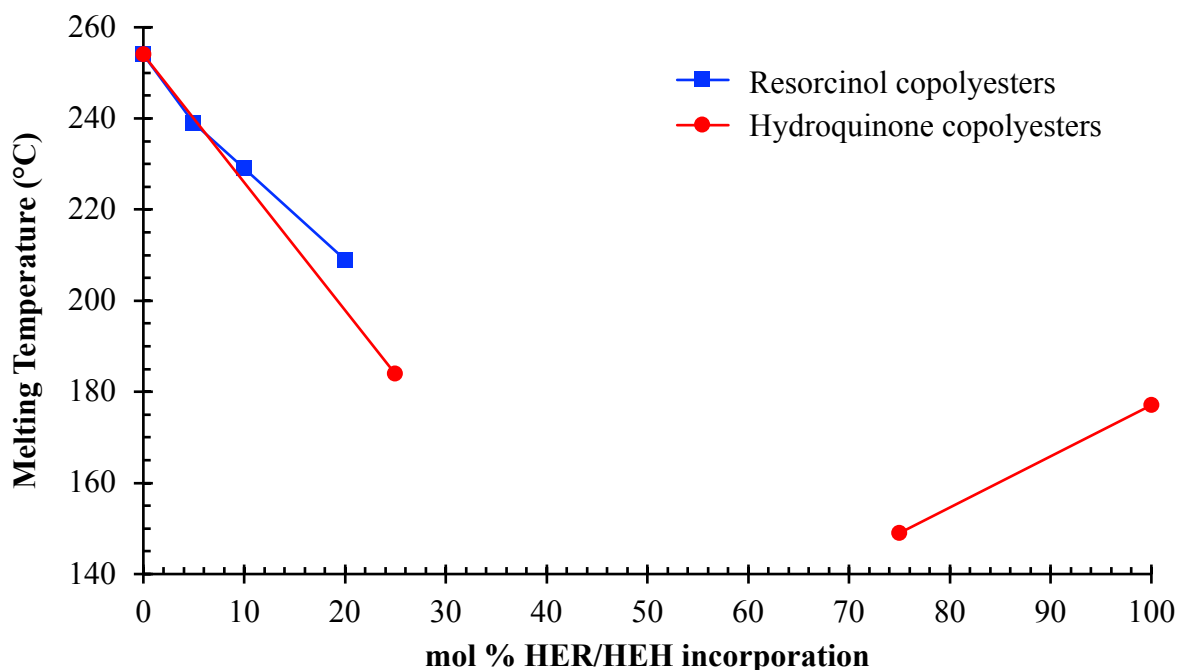


Figure 5.2. Melting temperature (T_m) versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red circle).

Dynamic mechanical analysis (DMA) corroborated DSC T_g s, as summarized in **Table 5.1**, while also probing sub T_g relaxations. All (co)polyesters displayed a similar temperature-insensitive glassy modulus from -150 °C up until the T_g (Figures S5.8. & S5.9.). All (co)polyesters exhibited an onset of flow temperature (T_{flow}) around 120 °C. Low temperature β -relaxations (T_β), analyzed from $\tan \delta$ curves, represent short range motions such as ring rotations, chair conformation flips, etc.^{2, 22, 48-50} and are associated with barrier performance^{14, 22, 37, 48, 51-52} and impact resistance.⁵³⁻⁵⁶ Incorporation of HER or HEH decreased β -relaxation intensity while also shifting T_β to lower temperatures, as seen in **Figure 5.3** and **Figure 5.4** and summarized in **Table 5.1**. HER-based (co)polyesters exhibited larger decreases in β -relaxation intensity due to the *meta*-substitution limiting ring-rotation compared to the *para*-substituted HEH (co)polyesters, as well as a likely higher density of fully amorphous sample, similar to other *meta* versus *para*

(co)polyesters.²² Higher HER levels also resulted in lower T_β indicating shorter relaxation times for conformational changes compared to the HEH-based (co)polyesters.

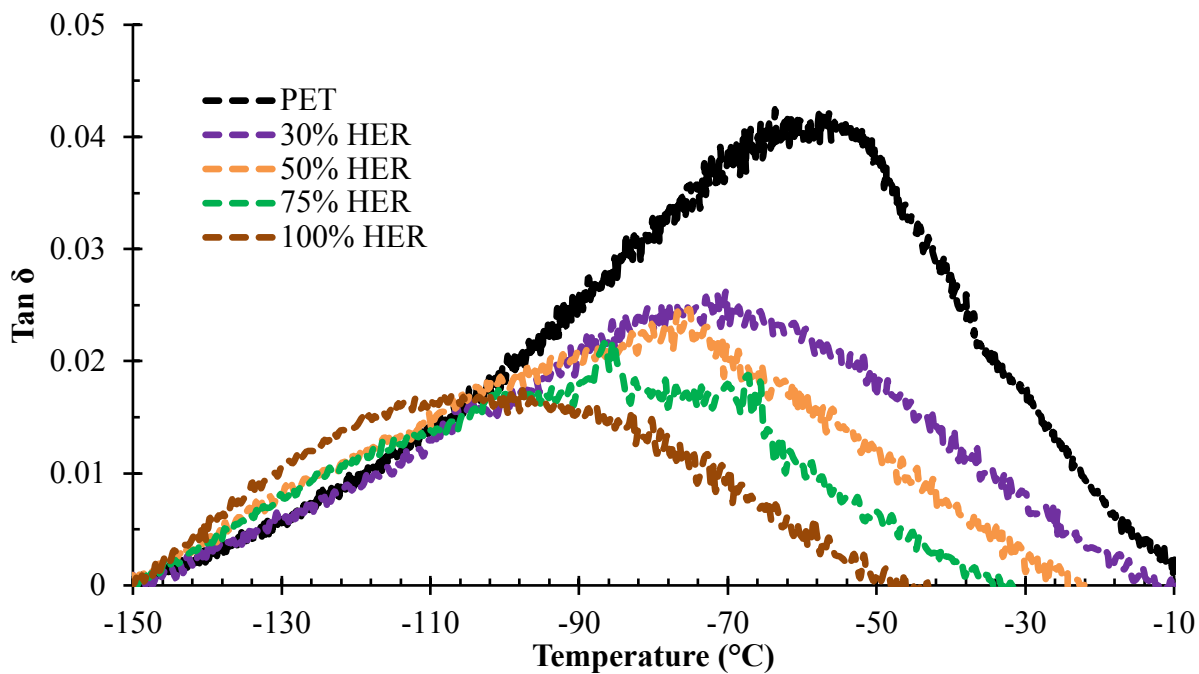


Figure 5.3. Sub- T_g relaxation analysis of poly(E_x -co- HER_y terephthalate) (co)polyesters from $\tan \delta$ versus temperature using DMA.

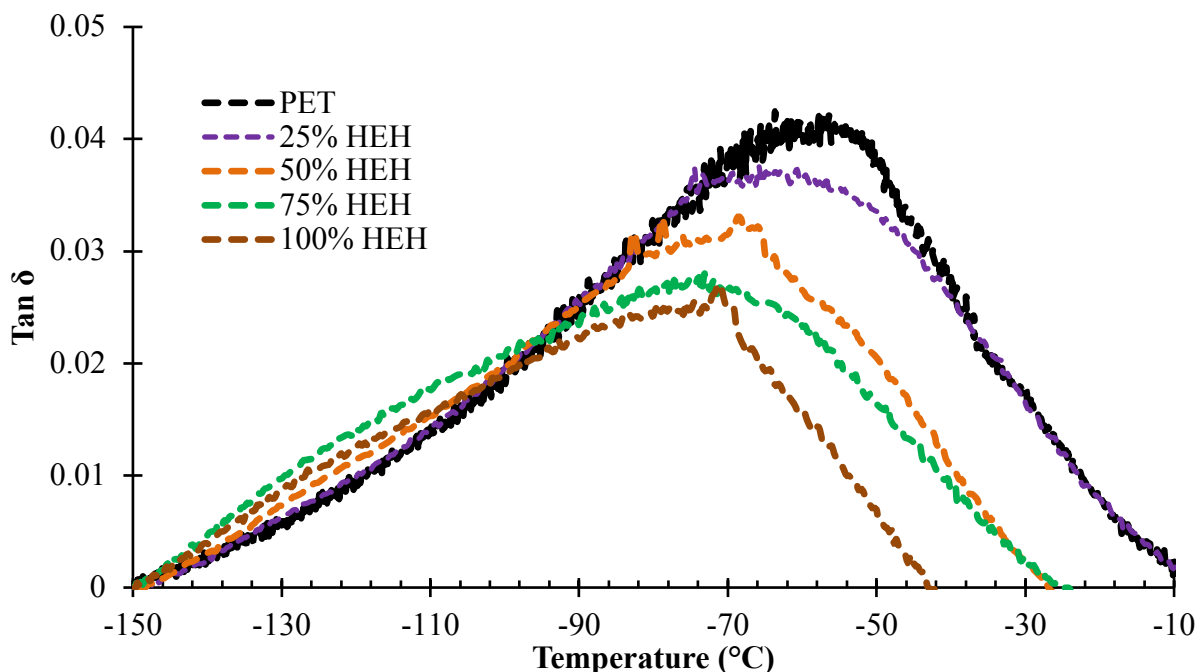


Figure 5.4. Sub- T_g relaxation analysis of poly(E_x -co- HEH_y T) (co)polyesters from $\tan \delta$ versus temperature using DMA.

Table 5.1. Summary of thermal properties for poly[ethylene-co-hydroxyethyl(resorcinol/hydroquinone) terephthalate] (co)polyesters.

Comonomer	Mol % HER/HEH	T_g (DSC) ^a	T_g (DMA) ^b	T_m (DSC) ^a	T_β (DMA) ^b
		°C	°C	°C	°C
PET	0	81	90	254	-55
PET-HER	30	71	80	ND	-69
	50	69	76	ND	-74
	75	65	75	ND	-84
	100	64	73	ND	-101
PET-HEH	25	76	85	184	-66
	50	72	80	ND	-69
	75	69	78	149	-71
	100	67	76	177	-75

^b DSC: heat/cool/heat, second heat; N₂, 10 °C/min. T_g reported as midpoint of step transition, T_m reported as peak maximum of endothermic event.

^c DMA: tension mode, 1 Hz, 3 °C/min. T_g reported as peak maximum in $\tan \delta$ curve, T_{flow} reported as temperature prior to modulus approaching zero.

Further analysis into chain relaxations and viscoelastic polymer properties required melt rheology. Storage (G') and loss (G'') moduli values from different temperatures were shifted to overlay across eight decades of angular frequencies. The generated master curves, which obeyed time-temperature-superposition (TTS) guidelines, allowed for determination of shift factors, a_T , and analysis utilizing the Williams-Landel-Ferry (WLF) equation determined universal constants C_1 and C_2 , summarized in **Table 5.2**. Crossovers between G' and G'' determined the reciprocal of characteristic relaxation times of reptation ($1/\tau_{\text{rep}}$), entanglement ($1/\tau_e$), and segmental motion ($1/\tau_0$), at a common reference temperature (T_r) of 160 °C for all compositions, as seen in **Figure 5.5**.

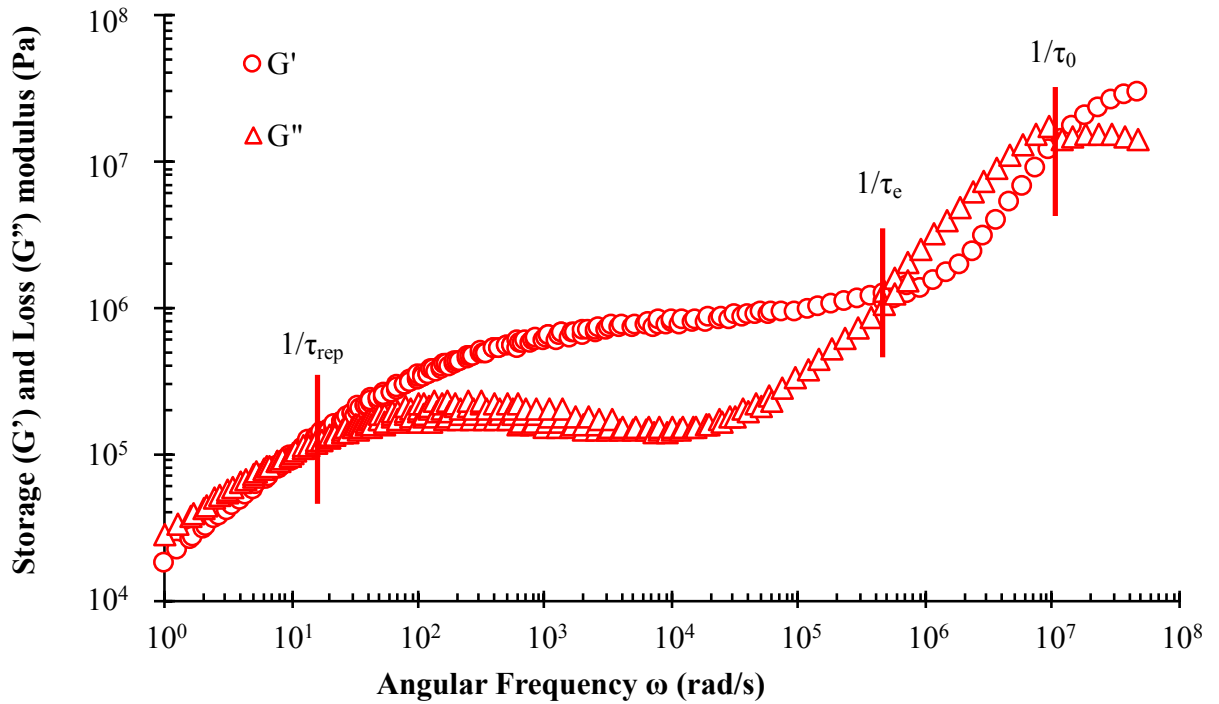


Figure 5.5. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(E₂₅-co-HER₇₅ T). Characteristic relaxation crossovers $1/\tau_{\text{rep}}$, $1/\tau_e$, and $1/\tau_0$ are marked.

Calculating universal constants C_1^g and C_2^g utilizing eq. 5.1 and 5.2, allowed for direct comparison to literature values. These universal constants agreed well with other

linear, nonassociating polymers.^{36-38, 57} Further application of the universal constants to eq. 5.3 provided fractional free volume analysis at the T_g (f_g) as seen in **Figure 5.6** and summarized in **Table 5.2**. Incorporation of HER systematically lowered f_g while higher levels of HEH increased f_g . The *meta*-substitution and thus kinked nature of HER allows for denser chain packing²² and melt density, thus a smaller f_g upon higher incorporation. Alternatively, the *para*-substitution and linear nature of HEH limits chain packing compared to HER,³⁹ thus a larger f_g upon higher incorporation.

$$C_1^g = \frac{C_1 C_2}{C_2 + (T_g - T_r)} \quad \text{Eq. 1}$$

$$C_2^g = C_2 + (T_g - T_r) \quad \text{Eq. 2}$$

$$f_g = \frac{B}{2.303 C_1^g} \quad \text{Eq. 3}$$

Table 5.2. Summary of WLF parameters, fractional free volumes, and melt flow activation energies of poly[ethylene-co-hydroxyethyl(resorcinol/hydroquinone) terephthalate] (co)polyesters.

		C_1	C_2	C_1^g	C_2^g	f_g	E_a	M_e
	Mol %		K		K		kJ mol^{-1}	g mol^{-1}
HER	30	1.4	238.4	8.7	39.4	0.050	48.2	2500
	50	1.8	249.0	9.2	48.0	0.047	47.8	2900
	75	1.4	240.6	9.6	35.6	0.045	46.4	3200
	100	1.4	240.2	10.0	34.2	0.043	45.1	3400
HEH	25	1.9	248.2	8.7	54.2	0.050	55.2	2200
	50	2.4	280.9	8.1	82.9	0.054	53.9	2400
	75	2.4	305.7	7.4	99.7	0.059	50.1	2700

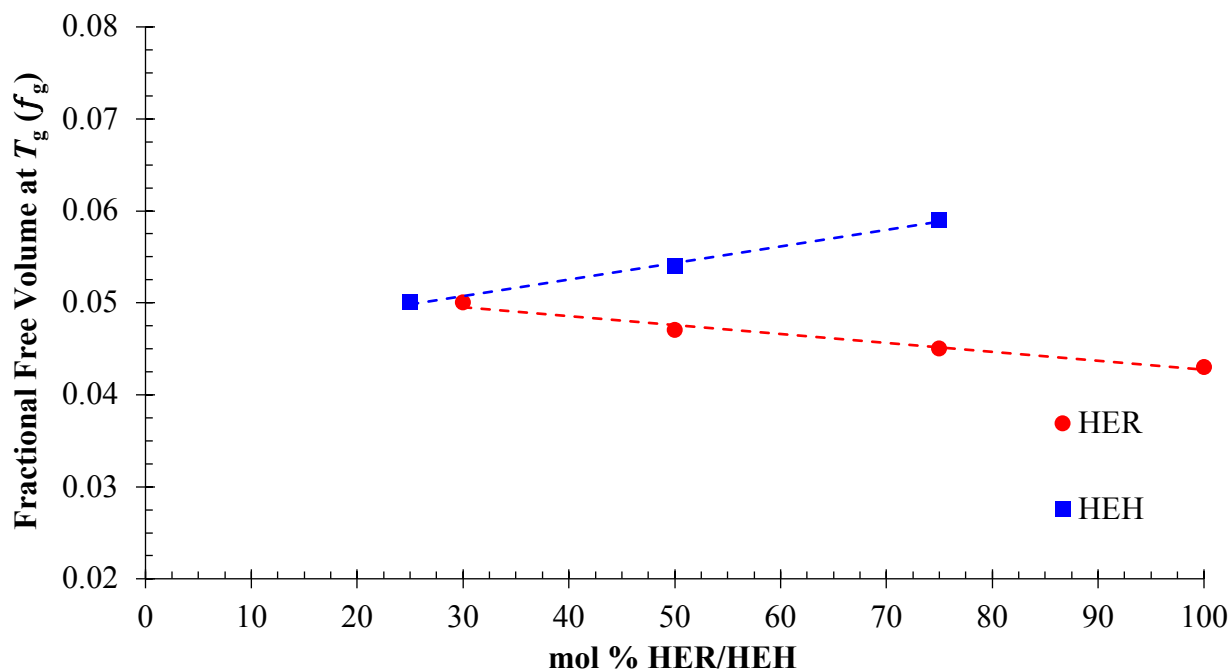


Figure 5.6. Fractional free volumes at T_g (f_g) from WLF analysis of TTS shift factors versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

Arrhenius analysis of shift factors at high temperatures allowed for the determination of melt flow activation energy (E_a). As seen in **Figure 5.7**, incorporation of both HER and HEH decrease the E_a compared to PET. Both comonomers contain flexible ether linkages and space out the terephthalate unit more than EG, thus HER or HEH incorporation into PET reduces the energy requirement for flow. HEH requires a larger amount of energy to undergo flow relative to HER-based (co)polyesters at similar mol % incorporations. The linear, *para*-substitution of HEH hinders rotational freedom and conformational perturbations³⁶ while also possessing a slightly higher T_g compared to the kinked, *meta*-substituted HER. Thus more energy is needed in the system for the chains to undergo reptation and subsequent flow.³⁵

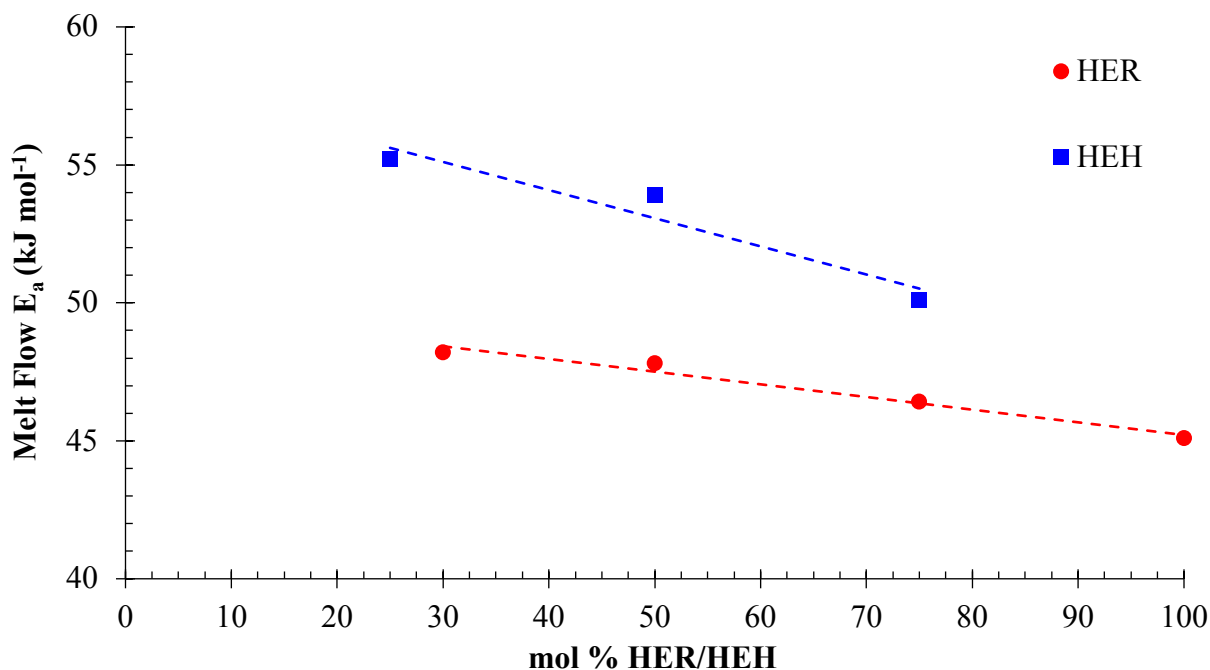


Figure 5.7. Melt flow activation energy (E_a) from Arrhenius analysis of TTS shift factors versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

Further analysis of the (co)polyesters master curves reveal characteristic viscoelastic behavior. At frequencies greater than $1/\tau_0$, the polymer behaves as a rigid glass, similar to below T_g . At frequencies below $1/\tau_0$ and until $1/\tau_{rep}$, the master curve reveals rubbery behavior with a characteristic storage modulus plateau. The breadth of this plateau is directly correlated to the number of entanglements per chain,^{35, 57-59} while the modulus of this plateau (G_N^0) is directly related to the molecular weight of entanglement (M_e) for linear, non-associating polymer chains (eq. S5.1).^{35, 58-59} As seen in **Figure 5.8** and summarized in **Table 5.2**, the M_e is greater for both HER- and HEH-based (co)polyesters compared to PET.²² The kinked, *meta*-substituted HER likely possesses a smaller coil size than PET and P(E-co-HEH T), thus a higher M_e , similar to the kinked poly(ethylene isophthalate) (PEI).^{5, 60} A larger coil size for HEH-based (co)polyesters promotes entanglements resulting in a lower M_e compared to PET.

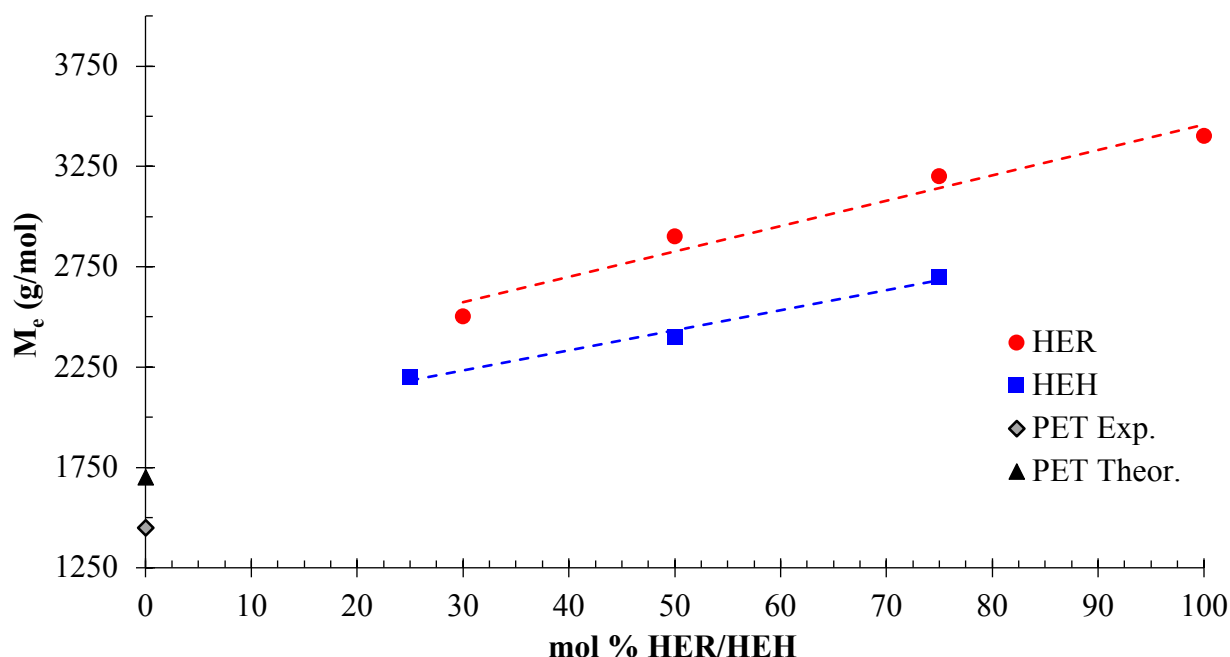


Figure 5.8. Molecular weight of entanglement (M_e) determined from storage modulus (G') plateau of TTS master curves versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

Tensile testing probed the influence of HER and HEH incorporation on mechanical integrity. Stress versus strain curves elucidated tensile deformation behavior and analysis resulted in Young's modulus and yield strength measurements. As seen in **Figure 5.9**, Young's modulus increases with increasing incorporation of HER or HEH. HER incorporation increases Young's modulus more than HEH due the kinked nature of the backbone, consistent with previous literature.^{14, 35, 37} Although the Young's modulus initially increases, greater backbone flexibility due to the ether linkages limits the overall increase as HER incorporation increases. Yield strength measurements follows a similar trend as Young's modulus, as seen in **Figure 5.10**. All samples yielded around 4% strain, thus a similar trend is expected for the yield strength as Young's modulus.

HER-based (co)polyesters exhibited brittle fracture soon after yielding, around 4.5% strain (Figure S5.22.). HEH-based (co)polyesters reached 200-250% strain,

consistent with PET elongation (Figures S.22. & S.23.). The increase in elongation to break for the HEH-based (co)polyesters results from the lower M_e as well as the higher molecular weight, suggested by the higher zero-shear viscosity analyzed by melt rheology. HEH-based (co)polyesters exhibit a slightly earlier onset of strain hardening (~100% strain) compared to PET. Increasing the mol % of HEH also increased the strain hardening slope, consistent with previous literature which incorporated more rigid and linear comonomers.³⁵ Strain hardening is a desirable property for PET and polyesters due processing methods applying high amounts of strain as well as pressurized applications. Thus, the increase in strain hardening of the HEH-based (co)polyesters is interesting for applications in packaging and oriented films.

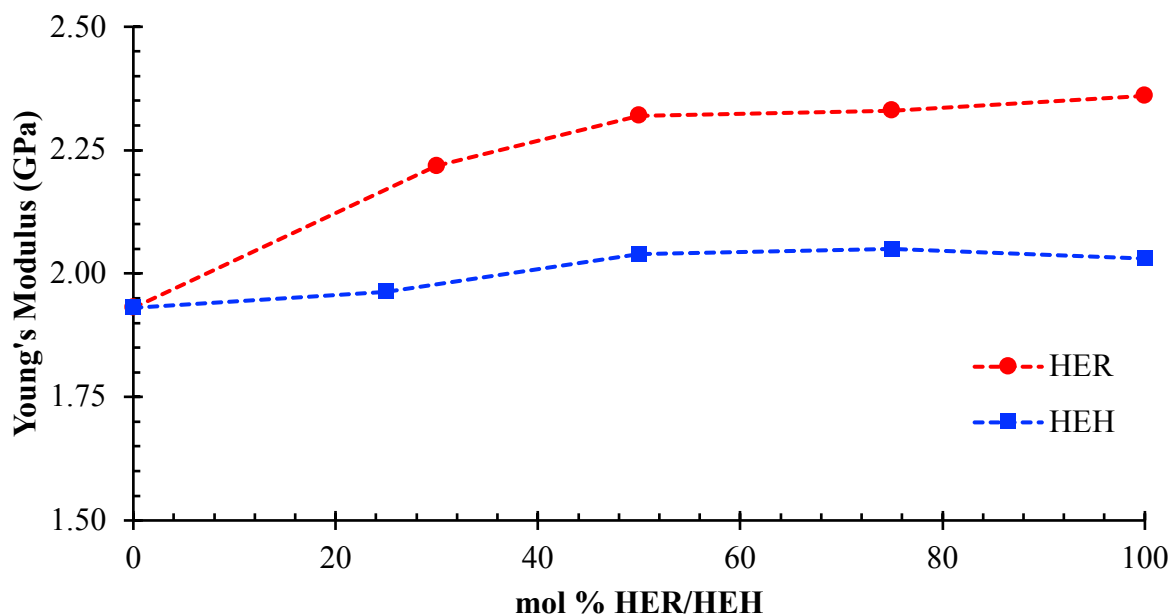


Figure 5.9. Young's moduli from tensile analysis versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

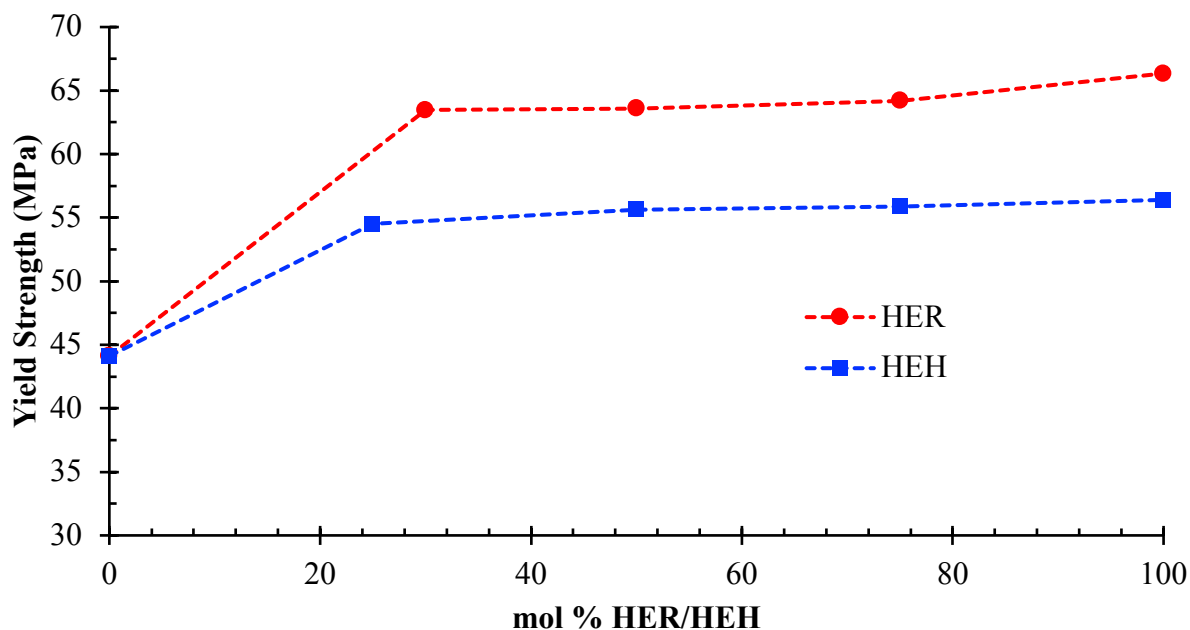


Figure 5.10. Tensile yield strengths versus mol % incorporation of hydroxyethylresorcinol (HER; blue, square) or hydroxyethylhydroquinone (HEH; red, circle).

5.5 Conclusions

Enhancing properties through comonomer incorporation continues to interest polymer chemists. Although new monomers with increasing complexity target vast enhancement of desired properties, sometimes subtle monomer changes, such as altering regiochemistry, produce the desired improvement without compromising other key properties. Although subtle, the interplay between polyester regioisomers structure, chain packing, and thermal/rheological/mechanical properties is yet to be fully understood.

In this study, PET-based (co)polyesters incorporating regioisomeric HER or HEH were synthesized and corresponding analysis determined the influence of backbone regiochemistry on thermal, rheological, and mechanical properties. HER-based (co)polyesters are of great interest due to the polyesters improved barrier performance over PET.^{10, 31, 33} Through systematic studies of thermomechanical and rheological behavior,

this decrease is attributed to more hindered short-chain relaxations, characterized by low temperature DMA, as well as a lower f_g , determined by WLF analysis of melt rheology. The corresponding analysis of the HER-based (co)polyesters' regioisomer, based on HEH, allowed for direct comparison of the backbone regiochemistry's impact on E_a , f_g , M_e , T_g , T_m , T_β , and tensile properties Young's modulus and yield strength.

Most polymer properties are highly influenced by the rigidity of the backbone and the change in density imparted by the kinked versus linear nature of the backbone. Thus, understanding the relationship between backbone structure, backbone regiochemistry, and chain rigidity helps predict the performance of next-generation thermoplastics.

Supporting Information.

^1H NMR spectra, DSC & TGA thermograms, TTS master curves of η^* and G' with G'' , WLF shift factor fittings, SEC chromatographs, DMA storage modulus graphs, tensile stress versus strain curves, and a summary table of tensile analysis.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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5.7 References

1. Mahendrasingam, A.; Blundell, D. J.; Martin, C.; Urban, V.; Narayanan, T.; Fuller, W., Time resolved WAXS study of the role of mesophase in oriented crystallisation of poly(ethylene terephthalate-co-isophthalate) copolymers. *Polymer* **2005**, *46* (16), 6044-6049.
2. Iyer, K. A., Chain mobility, secondary relaxation, and oxygen transport in terephthalate copolyesters with rigid and flexible cyclic diols. *Polymer* **2017**, *129*, 117-126.
3. Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of cold-drawn polyesters. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40* (9), 862-877.
4. Hu, Y. S.; Liu, R. Y. F.; Rogunova, M.; Schiraldi, D. A.; Nazarenko, S.; Hiltner, A.; Baer, E., Oxygen-barrier properties of cold-crystallized and melt-crystallized poly(ethylene terephthalate-co-4,4'-bibenzoate). *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40* (22), 2489-2503.
5. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Improving oxygen barrier properties of poly(ethylene terephthalate) by incorporating isophthalate. I. Effect of orientation. *J. Appl. Polym. Sci.* **2005**, *98* (4), 1615-1628.
6. Mohan, T. P.; George, A. P.; Kanny, K., Combined effect of isophthalic acid and polyethylene glycol in polyethylene terephthalate polymer on thermal, mechanical, and gas transport properties. *J. Appl. Polym. Sci.* **2012**, *126* (2), 536-543.
7. Finelli, L.; Fiorini, M.; Siracusa, V.; Lotti, N.; Munari, A., Synthesis and characterization of poly(ethylene isophthalate-co-ethylene terephthalate) copolyesters. *J. Appl. Polym. Sci.* **2004**, *92* (1), 186-193.
8. Hill, A. J.; Weinhold, S.; Stack, G. M.; Tant, M. R., Effect of copolymer composition on free volume and gas permeability in poly(ethylene terephthalate)-poly(1,4 cyclohexylenedimethylene terephthalate) copolyesters. *Eur. Polym. J.* **1996**, *32* (7), 843-849.
9. McGonigle, E. A.; Liggat, J. J.; Pethrick, R. A.; Jenkins, S. D.; Daly, J. H.; Hayward, D., Permeability of N₂, Ar, He, O₂ and CO₂ through biaxially oriented polyester films - dependence on free volume. *Polymer* **2001**, *42* (6), 2413-2426.
10. Gohil, R. M., Designing polyethylene terephthalate-based barrier resins. *J. Appl. Polym. Sci.* **2012**, *126* (1), 260-272.
11. Schiraldi, D. A.; Lee, J. J.; Gould, S. A. C.; Occelli, M. L., Mechanical properties and atomic force microscopic cross sectional analysis of injection molded poly(ethylene terephthalate-co-4,4'-bibenzoate). *Journal of Industrial and Engineering Chemistry* **2001**, *7* (2), 67-71.
12. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Comparison of statistical and blocky copolymers of ethylene terephthalate and ethylene 4,4'-bibenzoate based on thermal behavior and oxygen transport properties. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41* (3), 289-307.
13. Ha, W. S. C.; Y. K.; Jang, S. S.; Rhee, D. M.; Park, C. R., Preparation of Poly(ethylene terephthalate-co-isophthalate) by Ester Interchange Reaction in the PET/PEI Blend System. *J Polym Sci Pol Phys* **1997**, *35*, 309-315.

14. Edling, H. E.; Liu, H.; Sun, H.; Mondschein, R. J.; Schiraldi, D. A.; Long, T. E.; Turner, S. R., Copolyesters based on bibenzoic acids. *Polymer* **2018**, *135*, 120-130.
15. Kang, H. Y.; Lin, Q.; Armentrout, R. S.; Long, T. E., Synthesis and characterization of telechelic poly(ethylene terephthalate) sodiosulfonate ionomers. *Macromolecules* **2002**, *35* (23), 8738-8744.
16. Groeninckx, G.; Reynaers, H.; Berghmans, H.; Smets, G., Morphology and Melting Behavior of Semi-Crystalline Poly(Ethylene-Terephthalate) .1. Isothermally Crystallized Pet. *J Polym Sci Pol Phys* **1980**, *18* (6), 1311-1324.
17. Roberts, R. C., Poly(Ethylene Terephthalate) .2. Morphological Changes on Annealing. *Polymer* **1969**, *10* (2), 117-&.
18. Pegoretti, A.; Kolarik, J.; Peroni, C.; Migliaresi, C., Recycled poly(ethylene terephthalate)/layered silicate nanocomposites: morphology and tensile mechanical properties. *Polymer* **2004**, *45* (8), 2751-2759.
19. Di Lorenzo, M. L.; Errico, M. E.; Avella, M., Thermal and morphological characterization of poly(ethylene terephthalate)/calcium carbonate nanocomposites. *J Mater Sci* **2002**, *37* (11), 2351-2358.
20. Zekriardehani, S.; Joshi, A. S.; Jabarin, S. A.; Gidley, D. W.; Coleman, M. R., Effect of Dimethyl Terephthalate and Dimethyl Isophthalate on the Free Volume and Barrier Properties of Poly(ethylene terephthalate) (PET): Amorphous PET. *Macromolecules* **2018**, *51* (2), 456-467.
21. Burgess, S. K.; Lee, J. S.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J., Caffeine antiplasticization of amorphous poly(ethylene terephthalate): Effects on gas transport, thermal, and mechanical properties. *Polymer* **2015**, *65*, 34-44.
22. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of copolymers based on ethylene terephthalate. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (16), 1889-1899.
23. Asrar, J., High performance polyesters based on 4,4'-biphenyl dicarboxylic acid. In *Specialty polyesters*, Shotland Business Research, Skillman, NJ: 1995.
24. Krigbaum, W. R.; Asrar, J.; Toriumi, H.; Ciferri, A.; Preston, J., Aromatic polyesters forming thermotropic smectic mesophases. *Journal of Polymer Science: Polymer Letters Edition* **1982**, *20* (2), 109-115.
25. Karayannidis, G. P.; Bikiaris, D. N.; Papageorgiou, G. Z.; Pastras, S. V., Synthesis and characterization of poly(ethylene terephthalate-co-isophthalate)s with low content of isophthalate units. *J. Appl. Polym. Sci.* **2002**, *86* (8), 1931-1941.
26. de Ilarduya, A. M.; Kint, D. P. R.; Munoz-Guerra, S., Sequence analysis of poly(ethylene terephthalate-co-isophthalate) copolymers by C-13 NMR. *Macromolecules* **2000**, *33* (12), 4596-4598.
27. Lee, S. W.; Ree, M.; Park, C. E.; Jung, Y. K.; Park, C. S.; Jin, Y. S.; Bae, D. C., Synthesis and non-isothermal crystallization behaviors of poly(ethylene isophthalate-co-terephthalate)s. *Polymer* **1999**, *40* (25), 7137-7146.
28. Dickerson, J. P. B., A. E.; Oshinski, A. J.; Seo, K. S. Copolyesters based on 1,4-cyclohexanedimethanol having improved stability. US5773554A, 1998.
29. Turner, S. R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *J Polym Sci Pol Chem* **2004**, *42* (23), 5847-5852.
30. Turner, S. R.; Seymour, R. W.; Dombroski, J. R., Amorphous and Crystalline Polyesters based on 1,4-Cyclohexanedimethanol. In *Modern Polyesters: Chemistry and*

Technology of Polyesters and Copolyesters, Scheirs, J.; Long, T. E., Eds. John Wiley & Sons, Ltd: 2003.

31. Durairaj, R. B., Resorcinol additives for packaging extend product life for food and drink. *Plastics, Additives, and Compounding* **1999**, *1* (5), 30-34.
32. Gioia, C.; Banella, M. B.; Vannini, M.; Celli, A.; Colonna, M.; Caretti, D., Resorcinol: A potentially bio-based building block for the preparation of sustainable polyesters. *Eur. Polym. J.* **2015**, *73*, 38-49.
33. Pavel, D.; Shanks, R., Molecular dynamics simulation of diffusion of O₂ and CO₂ in blends of amorphous poly(ethylene terephthalate) and related polyesters. *Polymer* **2005**, *46* (16), 6135-6147.
34. Moad, G. G., A.; O'Shea, M.; Tozer, R. Polyester resins with improved properties. 2004.
35. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R.; Sirrine, J. M.; Weiseman, T. F.; Nazarenko, S.; Colby, R. H.; Turner, S. R.; Long, T. E., Influence of Bibenzoate Regioisomers on Cyclohexanedimethanol-based (Co)polyester Structure-Property Relationships. *Macromolecules* **2018**, *Submitted*.
36. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E., Influence of cyclobutane segments in cycloaliphatic decahydronaphthalene-containing copolyesters. *High Perform. Polym.* **2017**, *29* (6), 750-756.
37. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R. K.; Nazarenko, S.; Turner, S. R.; Long, T. E., Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance. *Macromolecules* **2017**, *50* (19), 7603-7610.
38. Dennis, J. M.; Enokida, J. S.; Long, T. E., Synthesis and Characterization of Decahydronaphthalene-Containing Polyesters. *Macromolecules* **2015**, *48* (24), 8733-8737.
39. Andrade, G. S.; Collard, D. M.; Schiraldi, D. A.; Hu, Y. S.; Baer, E.; Hiltner, A., Oxygen barrier properties of PET copolymers containing bis(2-hydroxyethyl)hydroquinones. *J. Appl. Polym. Sci.* **2003**, *89* (4), 934-942.
40. Dennis, J. M.; Fahs, G. B.; Moon, N. G.; Mondschein, R. J.; Moore, R. B.; Wilkes, G. L.; Long, T. E., Synthesis of Polysulfone-Containing Poly(butylene terephthalate) Segmented Block Copolymers: Influence of Segment Length on Thermomechanical Performance. *Macromolecules* **2017**, *50* (13), 5107-5113.
41. Cimecioglu, A. L.; Zeronian, S. H.; Alger, K. W.; Collins, M. J.; East, G. C., Properties of oligomers present in poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1986**, *32* (4), 4719-4733.
42. Ross, S. D.; Coburn, E. R.; Leach, W. A.; Robinson, W. B., Isolation of a cycle trimer from polyethylene terephthalate film. *J Polym Sci* **1954**, *13* (70), 406-407.
43. Walker, G. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 4. Calculation of cyclic trimer content of poly(ethylene terephthalate). *Polymer* **1970**, *11* (9), 472-485.
44. Cooper, D. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 11. Cyclics in poly(ethylene terephthalate). *Polymer* **1973**, *14* (5), 185-192.

45. Holland, B. J.; Hay, J. N., Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate). *Polymer* **2002**, *43* (6), 1797-1804.
46. Peebles, L. H.; Huffman, M. W.; Ablett, C. T., Isolation and identification of the linear and cyclic oligomers of poly(ethylene terephthalate) and the mechanism of cyclic oligomer formation. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1969**, *7* (2), 479-496.
47. Harrison, A. G.; Taylor, M. J.; Scrivens, J. H.; Yates, H., Analysis of cyclic oligomers of poly(ethylene terephthalate) by liquid chromatography/mass spectrometry. *Polymer* **1997**, *38* (10), 2549-2555.
48. Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J., Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate). *Macromolecules* **2014**, *47* (4), 1383-1391.
49. Maxwell, A. S.; Ward, I. M.; Lauprêtre, F.; Monnerie, L., Secondary relaxation processes in polyethylene terephthalate-additive blends: 1. N.m.r. investigation. *Polymer* **1998**, *39* (26), 6835-6849.
50. Maxwell, A. S.; Monnerie, L.; Ward, I. M., Secondary relaxation processes in polyethylene terephthalate-additive blends: 2. Dynamic mechanical and dielectric investigations. *Polymer* **1998**, *39* (26), 6851-6859.
51. Burgess, S. K.; Kriegel, R. M.; Koros, W. J., Carbon Dioxide Sorption and Transport in Amorphous Poly(ethylene furanoate). *Macromolecules* **2015**, *48* (7), 2184-2193.
52. Light, R. R.; Seymour, R. W., Effect of sub-T_g relaxations on the gas transport properties of polyesters. *Polym. Eng. Sci.* **1982**, *22* (14), 857-864.
53. Eisenberg, A.; Eu, B. C., Mechanical Spectroscopy: An Introductory Review. *Annu. Rev. Mater. Sci.* **1976**, *6* (1), 335-359.
54. Knowles, K. R. Effect of Chain Rigidity on Network Architecture and Deformation Behavior of Glassy Polymer Networks. The University of Southern Mississippi, Hattiesburg, MS, 2017.
55. Wada, Y.; Tetsuo, K., Relation Between Impact Strength and Dynamic Mechanical Properties of Plastics. *J. Appl. Polym. Sci.* **1967**, *11*, 1661-1665.
56. Boyer, R. F., Dependence of Mechanical Properties on Molecular Motion in Polymers. *Polym. Eng. Sci.* **1968**, *8*, 161-185.
57. Ferry, J. D., *Viscoelastic Properties of Polymers*. John Wiley & Sons: New York: 1980.
58. Rubinstein, M.; Colby, R. H., *Polymer Physics*. Oxford University Press Inc.: New York, 2003.
59. Fetters, L. J.; Lohse, D. J.; Colby, R. H., Chain Dimensions and Entanglement Spacings. In *Physical Properties of Polymers Handbook*, Mark, J. E., Ed. Springer New York: 2007; pp 447-454.
60. Karayiannis, N. C.; Mavrantzas, V. G.; Theodorou, D. N., Detailed atomistic simulation of the segmental dynamics and barrier properties of amorphous poly(ethylene terephthalate) and poly(ethylene isophthalate). *Macromolecules* **2004**, *37* (8), 2978-2995.

5.8 Supplemental Information

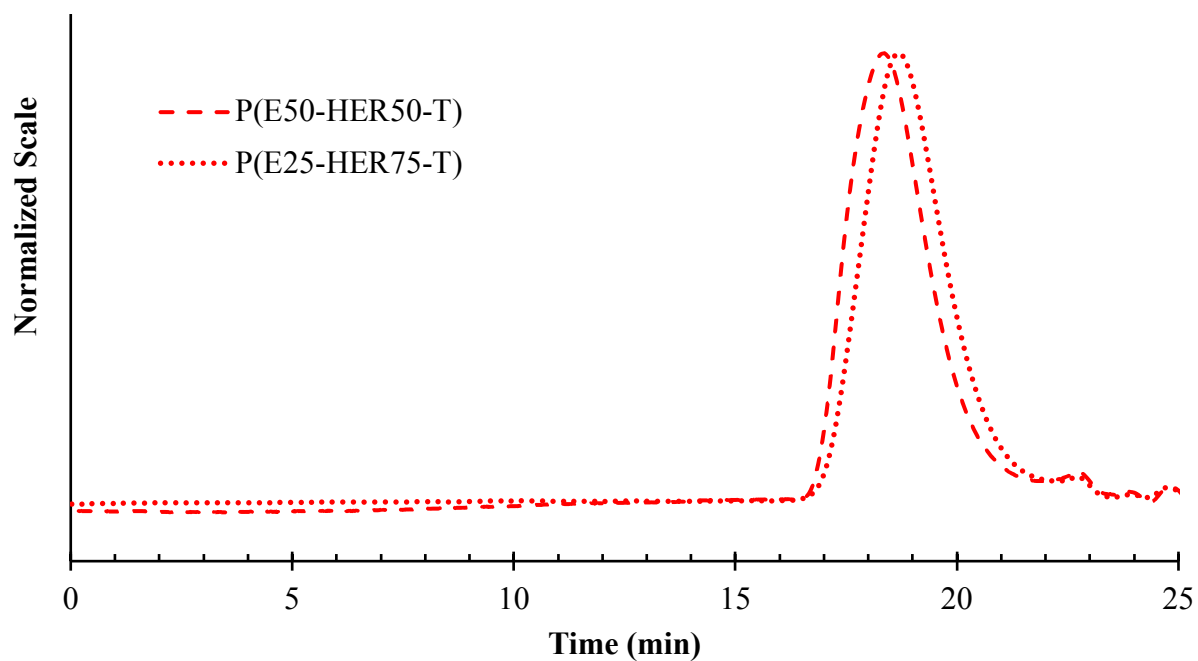


Figure S5.1. Size exclusion chromatograph of poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate): x:y = 50:50 (orange) and 25:75 (black).

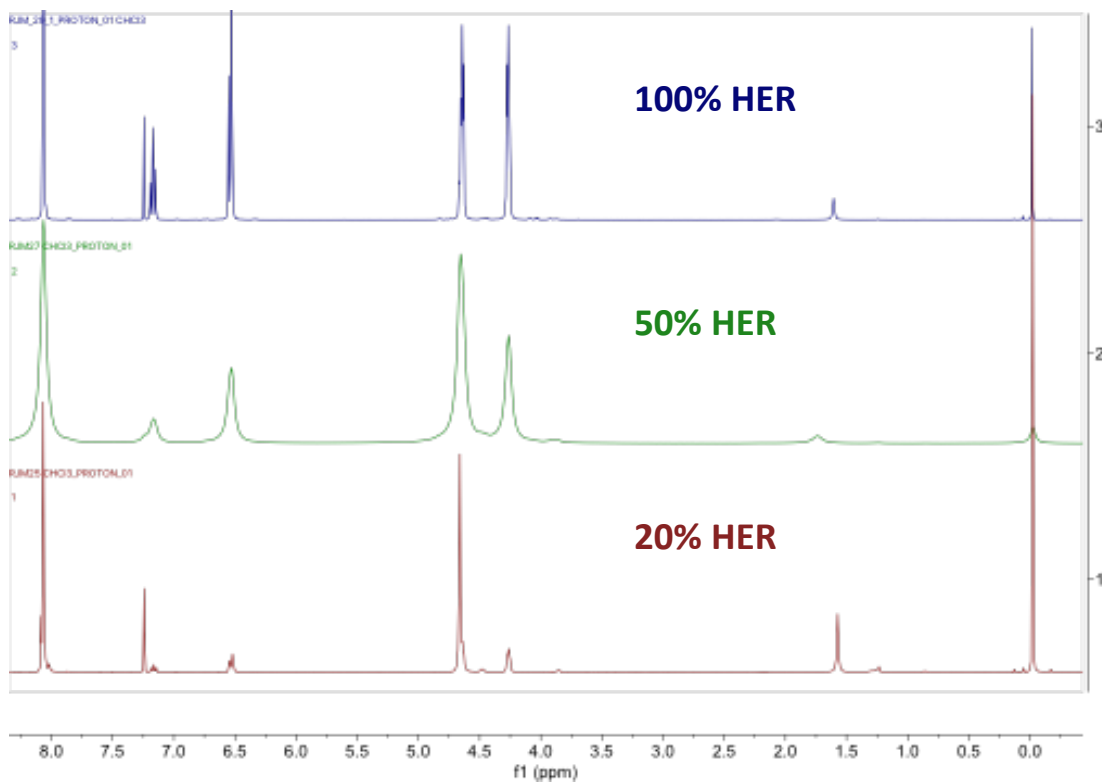


Figure S5.2. NMR spectra of poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate).

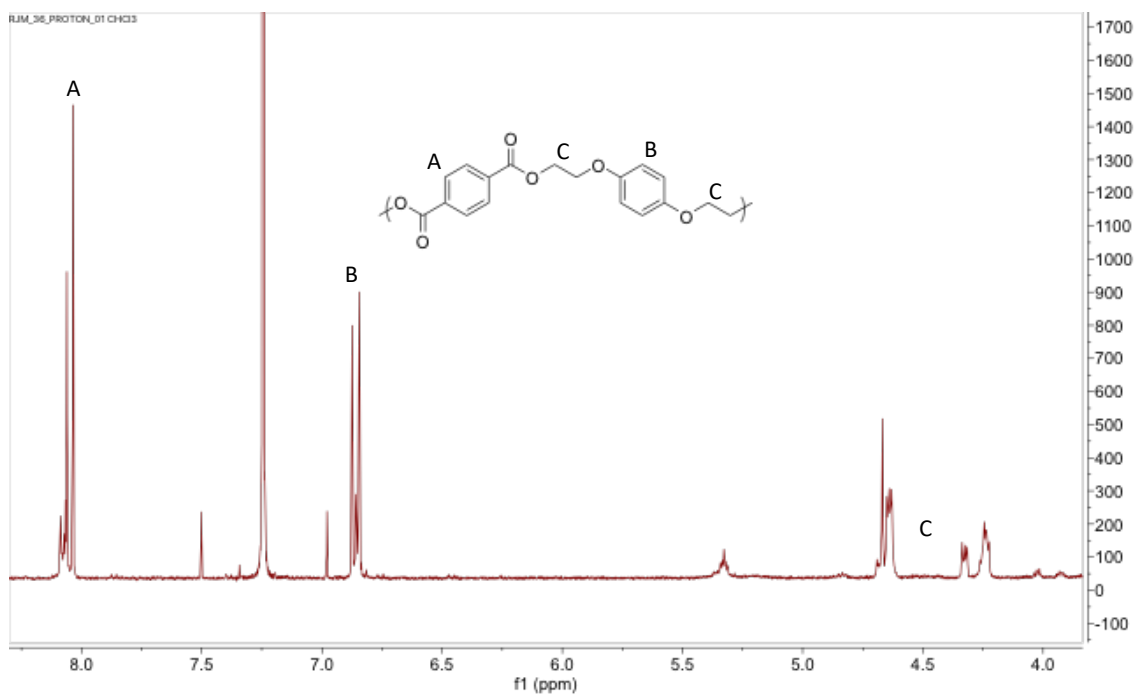


Figure S5.3. NMR spectra of poly(hydroquinone terephthalate).

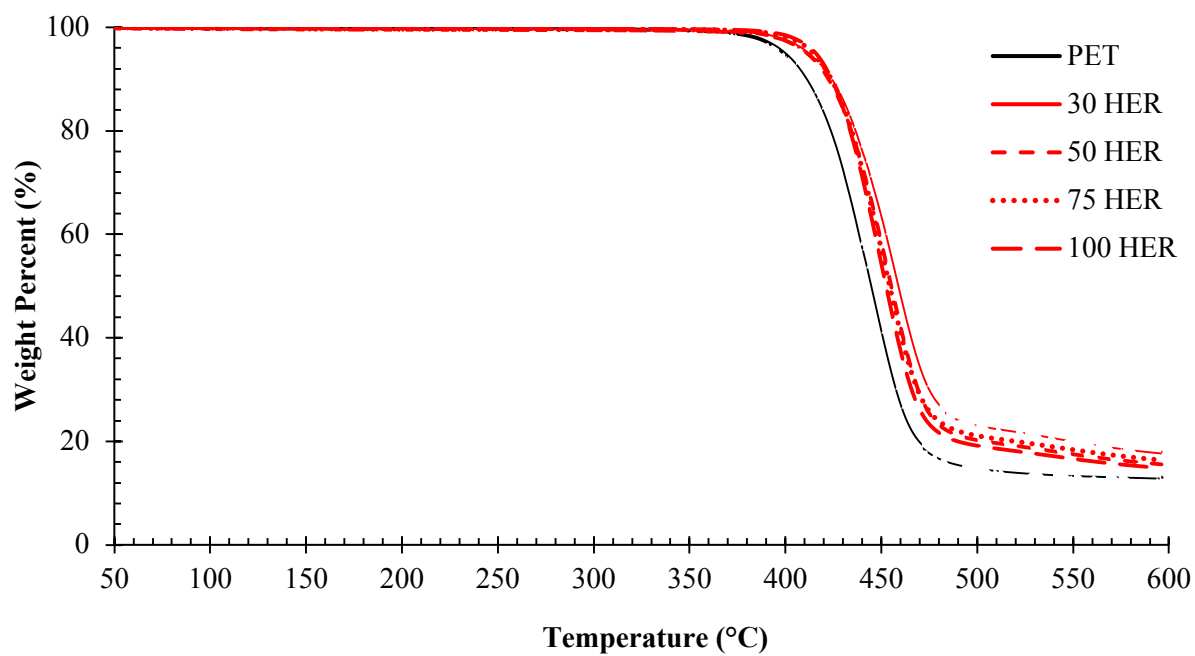


Figure S5.4. Thermogravimetric analysis (TGA) of poly(ethylene_x-co-hydroxyethylresorcinol) terephthalate).

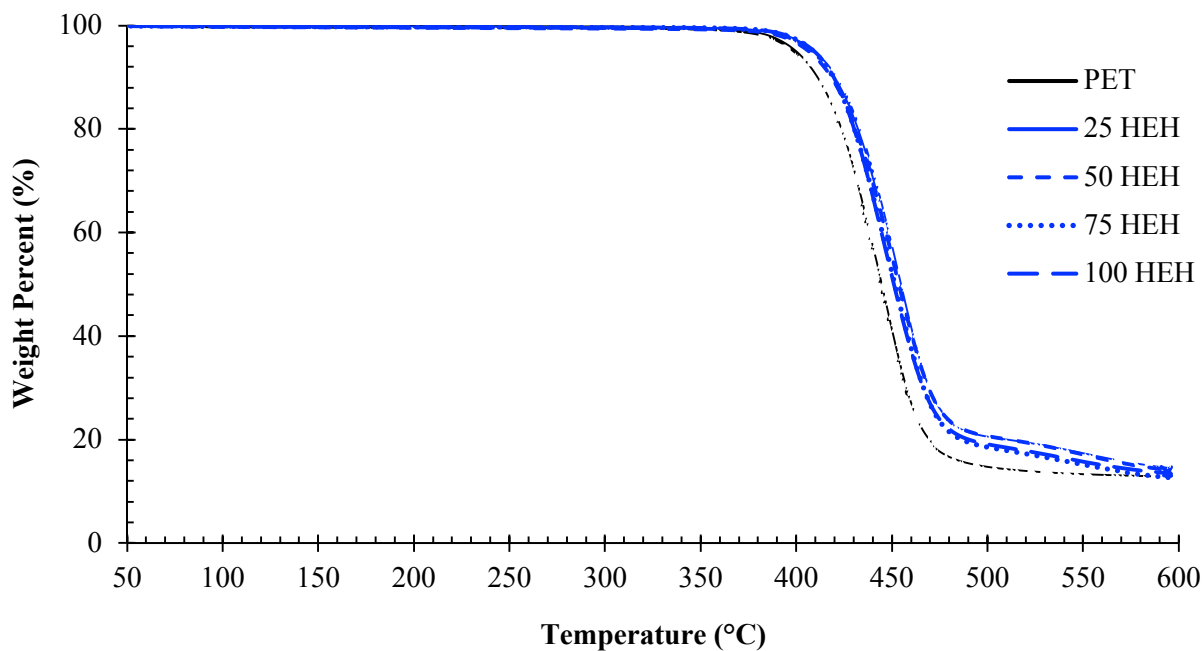


Figure S5.5. Thermogravimetric analysis (TGA) of poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate).

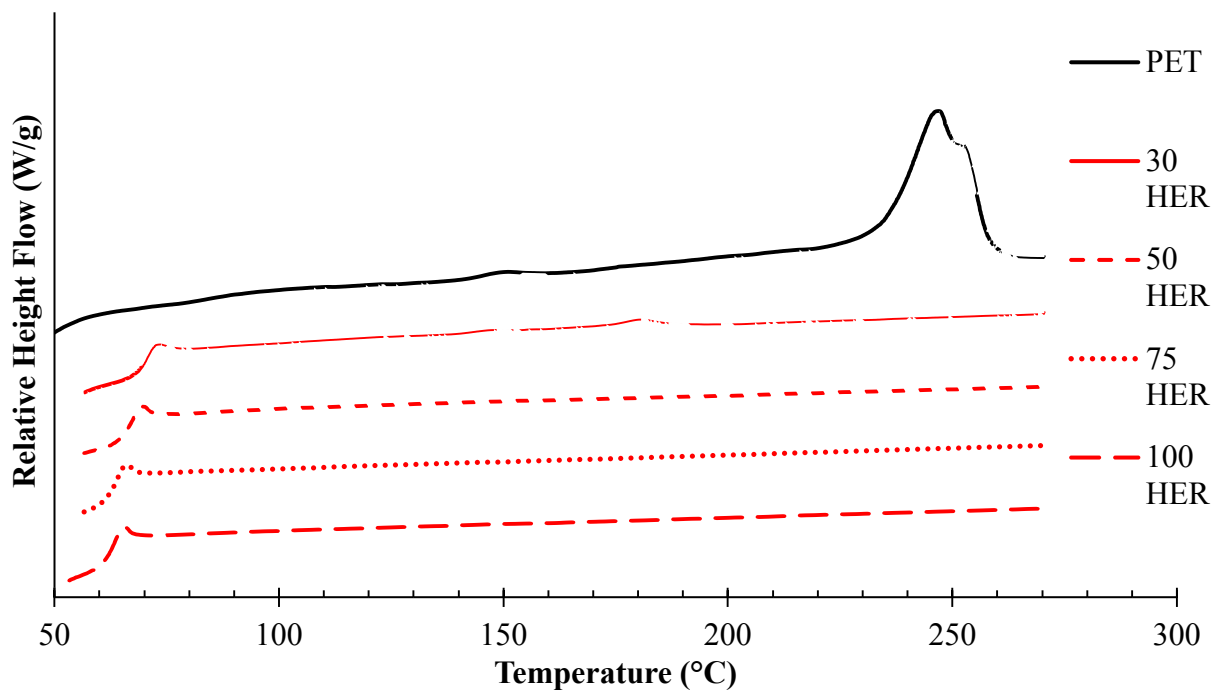


Figure S5.6. Differential scanning calorimetry (DSC) thermograms of poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate).

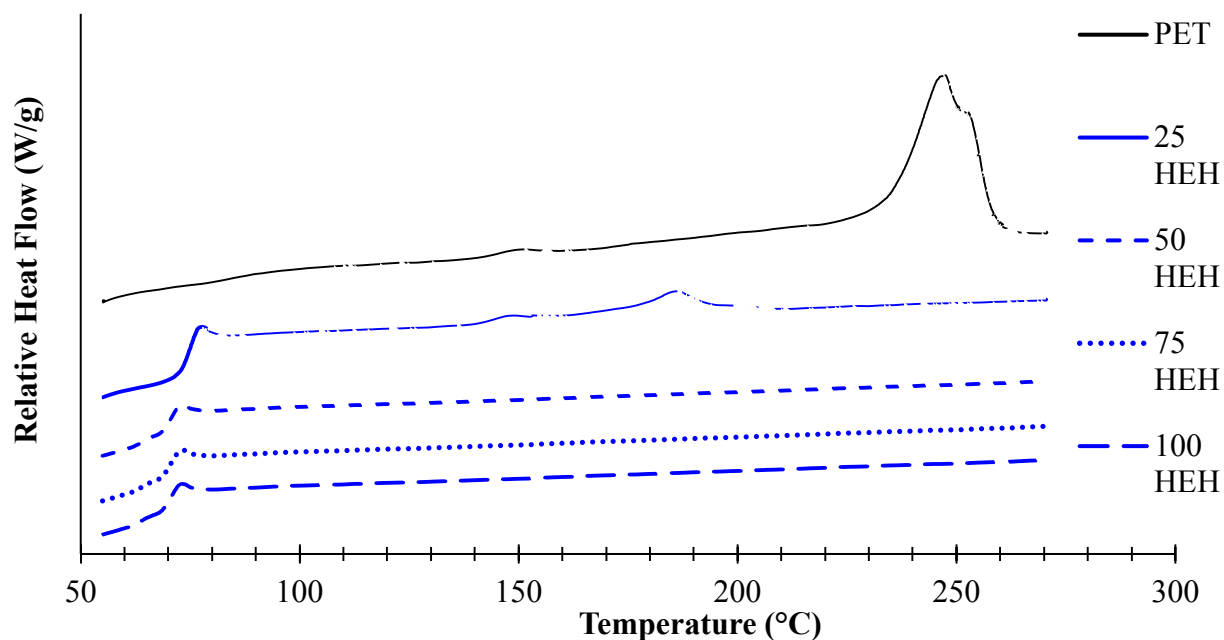


Figure S5.7. Differential scanning calorimetry (DSC) thermograms of poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate).

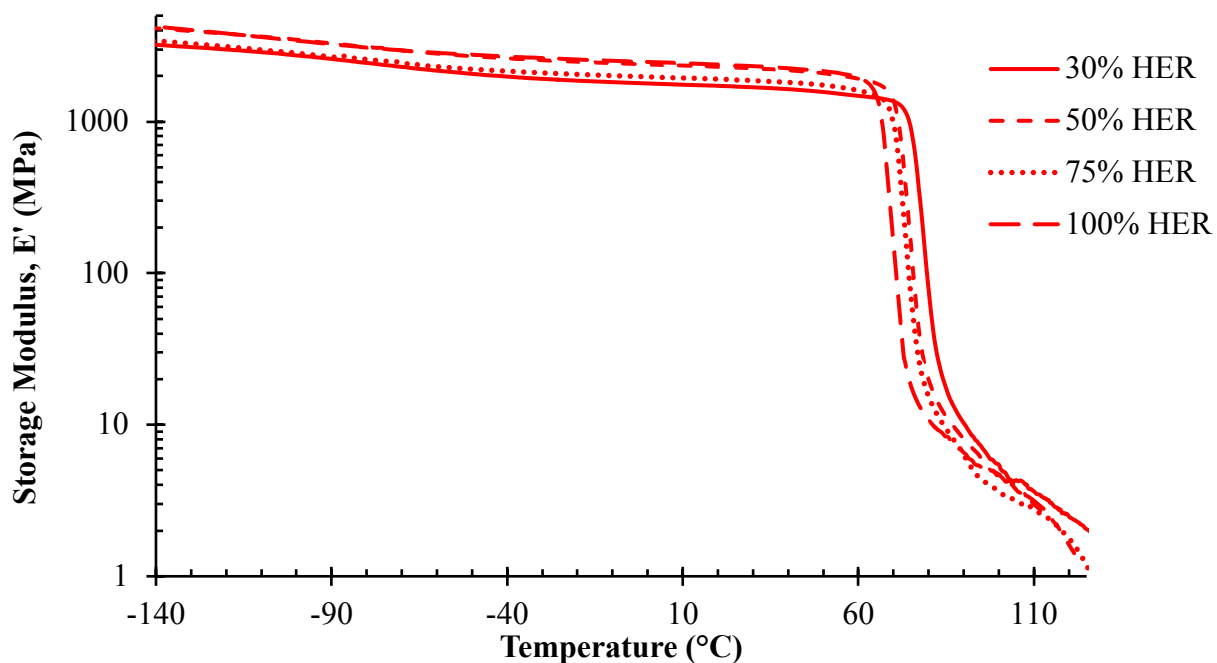


Figure S5.8. Storage modulus (E') versus temperature for poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate) (co)polyesters.

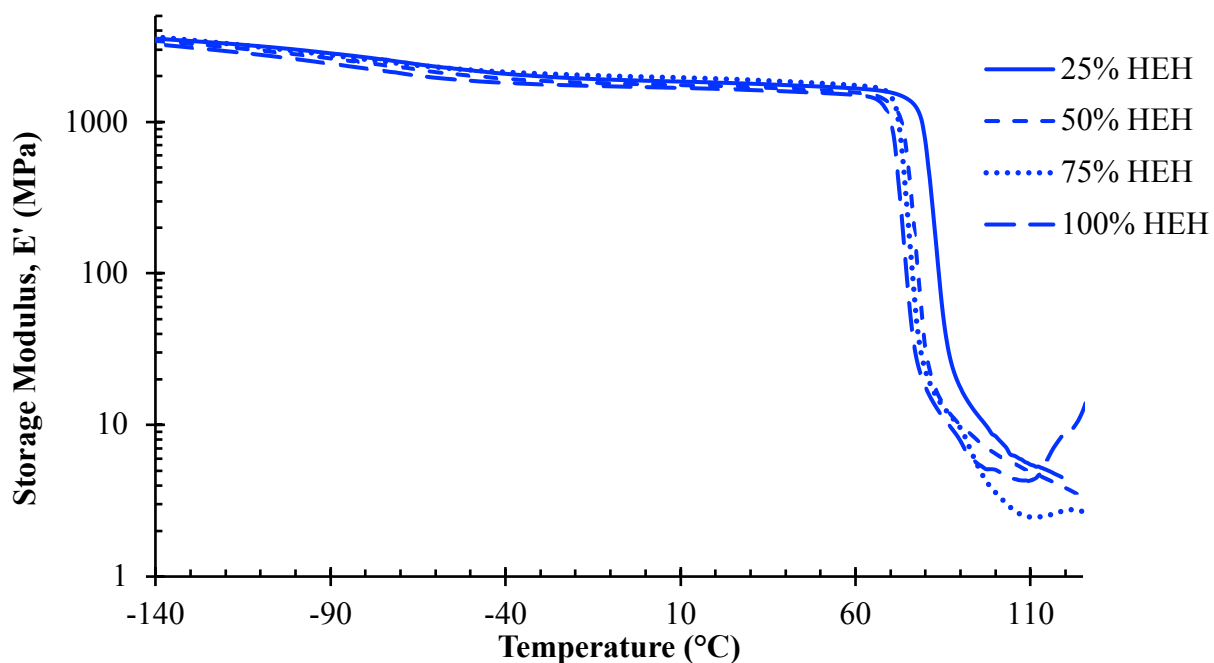


Figure S5.9. Storage modulus (E') versus temperature for poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate) (co)polyesters.

$$M_e = \frac{nRT}{G_N^0} \quad \text{eq. S5.1}$$

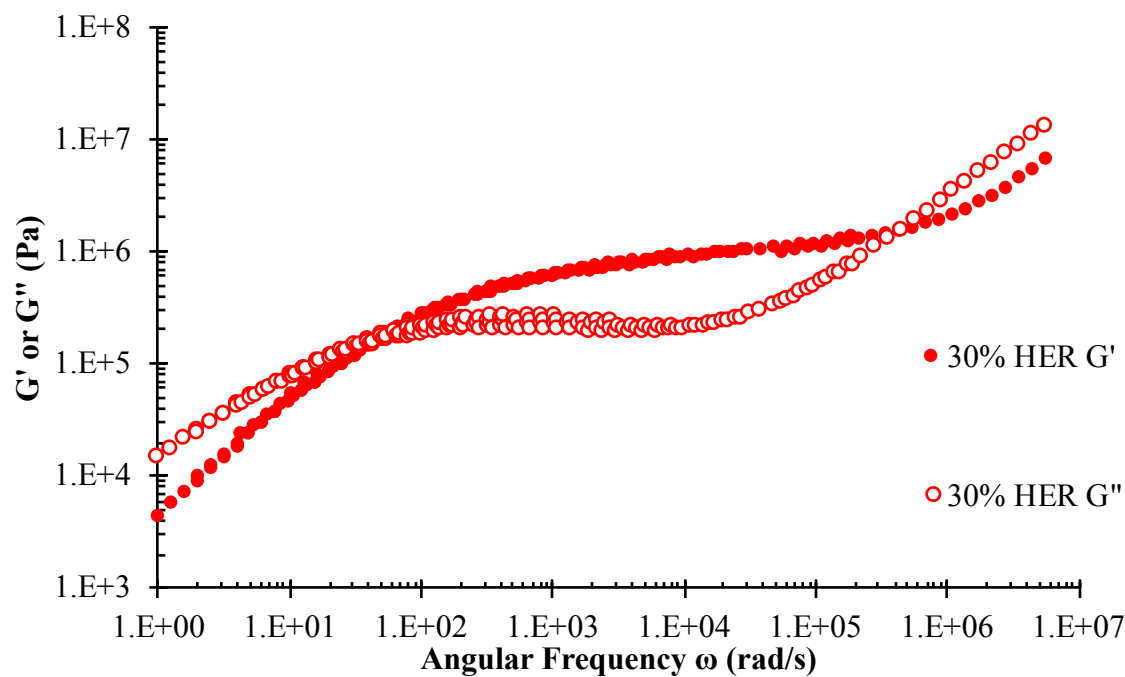


Figure S5.10. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(ethylene₇₀-co-hydroxyethylresorcinol₃₀ terephthalate).

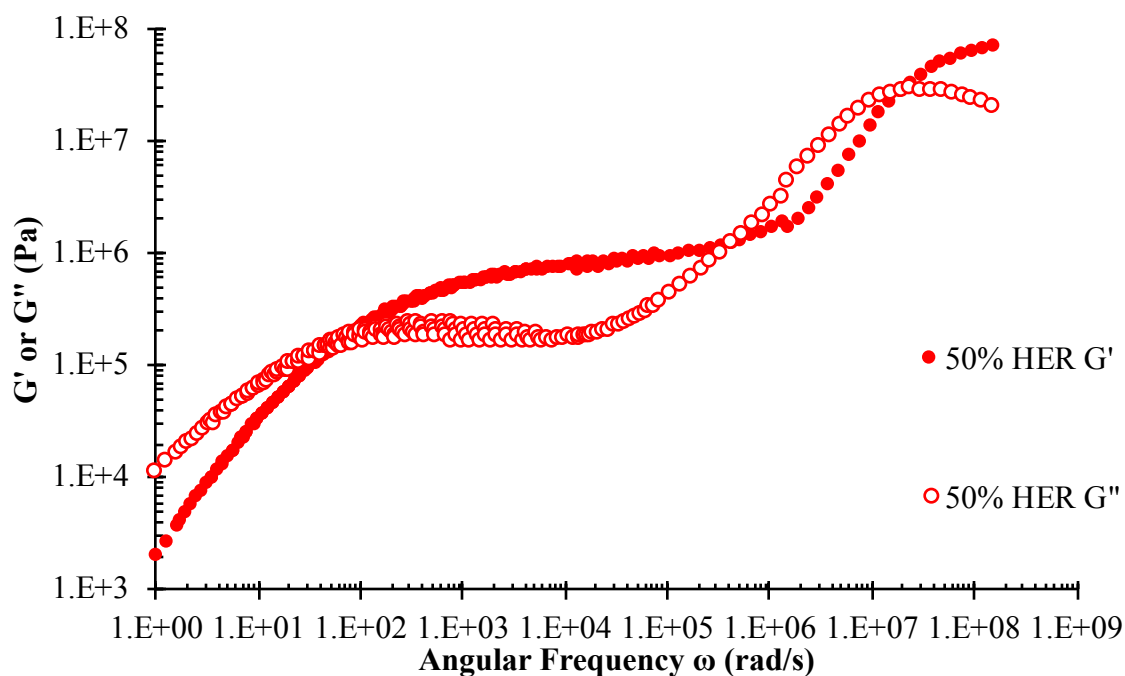


Figure S5.11. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(ethylene₅₀-co-hydroxyethylresorcinol₅₀ terephthalate).

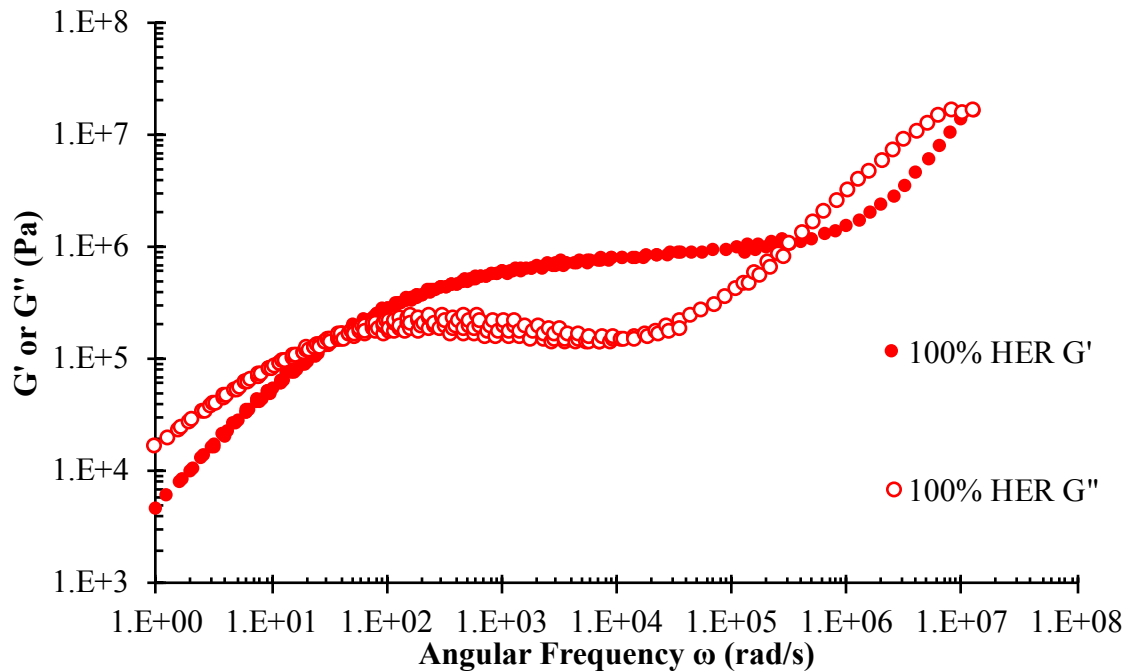


Figure S5.12. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(hydroxyethylresorcinol terephthalate).

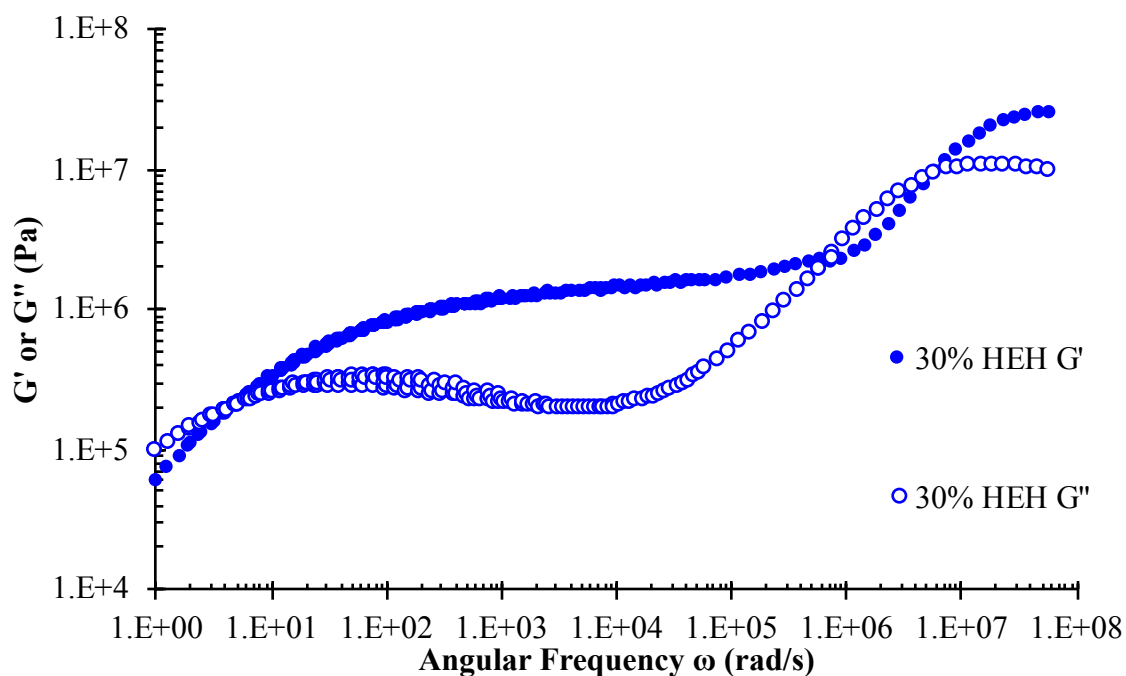


Figure S5.13. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(ethylene₇₅-co-hydroxyethylhydroquinone₂₅ terephthalate).

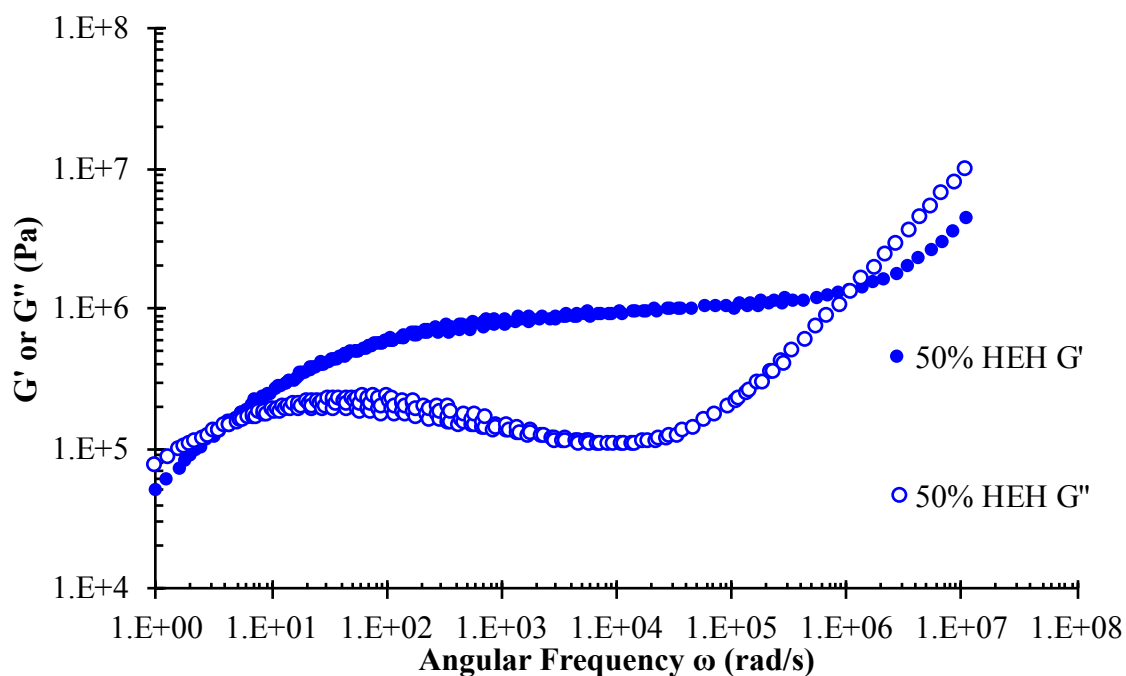


Figure S5.14. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(ethylene₅₀-co-hydroxyethylhydroquinone₅₀ terephthalate).

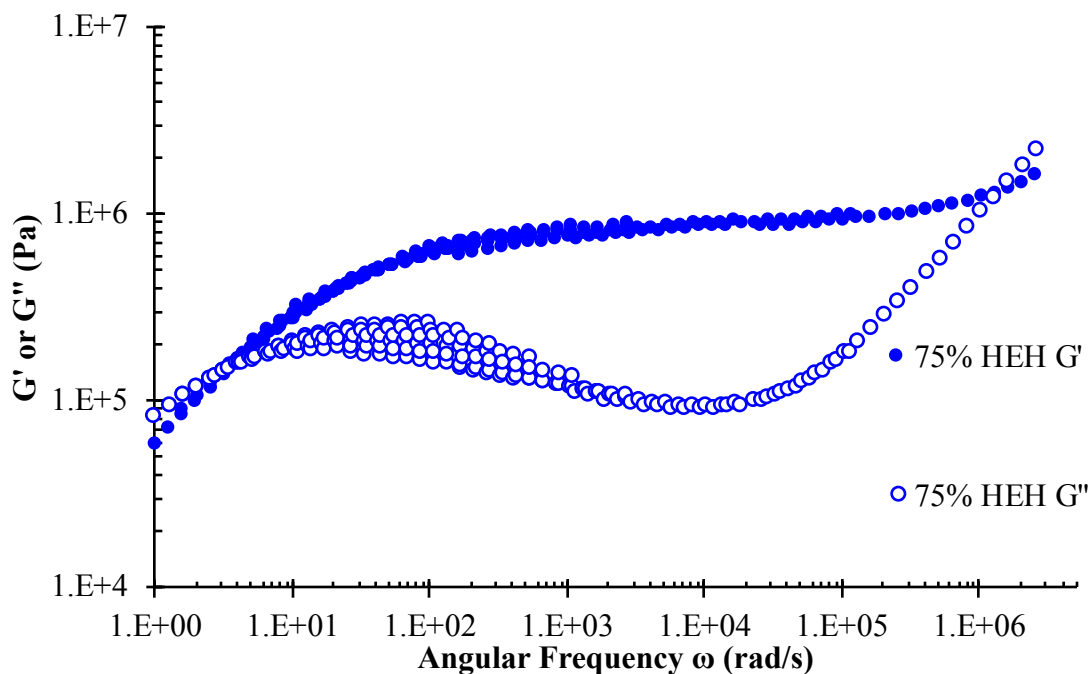


Figure S5.15. Representative TTS master curve of storage (G') and loss (G'') modulus versus angular frequency for poly(ethylene₂₅-co-hydroxyethylhydroquinone₇₅ terephthalate).

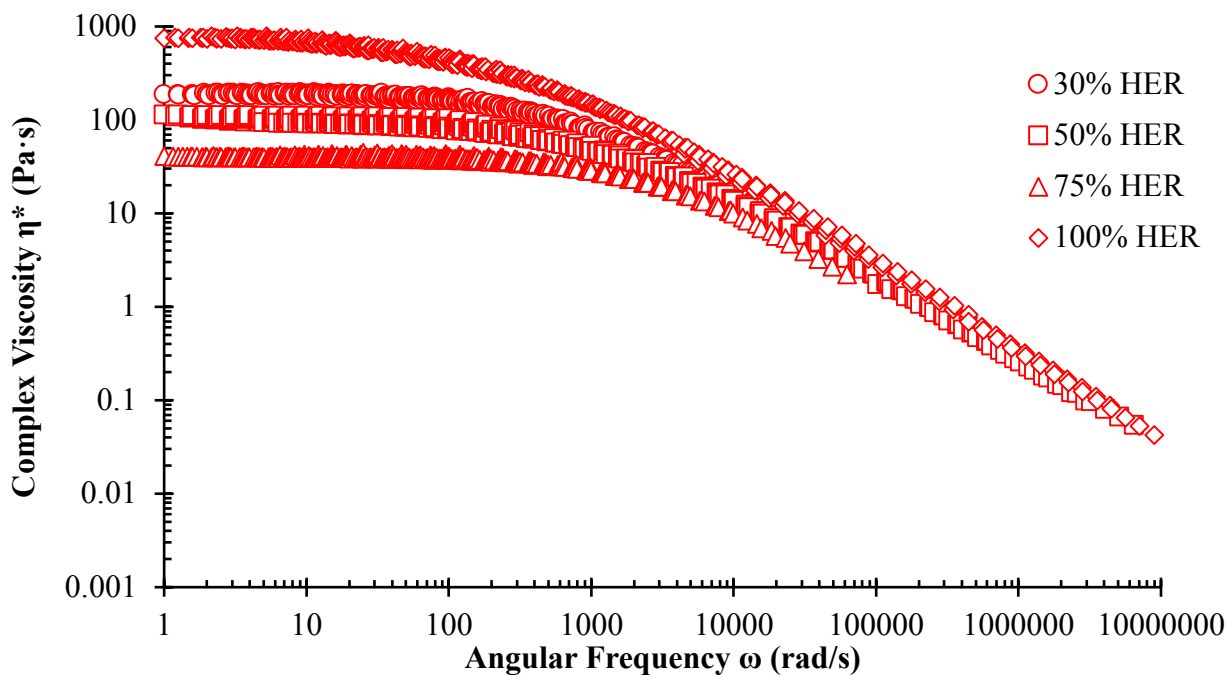


Figure S5.16. TTS master curves of complex viscosity (η^*) versus angular frequency for poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate) copolyesters.

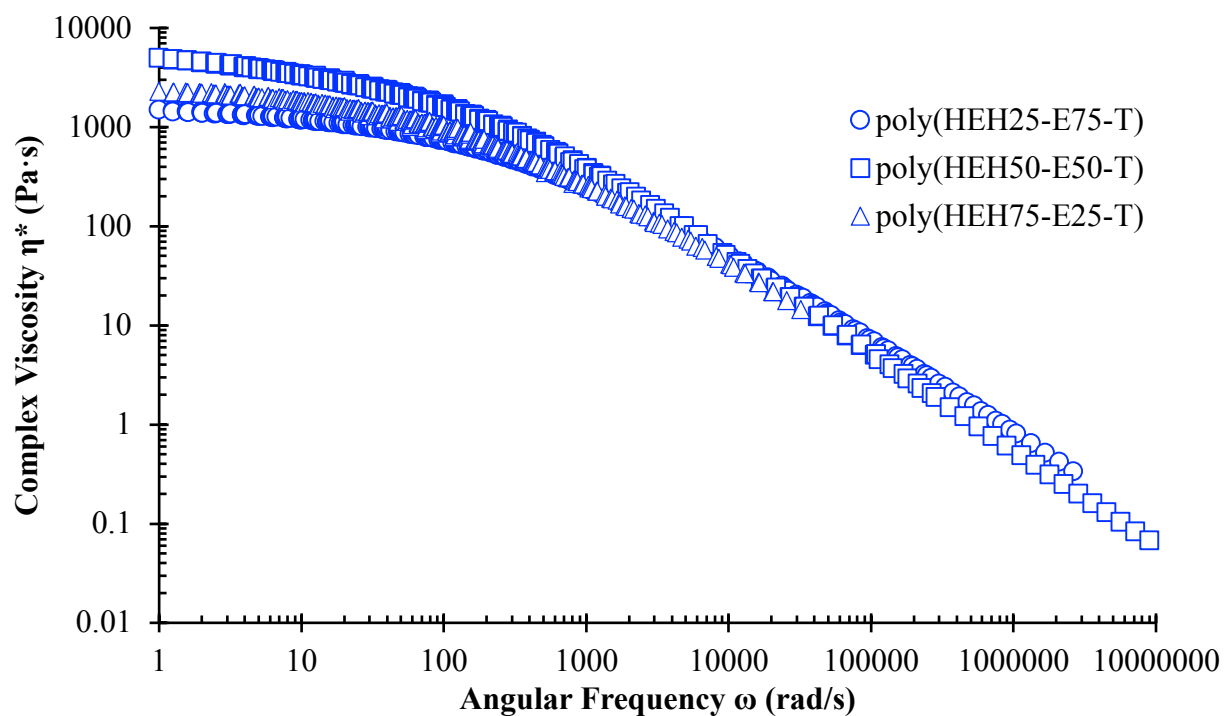


Figure S5.17. TTS master curves of complex viscosity (η^*) versus angular frequency for poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate) copolyesters.

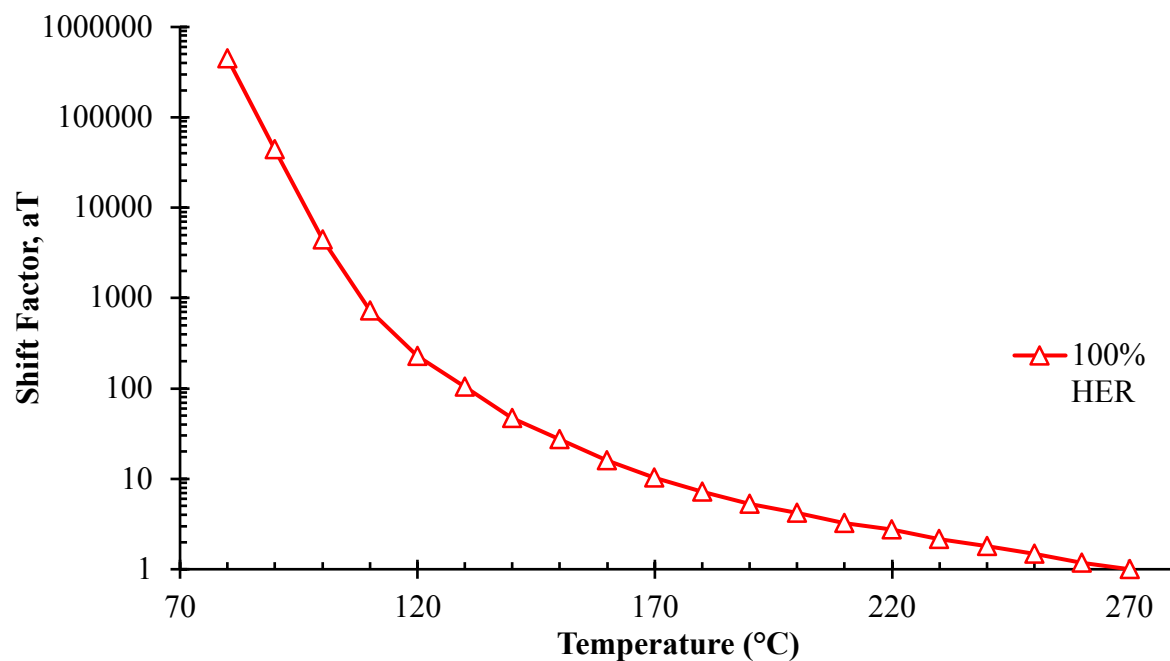


Figure S5.18. Representative shift factor versus temperature for poly(hydroxyethylresorcinol terephthalate).

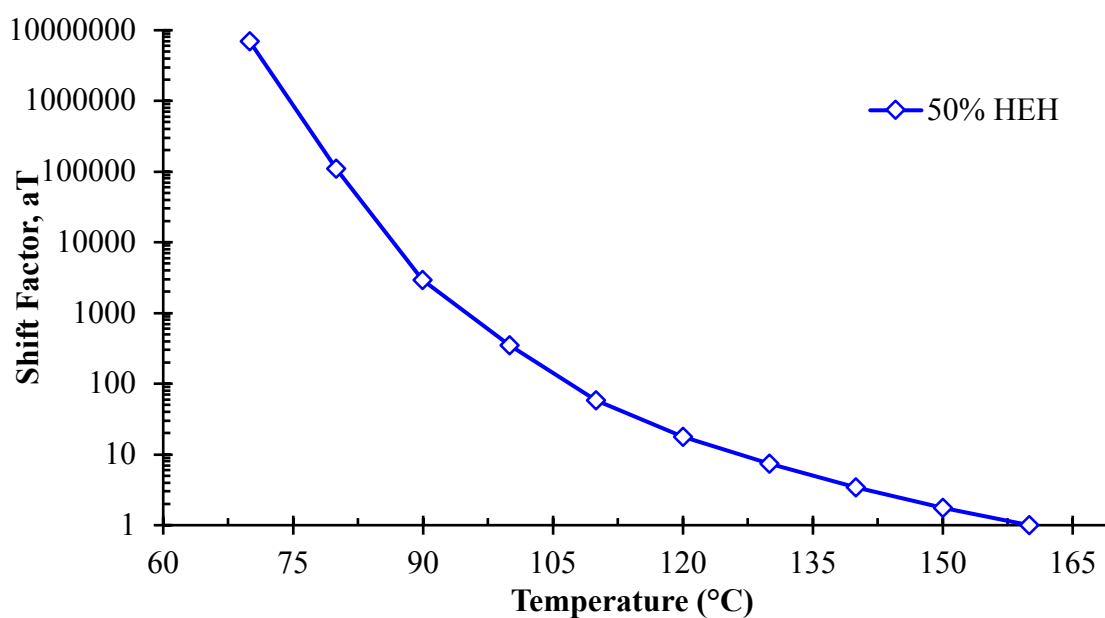


Figure S5.19. Representative shift factor versus temperature for poly(ethylene₅₀-co-hydroxyethylhydroquinone₅₀ terephthalate).

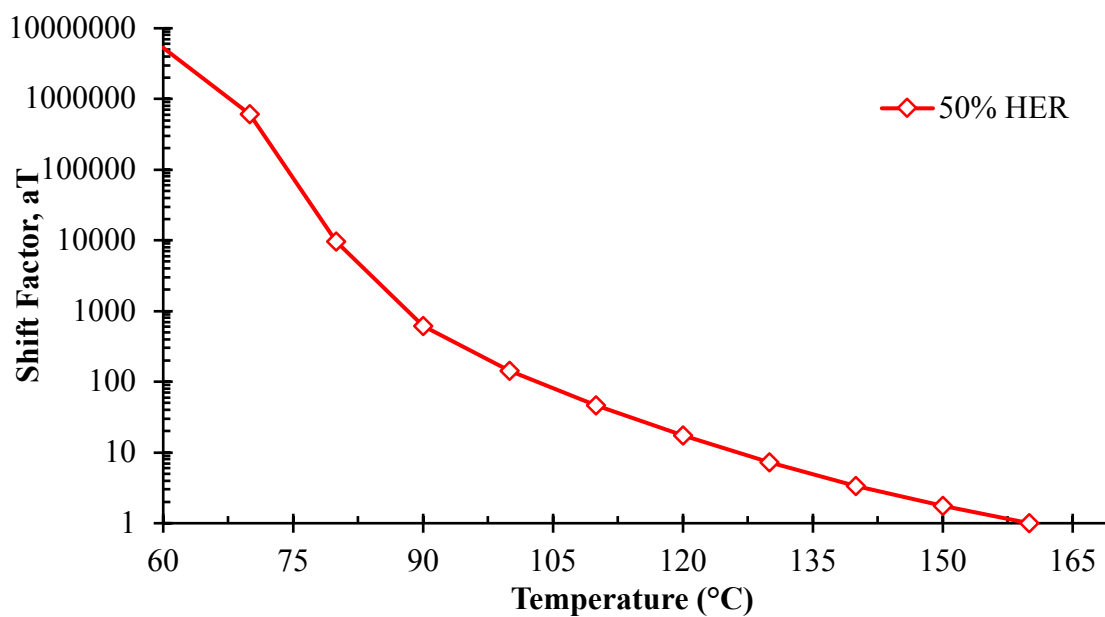


Figure S5.20. Representative shift factor versus temperature for poly(ethylene₂₅-co-hydroxyethylresorcinol₇₅ terephthalate).

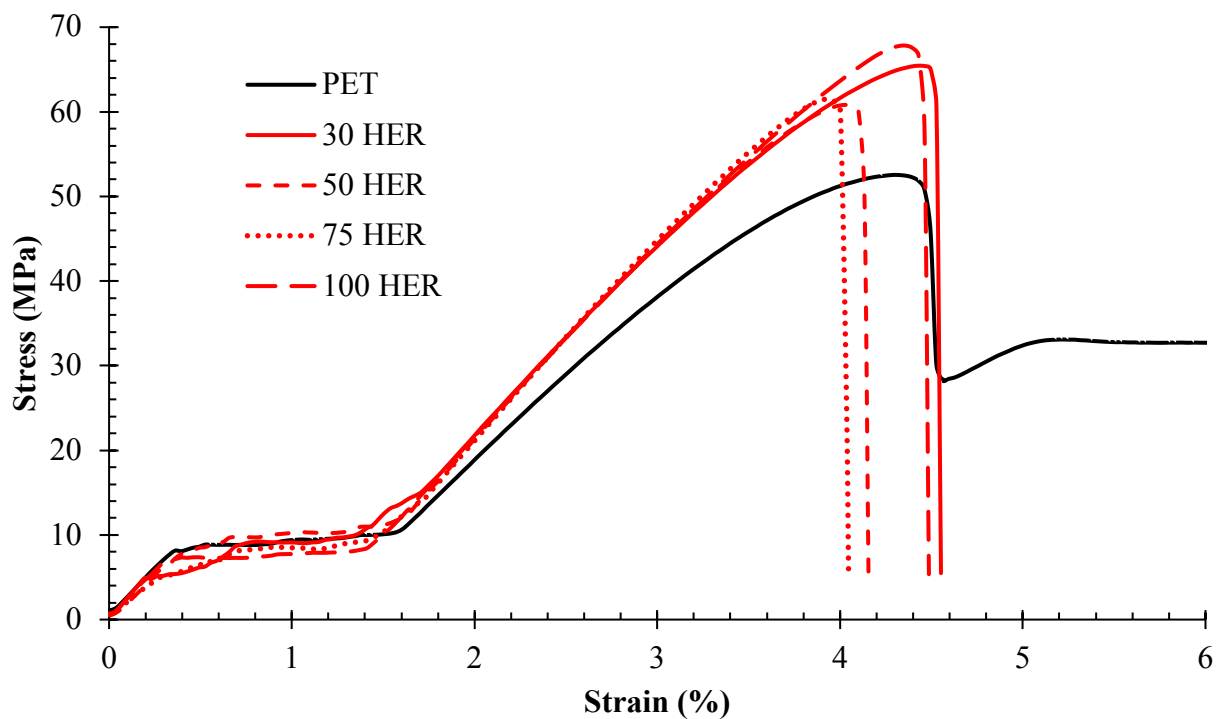


Figure S5.21. Representative tensile stress versus strain curve for poly(ethylene_x-co-hydroxyethylresorcinol_y terephthalate).

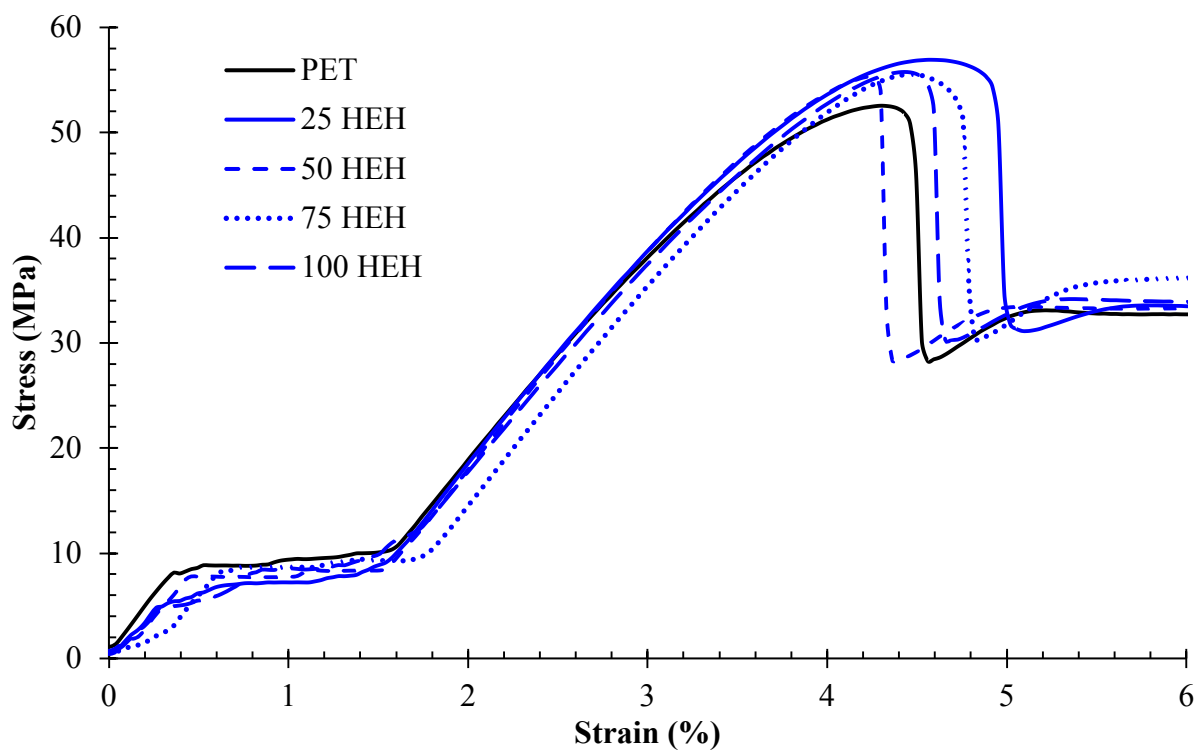


Figure S5.22. Representative tensile stress versus strain curve for poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate) at low strain %.

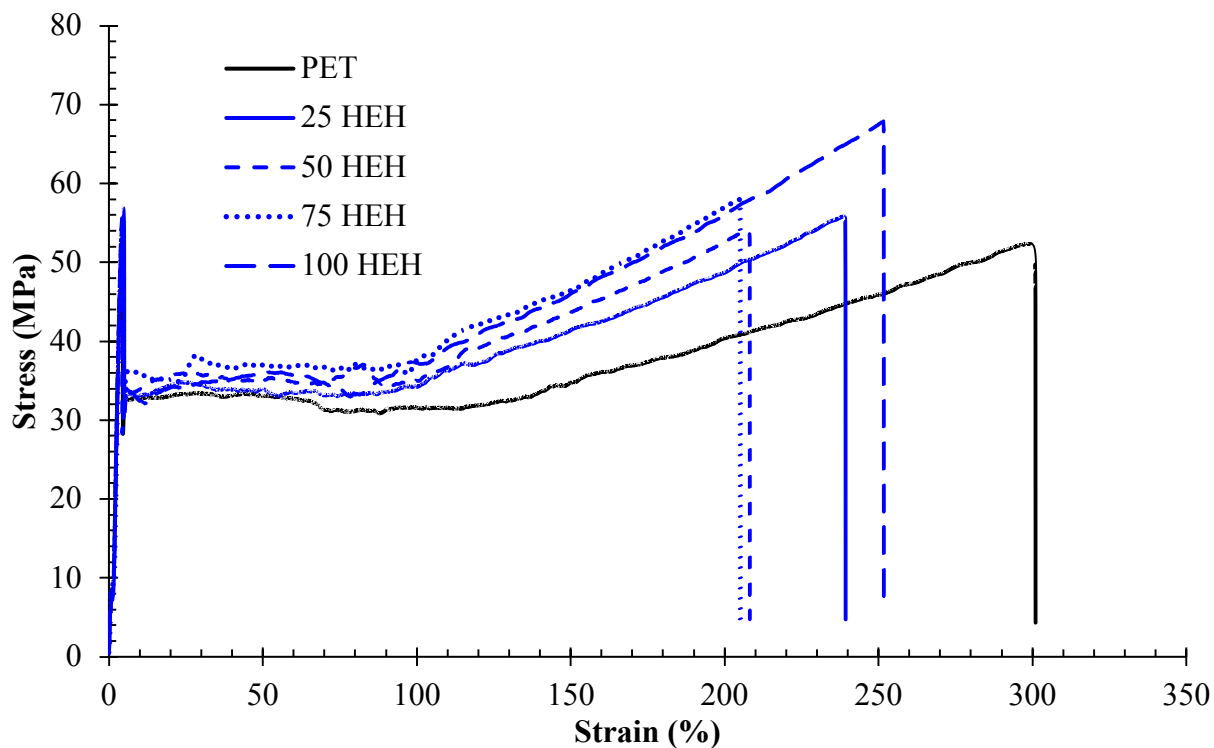


Figure S5.23. Representative tensile stress versus strain curve for poly(ethylene_x-co-hydroxyethylhydroquinone_y terephthalate) at low strain %.

Table S5.1. Summary of mechanical properties for poly[ethylene-co-hydroxyethyl(resorcinol/hydroquinone) terephthalate] (co)polyesters.

	Mol %	Yield Strength (MPa)	Young's Modulus (GPa)	Elongation to Break (%)
PET	0	44.1 ± 8.3	1.93 ± 0.14	293 ± 23
HER	30	63.5 ± 2.2	2.22 ± 0.09	13 ± 19
	50	61.0 ± 6.3	2.33 ± 0.03	4 ± 1
	75	57.1 ± 6.5	2.21 ± 0.39	6 ± 3
	100	66.3 ± 4.6	2.32 ± 0.04	10 ± 13
HEH	25	56.7 ± 0.8	1.96 ± 0.10	202 ± 109
	50	54.6 ± 2.3	2.04 ± 0.10	175 ± 73
	75	53.8 ± 1.6	2.00 ± 0.21	204 ± 10
	100	55.8 ± 1.3	1.99 ± 0.11	203 ± 64

Chapter 6: Characterization of Cyclics in (Co)polyester Regioisomers Incorporating Hydroxyethylresorcinol (HER) and Hydroxyethylhydroquinone (HEH)

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Keywords: Polyester, Hydroxyethylresorcinol, HER, Cyclics, Hydroxyethylhydroquinone, Regioisomers

6.1 Abstract

Melt polymerization enabled the synthesis of (co)polyesters incorporating regioisomers hydroxyethylresorcinol (HER) and hydroxyethylhydroquinone (HEH). NMR spectroscopy confirmed the polyester compositions and differential scanning calorimetry (DSC) determined glass transition temperatures (T_g)s. Advanced permeation chromatography (APC) targeted separation of low molecular weight species, specifically targeting analysis of low molecular weight cyclic species, including dimer, trimers, tetramers, and pentamers. Mass spectrometry (MS) confirmed the presence of low molecular weight cyclics rather than the linear dimer, trimer, etc. analogue. Analysis of the refractive index graphs quantified the relative amounts of each low molecular weight species. Polyesters with increased *meta*-substituted HER incorporation possessed more low molecular weight cyclic. Introduction of the *para*-substituted HEH systematically reduced the relative amount of cyclic species present.

6.2 Introduction

Hydroxyethylresorcinol (1,3-bis(2-hydroxyethyl)resorcinol; HER) or hydroxyethylhydroquinone (1,3-bis(2-hydroxyethyl)hydroquinone; HEH) incorporation

into PET-based (co)polyesters affords polymers with improved barrier performance,¹⁻² mechanical properties, and melt flow behavior compared to PET. Thus, interest remains in developing polyesters utilizing these monomers for applications in food packaging and consumer thermoplastic applications. For HER-based (co)polyesters, the increase in barrier properties is attributed to decreased free volume as well as hindered short range relaxations, mainly the aromatic ring rotation around the *meta* linkage. The improved mechanical properties are attributed to the increased amorphous density of the polymers. The *meta* linkage imparts more *trans* conformations in the backbone, thus leading to a smaller coil and denser packing. For HEH-based (co)polyesters, the increase in barrier properties is attributed to decrease in oxygen gas solubility.¹ Although these results are consistent with previous structure-property relationships of polyesters and barrier performance,³⁻⁹ there is no consideration of the amount of cyclic species produced based on monomer regiochemistry, and the cyclics resulting impact on permeability or mechanical properties.

Poly(ethylene terephthalate) (PET) contains up to 3 wt % cyclics at bottle grade molecular weight (0.7-0.8 dL/g I.V.) with dimer to nonamer cyclic species present.¹⁰⁻¹³ The trimer is commonly the highest fraction of the cyclics and can be isolated through various techniques.^{12, 14} PET's *meta* regioisomer, poly(ethylene isophthalate) (PEI), contains up to 10 wt % cyclics.¹⁵⁻¹⁶ Thus, the change from primarily *para* backbone regiochemistry to *meta* backbone regiochemistry influences the size and amount of low molecular weight cyclic formation drastically. Low molecular weight species are known to improve barrier properties. Introducing small molecules dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI) into PET decreased free volume and changed the free volume distribution. This reduction in free volume coupled with the decrease in short range chain

mobility through the small molecules role as an antiplasticizer significantly lowered the permeability to carbon dioxide, oxygen and helium gas.¹⁷ Similarly, incorporating hydroxynaphthalenes, caffeine, or bishydroxy benzenes in 3-5 wt % improved barrier performance 2-10 times.¹⁸⁻²⁰ Thus, understanding the amount of cyclics in HER/HEH-based (co)polyesters affords insight into the influence of regiochemistry on cyclic formation as well as the cyclics impact on barrier performance.

Incorporating HER or HEH into PET-based (co)polyesters improves solubility in common organic solvents. In order to compare polyesters with and without cyclics, solution processing is required. Since cyclics form due to entropic gain at elevated temperature and the cyclics are at an equilibrium amount at high temperatures, melt processing polyesters with cyclics removed will result in the reformation of cyclics and make characterizing polyesters with no cyclics difficult. Since the HER- and HEH-based (co)polyesters are soluble and regioisomers, polyesters incorporating both HER and HEH as co-diols should provide soluble (co)polyester regioisomers. These polyester compositions are ideal to study the influence of backbone regiochemistry on cyclic formation and their solubility enables use of purification techniques such as dialysis to isolate low molecular weight cyclic species from the high molecular weight linear polymer. Solution casting films of these polyesters with cyclics and the same compositions with cyclics extracted will allow for direct and systematic comparison of polyester compositions and properties with and without cyclics.

This report highlights and describes the synthesis and characterization of poly(hydroxyethylresorcinol-co-hydroxyethylhydroquinone terephthalate) (poly(HER-co-HEH T) (co)polyesters. Melt polymerization including transesterification and

polycondensation produced a series of (co)polyesters with targeted amounts of HER/HEH incorporation. NMR spectroscopy confirmed final polymer compositions. Thermal property analysis probed the bishydroxyethyl benzene regiochemistries' influence on the glass transition temperature (T_g). Chromatography targeting separation of low molecular weight species probed cyclic species present. Analyzing the area of the refractive index (RI) traces quantified the amount of low molecular weight species for the various (co)polyesters. Mass spectrometry confirmed the molar mass of cyclic species.

6.3 Experimental

6.3.1 Materials. 1,3-bis(2-hydroxyethyl)resorcinol (HER) (>98.0%) supplied by TCI America and 1,4-bis(2-hydroxyethyl)hydroquinone (HEH) (98%) and dimethyl terephthalate (DMT) (ReagentPlus $\geq 99\%$) supplied by MilliporeSigma were used as received. Ethylene glycol (EG) was supplied by Sigma-Aldrich ($\geq 99\%$) and used as received. Titanium tetra(isopropoxide) (99%) was supplied by Sigma-Aldrich, and a 0.01 g/mL titanium solution in anhydrous 1-butanol was made according to previously detailed procedures.²¹ All solvents (Spectrum) were used as received. Nitrogen gas (N_2) (Praxair, 99.999%) was used as received.

6.3.2 Analytical Methods. A Waters ACQUITY Advanced Permeation Chromatograph (APC) utilized a column set of one 125 Å x 150 mm and two 45 Å x 150 mm XT columns and employed a Waters ACQUITY RI detector. At 40 °C, a 1.0 mL min⁻¹ flow rate in $CHCl_3$ afforded relative molecular weights using a polystyrene standard. Dynamic light scattering (DLS) analyzed all polymer solutions at 40 °C in $CHCl_3$ prior to APC analysis, to confirm no homogenous solutions. Quantification of the area under the peaks in APC analysis was conducted in Waters Empower software. Thermal transitions were analyzed

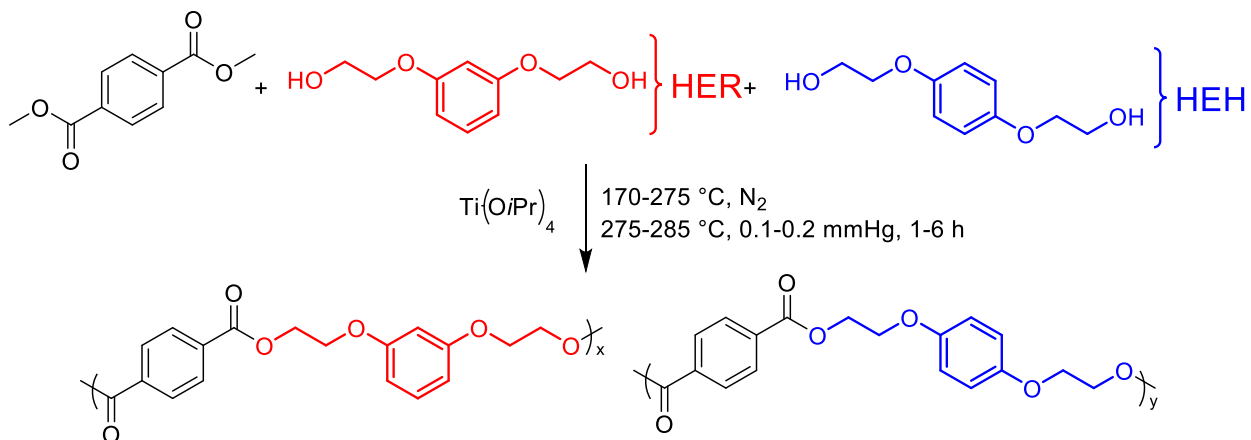
using a TA instruments Q1000 differential scanning calorimeter (DSC). The DSC was calibrated with indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards. The DSC employed a 50 mL min⁻¹ nitrogen flow and a 10 °C min⁻¹ heating/cooling rate. The second heating ramp was analyzed and the glass transition temperatures (T_g) were chosen to be the midpoint of step change. An Agilent 6220 liquid chromatograph with mass spectrometry (LCMS) equipped with a TOF analyzer utilized ESI in positive mode to determine accurate molar masses.

6.3.3 Synthesis of poly(HER-co-HEH T). The following is an example of the (co)polyesters synthetic procedure and the synthesis of 40:60 HER:HEH follows as an example. Reactions were conducted in a dried 100-mL round-bottomed flask. A nitrogen inlet, distillation apparatus, and overhead stirrer was equipped to the reaction. HER (7.24 g, 0.4 mol equiv), HEH (10.87 g, 0.6 mol equiv), EG (1.42 equiv), and DMT (17.74 g, 1.0 mol equiv) were added to the flask. 40 ppm of titanium tetra(isopropoxide) (0.15 mL; 0.01 g/mL (anhydrous 1-butanol)) catalyst was then introduced to the flask. Degassing to 0.2 mmHg and purging 3 times with nitrogen gas produced an oxygen free atmosphere for the reaction. The reaction started at 170 °C for 1 h and was increased to 200 °C for 1 h followed by 220 °C for 2 h and finally 275 °C for 1 h with 75-100 rpm stirring and nitrogen gas purge. Methanol condensate removal was monitored in a cooled round-bottomed flask to ensure progress of the reaction. Vacuum application to the system reduced the pressure to 0.1-0.2 mmHg and stirring continued at 275 °C until the melt viscosity stopped flow of the polymer. Polymer was collected by shattering the flask and isolating the polymer from the stir rod. Further purification was not needed.

6.4 Results and Discussion

Standard polyester melt polymerizations utilize an excess of diol monomer to ensure the stoichiometry always remains in favor of producing high molecular weight.^{3-4, 22-24} Since the polymerization takes place at elevated temperatures ($>200\text{ }^{\circ}\text{C}$) and with a constant nitrogen gas purge, low boiling temperature diols volatilize and leave the reaction flask, changing the charged stoichiometry throughout the reaction; thus the need for excess charged diol. In order for the stoichiometry to achieve the needed 1:1 ratio for high molecular weight, application of vacuum removes excess diol monomer, generated through transesterification at high temperatures. This method becomes difficult when diol monomers possess a high boiling point, making the excess difficult to remove or requiring long reaction times upon application of vacuum.

A standard method to avoid the longer reaction times is utilizing ethylene glycol (EG) as a sacrificial diol to ensure favorable stoichiometry. Exact mol equiv addition of dimethyl terephthalate (DMT), hydroxyethylresorcinol (HER), and hydroxyethylhydroquinone (HEH) to the reaction flask targeted desired final polyester compositions. 0.25 mol equiv of EG addition ensured excess diol and a volatile diol, which was easy to remove upon transesterification during high temperature and vacuum steps. As seen in **Scheme 6.1**, poly(HER-co-HEH T) synthesis followed previously reported procedures.^{4, 24} Reactions began at $170\text{ }^{\circ}\text{C}$ and increased up to $275\text{ }^{\circ}\text{C}$ over various temperature and time steps. A final step at $275\text{--}285\text{ }^{\circ}\text{C}$ under vacuum facilitated excess diol removal and high molecular weight polymer. ^1H NMR spectroscopy confirmed final chemical structures, as seen in **Figure 6.1**. No significant peaks related to PET repeat units confirms most of the excess EG was removed during the polymerization.



Scheme 6.1. Synthesis of (co)polyester regioisomers incorporating hydroxyethylresorcinol (HER; red) and hydroxyethylhydroquinone (HEH; blue) along with terephthalate

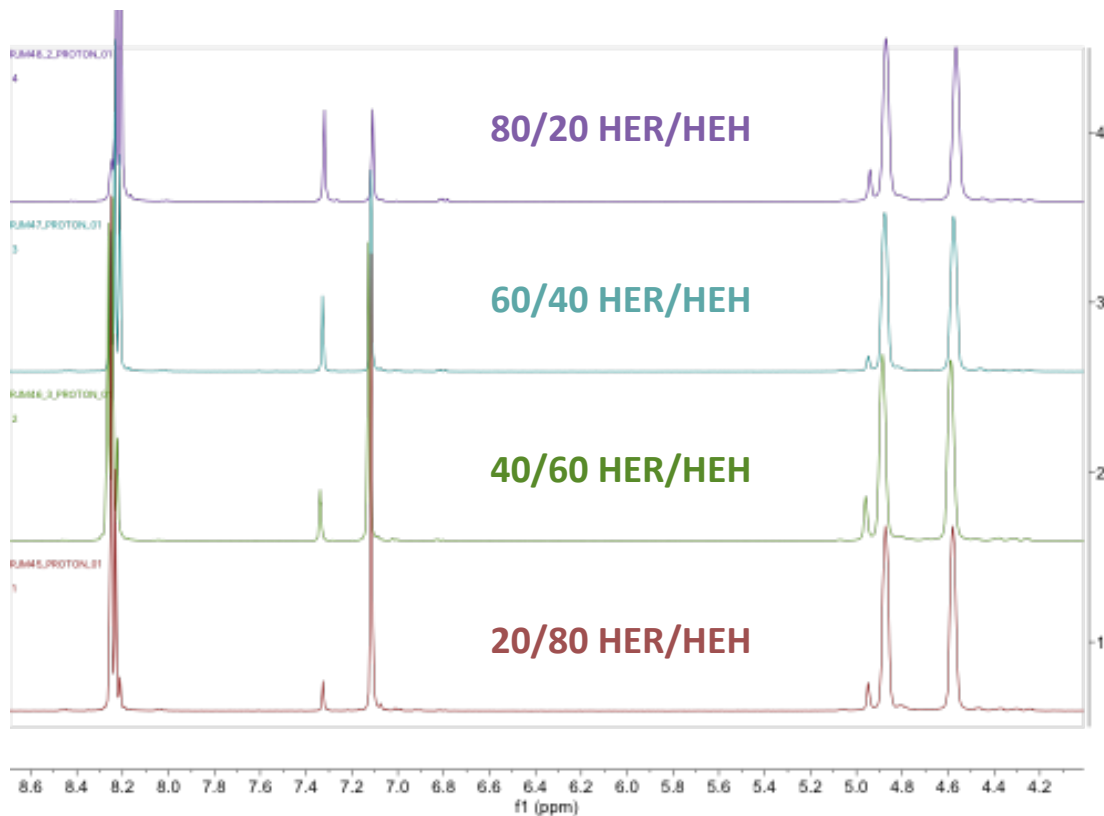


Figure 6.1. ^1H NMR spectra of poly(hydroxyethylresorcinol-co-hydroxyethylhydroquinone terephthalate) (co)polyesters

Differential scanning calorimetry (DSC) analyzed thermal transitions of the HER/HEH-based (co)polyesters. The glass transition temperature (T_g) of the homopolymers poly(HEH T) and poly(HER T) possess T_g s of 67 °C and 64 °C respectively, consistent with previous literature.¹⁻² As seen in **Figure 6.2**, T_g s of the copolyesters follow the Fox equation fit well, as expected for random amorphous copolymers. (Co)polyesters incorporating high levels of HER are amorphous until 80 mol % of HEH is incorporated. The homopolymer poly(HEH T) possesses a melting temperature (T_m) of 177 °C, consistent with pervious literature.¹ A slight melting point depression is observed when 20 mol % HER is incorporated, lowering the T_m as expected.

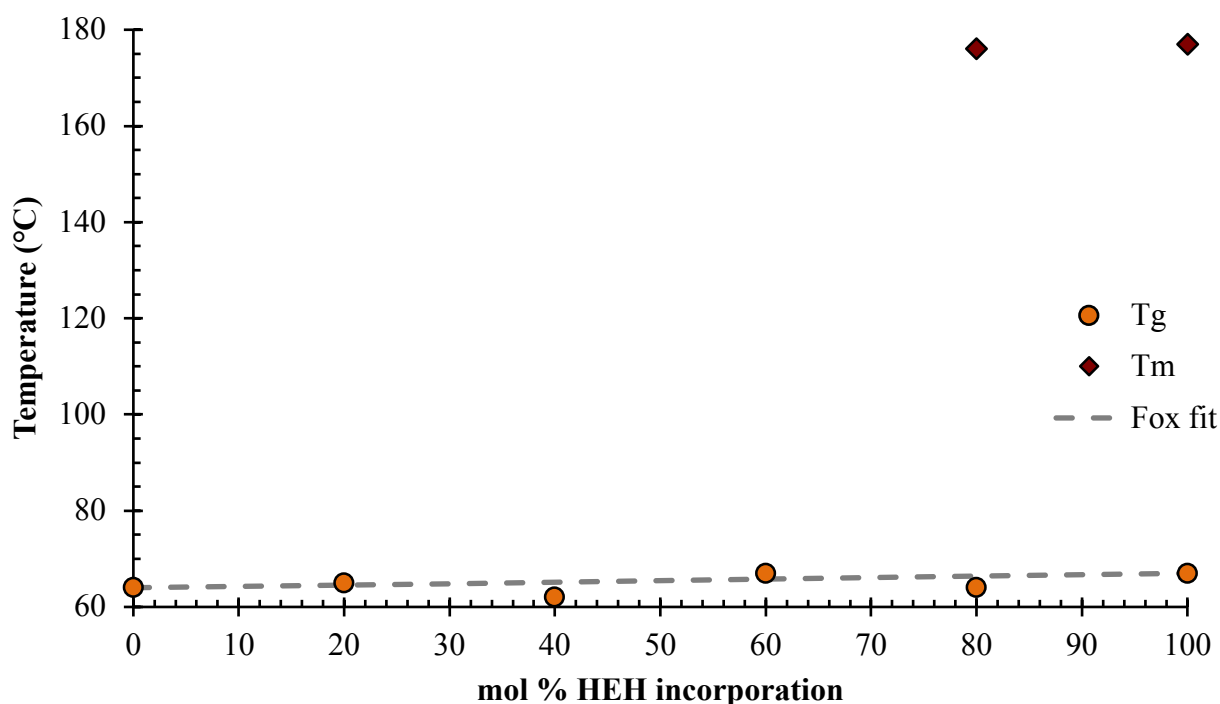


Figure 6.2. Glass transition temperatures (T_g ; orange circle) and melting temperatures (T_m ; brown diamond) of poly(hydroxyethylresorcinol-co-hydroxyethylhydroquinone terephthalate) (co)polyesters. The Fox equation fit is shown as a grey dotted line.

Step growth polymers are known to produce low molecular weight cyclics during polymerization along with the high molecular weight linear polymer.^{10, 16, 22, 25-26} The size

and wt % of cyclics greatly depends on the regiochemistry (bond angles) and structure of the monomers.^{10-11, 15, 27} Typically, *meta*-substituted monomers produce higher wt % of cyclics due to the lower ring strain as a result of the lower rigidity and kink imparted by the 1,3-linkage. Similarly, the *meta*-substituted linkage also favors smaller cyclics such as dimers. As seen in **Figure 6.3**, the HER/HEH-based (co)polyesters produce three potential regioisomer dimers, dependent on the incorporation of HER vs. HEH. Increasing the cyclic size to trimer, tetramer, etc. increases the complexity of the final structure due to many potential HER/HEH incorporation ratios as well as various potential sequences. Mass spectrometry (MS) in positive mode, confirmed the presence of cyclic dimer and trimer species. As seen in **Figure 6.4**, analysis of poly(hydroxyethylresorcinol₄₀-co-hydroxyethylhydroquinone₆₀ terephthalate) illustrates the dimer exhibited a much larger relative abundance, although further characterization is required to confirm relative amounts of cyclic species. All copolyesters exhibited similar trends (Figures S.6.1-6.3.)



Figure 6.3. Cyclic regioisomers of possible dimers produced during the synthesis of hydroxyethylresorcinol (HER; red) and hydroxyethylhydroquinone (HEH; blue)

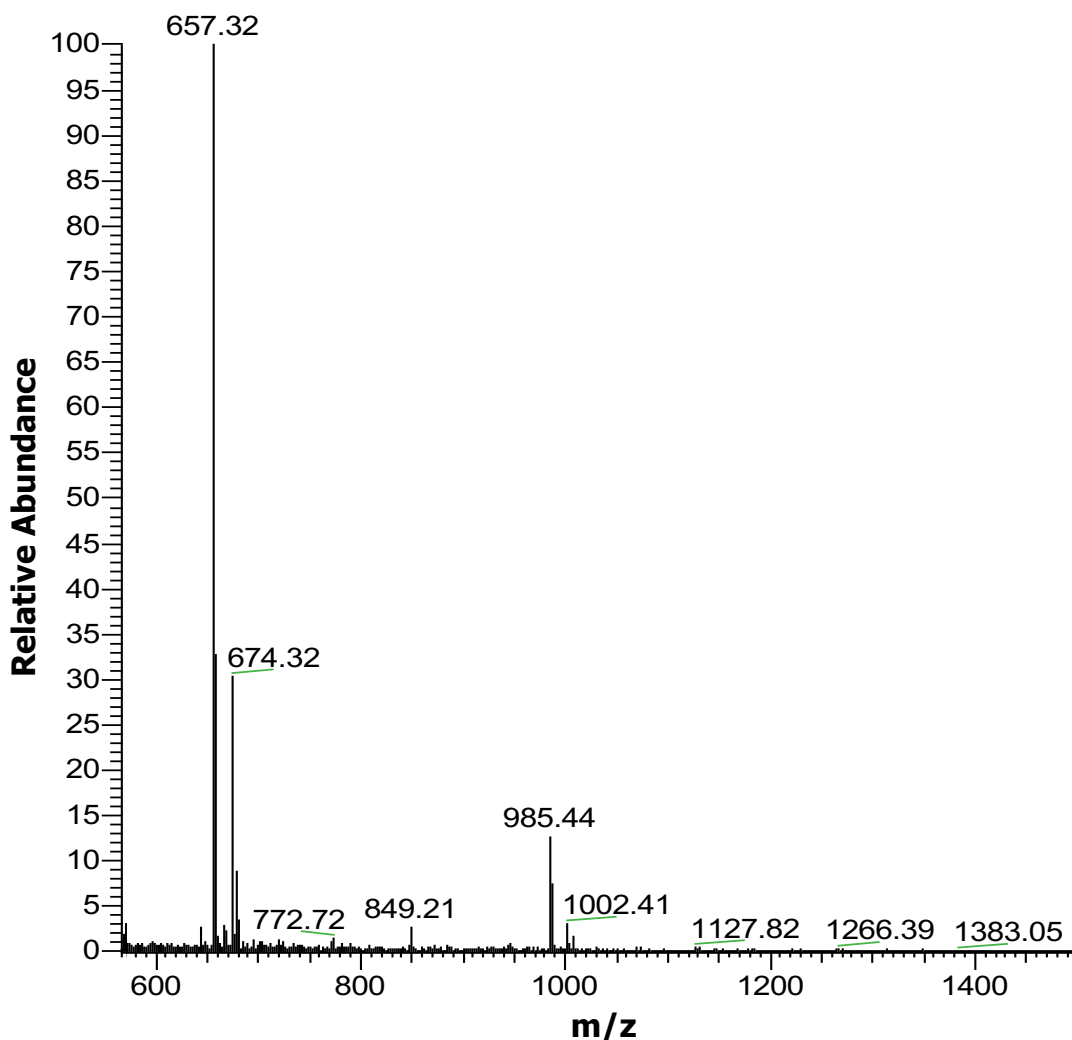


Figure 6.4. Mass spectrometry (MS) analysis of poly(hydroxyethylresorcinol₄₀-co-hydroxyethylhydroquinone₆₀ terephthalate) exhibiting m/z for dimer (657.32) and trimer (985.44) cyclic species

Advanced permeation chromatography (APC) enabled the separation of low molecular weight species utilizing two columns with 45 Å bead sizes as well as one column with 125 Å bead size. As seen in **Figure 6.5**, refractive index analysis detected sample elution at high retention times (5-6 min), typically where low molecular weight species such as cyclics elute. The 40 and 20 mol % HER samples possessed little RI detection at retention times expected for the high molecular weight copolyesters (3-4.5 min), due to

limited solubility of these polyesters in CHCl_3 . Although the high molecular weight polymer did not dissolve in the CHCl_3 , signal of low molecular weight species as well as detection of the cyclic species using MS, confirmed the solubility of the low molecular weight species in CHCl_3 . Thus, dissolving the samples for at least 72 h, allowed dissolution or extraction from the swollen insoluble polyesters and further analysis of the low molecular weight cyclic species.

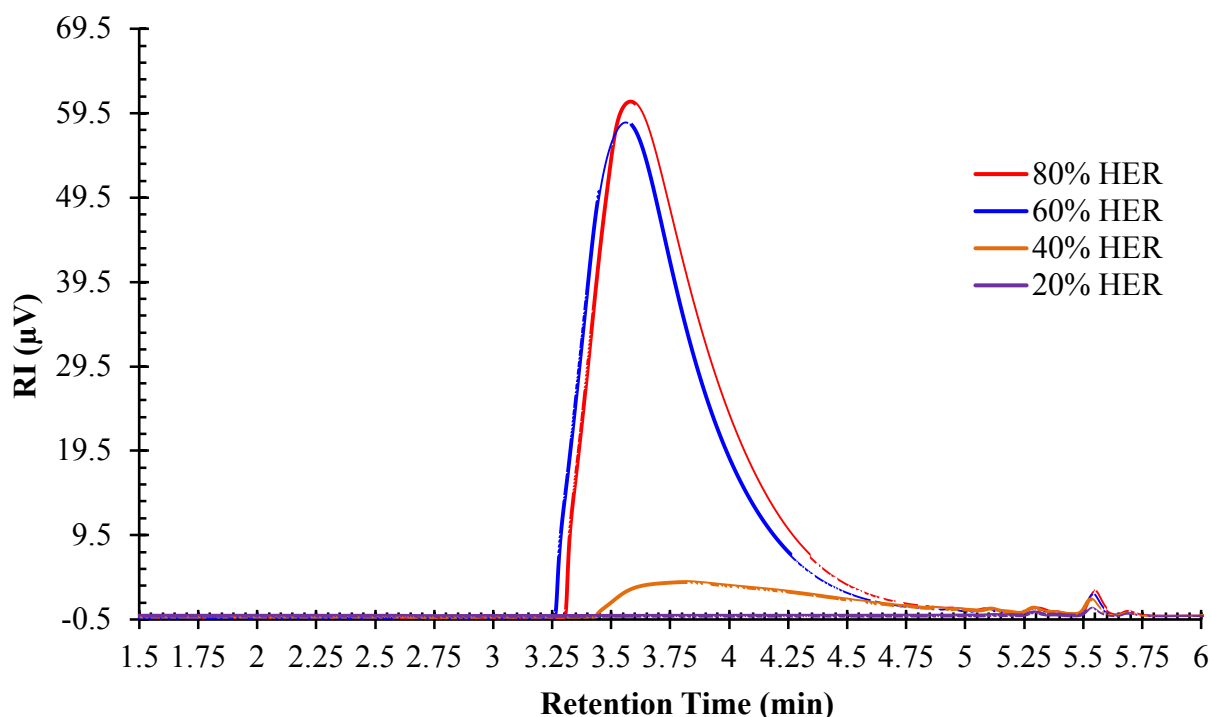


Figure 6.5. Advanced permeation chromatography (APC) of poly(HER/HEH T) copolyesters.

As seen in **Figure 6.6**, analysis of the APC chromatograms at high retention times afforded qualitative analysis of the different low molecular weight species, presumably different cyclic sizes. All copolyester samples possessed four peaks. Assuming the peak at the highest retention time is the cyclic dimer, the four peaks most likely correlate to the dimer (5.70 min), trimer (5.55 min), tetramer (5.30 min), and pentamer (5.10 min). The

trimer possesses the highest peak intensity, indicating the highest concentration of trimer relative to the other cyclics. A higher concentration of the trimer suggests it has the lowest ring strain and thus the highest probability to be produced during polymerization. Future computational studies are ongoing to determine which cyclic species possesses the lowest energy conformation and thus is most likely to form. The dimer and trimer peak possess the narrowest breadth of retention time, indicating the least variation of the coil size in solution. The dimer and trimer possess the least number of potential compositions from the three monomers, thus the most similar size in solution. The tetramer and pentamer peaks both broaden retention times due to the increased number of compositions influencing the size of the molecule in solution. Both comonomer incorporation as well as sequence will influence the size in solution, thus broadening the peak. Another possibility is the peak at 5.40 min is the linear trimer. The linear trimer would possess a larger coil size compared to the cyclic trimer, thus this linear species would elute at a lower retention time. Though the linear trimer is a possibility, the vacuum step at elevated temperatures at the end of the polymerization typically removes most of the linear low molecular weight species. Peak molecular weights were not determined due to the calibration curve necessary for relative molecular weight analysis not extending to low molecular weight species. Further analysis utilizing a light scattering detector and another 45 Å column will further separate the low molecular weight species as well as allow for determination of absolute molecular weights. More well resolved peaks as well as molecular weight analysis will help differentiate each peaks topology as well as composition. Although some uncertainty remains with respect to the true composition and topology of the peaks in the APC chromatogram, quantifying the area under the curve of each of the peaks allows for direct relative comparisons.

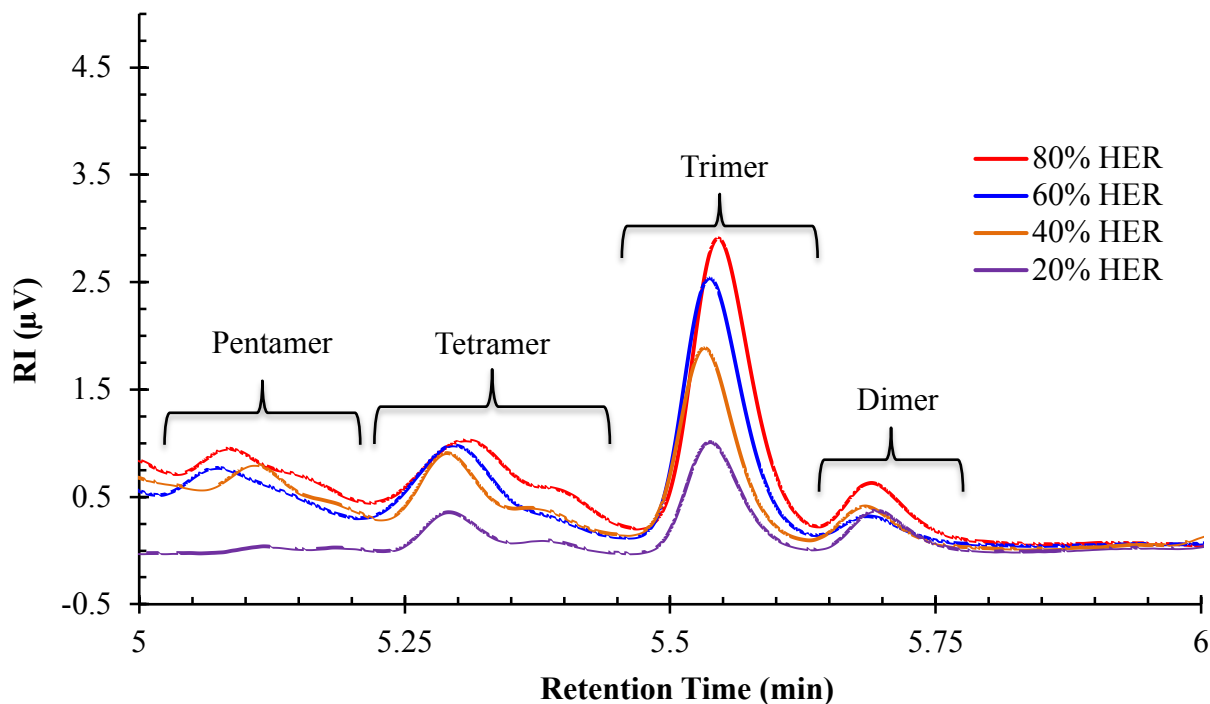


Figure 6.6. Advanced permeation chromatography (APC) analysis of low molecular weight species including cyclic dimer, trimer, tetramer, and pentamers.

Determining the area under each of the APC chromatogram peaks at high retention times enabled the relative comparison of amount of each presumed cyclic species. As seen in **Figure 6.7**, the higher HER incorporation resulted in a higher concentration of low molecular weight species. Overall, the trimer had the highest concentration for each of the copolyesters, followed by the tetramer, pentamer, and dimer. The relatively small concentration for the dimer suggests the ring strain of the dimer hinders its formation relative to the other cyclics. Overall cyclic wt % was not determined due to the limited solubility of the 20 and 40 mol % HER-based copolyesters, thus the main polymer chains were not able to be analyzed. Overall cyclic formation of the 60 and 80 wt % HER-based copolyesters was difficult due to the overlapping of the pentamer and main chain peak around 5.0 min retention time. Improved separation is required to accurately determine the

relative concentrations of the cyclic species and get an overall wt % of cyclics for each of the copolyester compositions.

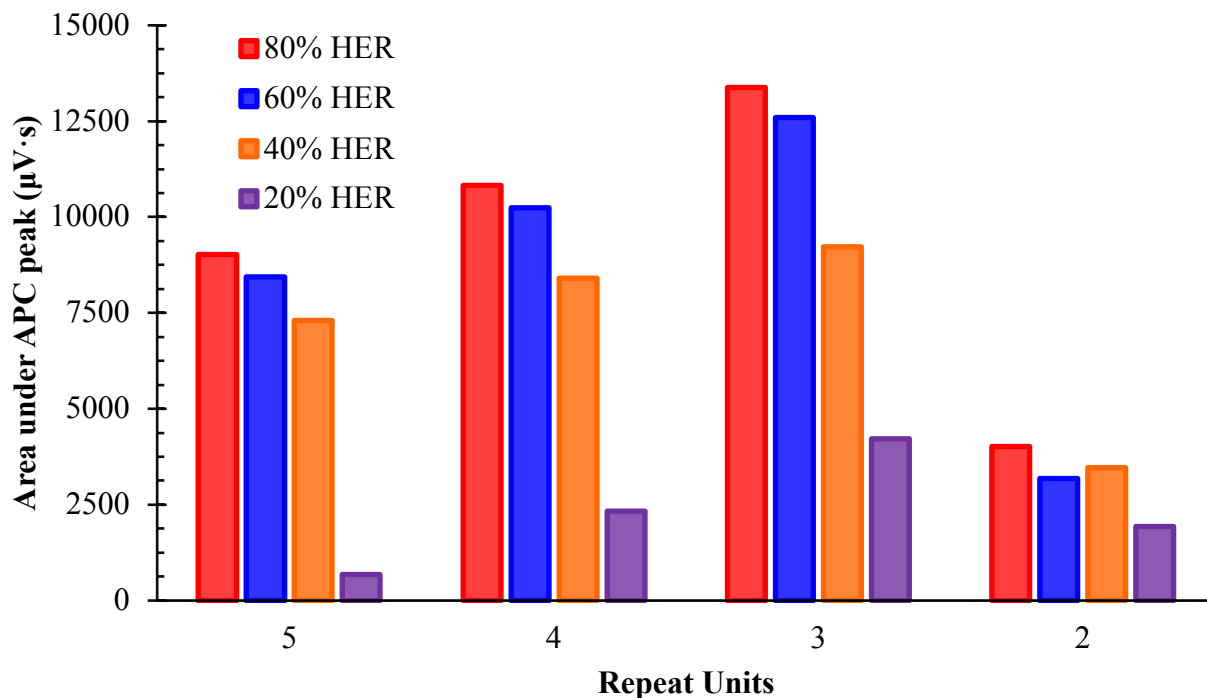


Figure 6.7. Absolute area of peaks related to the pentamer (5), tetramer (4), trimer (3), and dimer (2) low molecular weight species.

6.5 Conclusions

Step growth polymerization is known to produce cyclic species in equilibrium with high molecular weight linear chains. The influence of cyclics is also commonly overlooked when determining polymer structure-property relationships. Wt % of cyclic species in polymers can reach upward of 10 wt %. Additive addition into polymers drastically changes their properties as low as 1 wt %. Thus, it is important to consider the cyclics' produced in step growth polymerization impact to properties such as barrier and mechanical properties.

First, further understanding of monomer structure's relationship to cyclic formation needs to be determined. Kinked, *meta*-substituted monomers impart higher wt % of cyclics as well as lower repeat unit cyclics, due to decreased ring strain through the more favorable bond angles from the more kinked monomers. These cyclics typically act as additives, specifically like antiplasticizers. Thus, knowing the wt % of cyclics as well as the cyclics' size and shape is important to understand how they mix with the bulk polymer. A higher wt % of smaller size cyclics could fill free volume space, thus influencing barrier properties. This could help explain why HER and poly(ethylene isophthalate) (PEI) polyesters possess improved barrier performance over their *para*-substituted analogues. This relationship has never been confirmed or explored, thus further evaluation is needed to relate monomer/polymer structure, cyclic wt %/size, and bulk polymer properties.

A major challenge with understanding properties of polyesters void of cyclics compared to polymers incorporating cyclics is that most polyesters are synthesized in the melt as well as processed in the melt. Since cyclics are a thermodynamic equilibrium, removal of cyclics followed by melt processing, regenerates the cyclics, making cyclic free polymer property measurements difficult. Thus, soluble and solution processable polyesters are required to extract the cyclics from the high molecular weight polymers as well as process films. Solubility of semi-aromatic polyesters is limited; thus, careful consideration is needed when choosing monomers. HER- and HEH-based polyesters offer increased solubility compared to PET and PEI, although copolyesters with terephthalate offers partial solubility in some compositions. Synthesizing a series of polyesters incorporating HER/HEH with a diacid/diester to impart solubility and easy solution processing is required study the influence of cyclics on bulk polymer properties.

6.6 Acknowledgements

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6.7 References

1. Andrade, G. S.; Collard, D. M.; Schiraldi, D. A.; Hu, Y. S.; Baer, E.; Hiltner, A., Oxygen barrier properties of PET copolymers containing bis(2-hydroxyethyl)hydroquinones. *J. Appl. Polym. Sci.* **2003**, *89* (4), 934-942.
2. Durairaj, R. B., Resorcinol additives for packaging extend product life for food and drink. *Plastics, Additives, and Compounding* **1999**, *1* (5), 30-34.
3. Edling, H. E.; Liu, H.; Sun, H.; Mondschein, R. J.; Schiraldi, D. A.; Long, T. E.; Turner, S. R., Copolyesters based on bibenzoic acids. *Polymer* **2018**, *135*, 120-130.
4. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R. K.; Nazarenko, S.; Turner, S. R.; Long, T. E., Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance. *Macromolecules* **2017**, *50* (19), 7603-7610.
5. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of copolymers based on ethylene terephthalate. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (16), 1889-1899.
6. Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J., Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate). *Macromolecules* **2014**, *47* (4), 1383-1391.
7. Iyer, K. A., Chain mobility, secondary relaxation, and oxygen transport in terephthalate copolyesters with rigid and flexible cyclic diols. *Polymer* **2017**, *129*, 117-126.
8. Light, R. R.; Seymour, R. W., Effect of sub-T_g relaxations on the gas transport properties of polyesters. *Polym. Eng. Sci.* **1982**, *22* (14), 857-864.
9. Maxwell, A. S.; Ward, I. M.; Lauprêtre, F.; Monnerie, L., Secondary relaxation processes in polyethylene terephthalate-additive blends: 1. N.m.r. investigation. *Polymer* **1998**, *39* (26), 6835-6849.
10. Cooper, D. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 11. Cyclics in poly(ethylene terephthalate). *Polymer* **1973**, *14* (5), 185-192.
11. Harrison, A. G.; Taylor, M. J.; Scrivens, J. H.; Yates, H., Analysis of cyclic oligomers of poly(ethylene terephthalate) by liquid chromatography/mass spectrometry. *Polymer* **1997**, *38* (10), 2549-2555.
12. Ross, S. D.; Coburn, E. R.; Leach, W. A.; Robinson, W. B., Isolation of a cycle trimer from polyethylene terephthalate film. *J Polym Sci* **1954**, *13* (70), 406-407.
13. Walker, G. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 4. Calculation of cyclic trimer content of poly(ethylene terephthalate). *Polymer* **1970**, *11* (9), 472-485.
14. Peebles, L. H.; Huffman, M. W.; Ablett, C. T., Isolation and identification of the linear and cyclic oligomers of poly(ethylene terephthalate) and the mechanism of cyclic oligomer formation. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1969**, *7* (2), 479-496.
15. Berr, C. E., Isolation of a Cyclic Dimer during Synthesis of Polyethylene Isophthalate. *J Polym Sci* **1955**, *15* (80), 590-591.

16. Holland, B. J.; Hay, J. N., Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate). *Polymer* **2002**, *43* (6), 1797-1804.
17. Zekriardehani, S.; Joshi, A. S.; Jabarin, S. A.; Gidley, D. W.; Coleman, M. R., Effect of Dimethyl Terephthalate and Dimethyl Isophthalate on the Free Volume and Barrier Properties of Poly(ethylene terephthalate) (PET): Amorphous PET. *Macromolecules* **2018**, *51* (2), 456-467.
18. Shi, Y. Polyester Composition with Enhanced Gas Barrier, Articles Made Therewith, and Methods. 2005.
19. Shi, Y. S., R. J.; Walters, C.; Kriegel, R.; Huang, X. Polyester Container with Enhanced Gas Barrier and Method. 2006.
20. Shi, Y. S., F. M.; Weemes, D. A.; Weemes, M. K. Container and Composition for Enhanced Gas Barrier Properties. 2010.
21. Kang, H. Y.; Lin, Q.; Armentrout, R. S.; Long, T. E., Synthesis and characterization of telechelic poly(ethylene terephthalate) sodiosulfonate ionomers. *Macromolecules* **2002**, *35* (23), 8738-8744.
22. Scheirs, J.; Long, T. E., *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*. John Wiley & Sons, Ltd: 2003.
23. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E., Influence of cyclobutane segments in cycloaliphatic decahydronaphthalene-containing copolyesters. *High Perform. Polym.* **2017**, *29* (6), 750-756.
24. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R.; Sirrine, J. M.; Weiseman, T. F.; Nazarenko, S.; Colby, R. H.; Turner, S. R.; Long, T. E., Influence of Bibenzoate Regioisomers on Cyclohexanedimethanol-based (Co)polyester Structure-Property Relationships. *Macromolecules* **2018**, *Submitted*.
25. Semlyen, J. A., Ring-chain equilibria and the conformations of polymer chains. In *Mechanisms of Polyreactions-Polymer Characterization*, Springer: Berlin, Heidelberg, 1976; pp 41-75.
26. Carothers, W. H., Polymerization. *Chem. Rev.* **1931**, *8* (3), 353-426.
27. Heath, R., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 16. Theoretical and experimental investigations of cyclics prepared from poly(decamethylene fumarate) and poly(decamethylene maleate) ring-chain equilibrium reactions. *Polymer* **2000**, *41* (4), 1487-1495.

6.8 Supporting Information

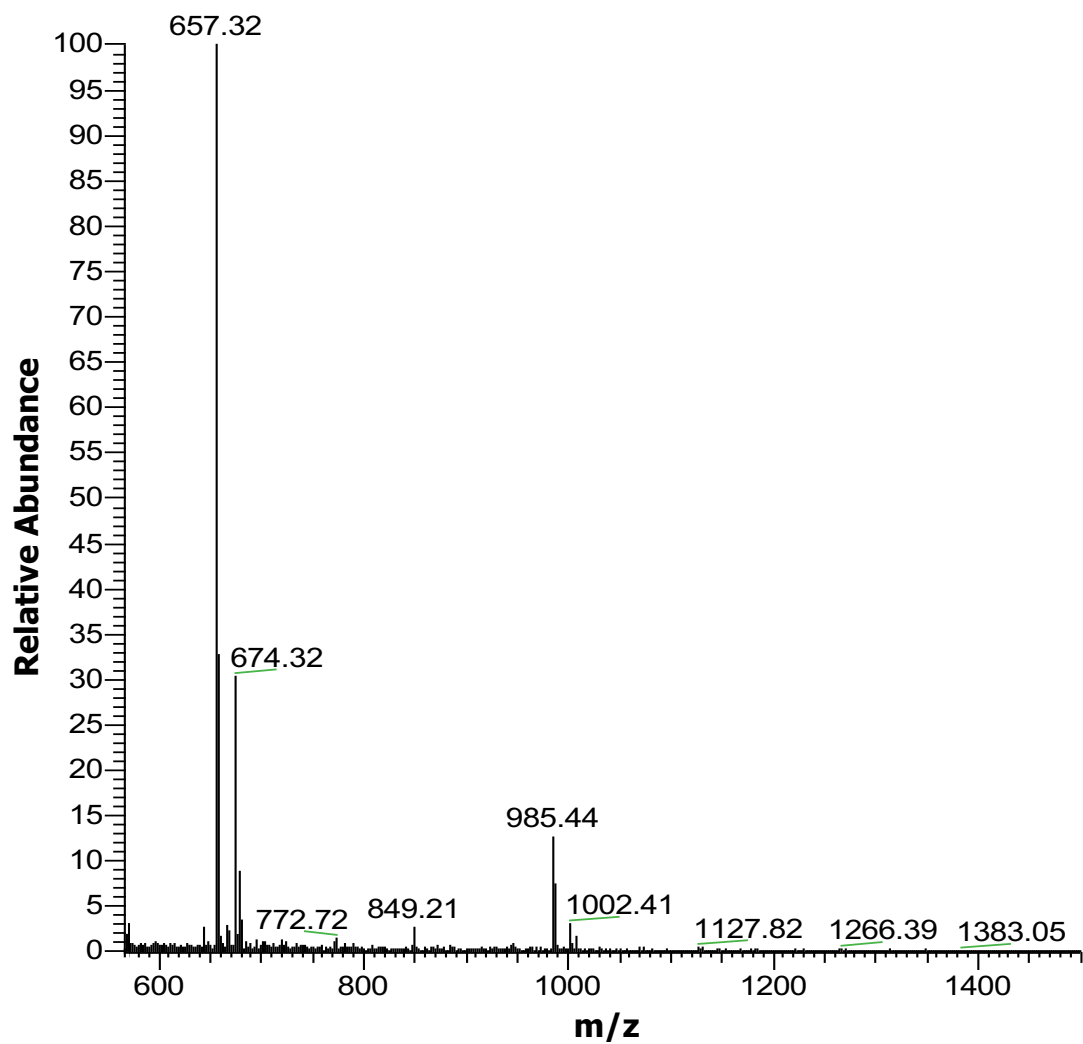


Figure S6.1. Mass spectrometry (MS) analysis of poly(hydroxyethylresorcinol₂₀-co-hydroxyethylhydroquinone₈₀ terephthalate) exhibiting m/z for dimer (657.32) and trimer (985.44) cyclic species

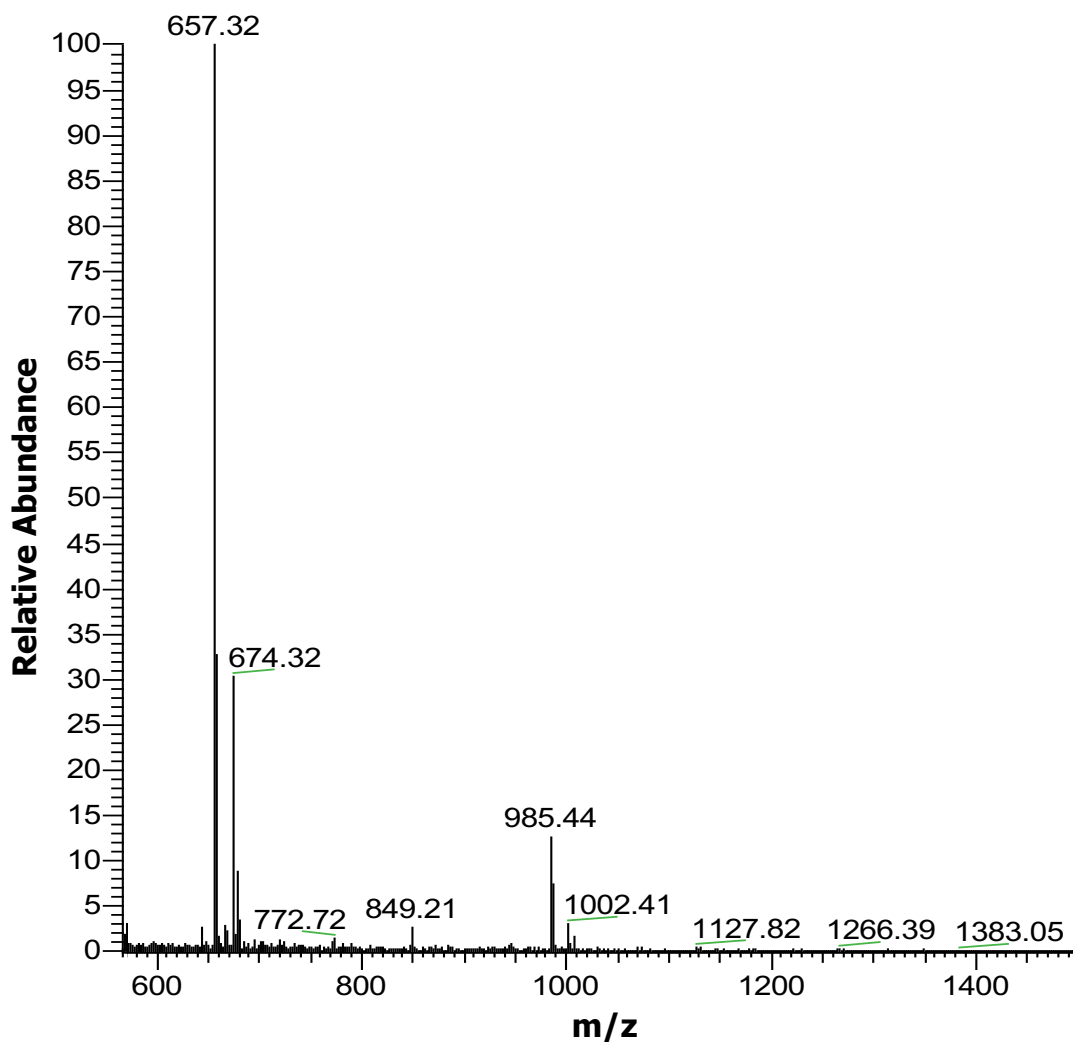


Figure S6.2. Mass spectrometry (MS) analysis of poly(hydroxyethylresorcinol₆₀-co-hydroxyethylhydroquinone₄₀ terephthalate) exhibiting m/z for dimer (657.32) and trimer (985.44) cyclic species

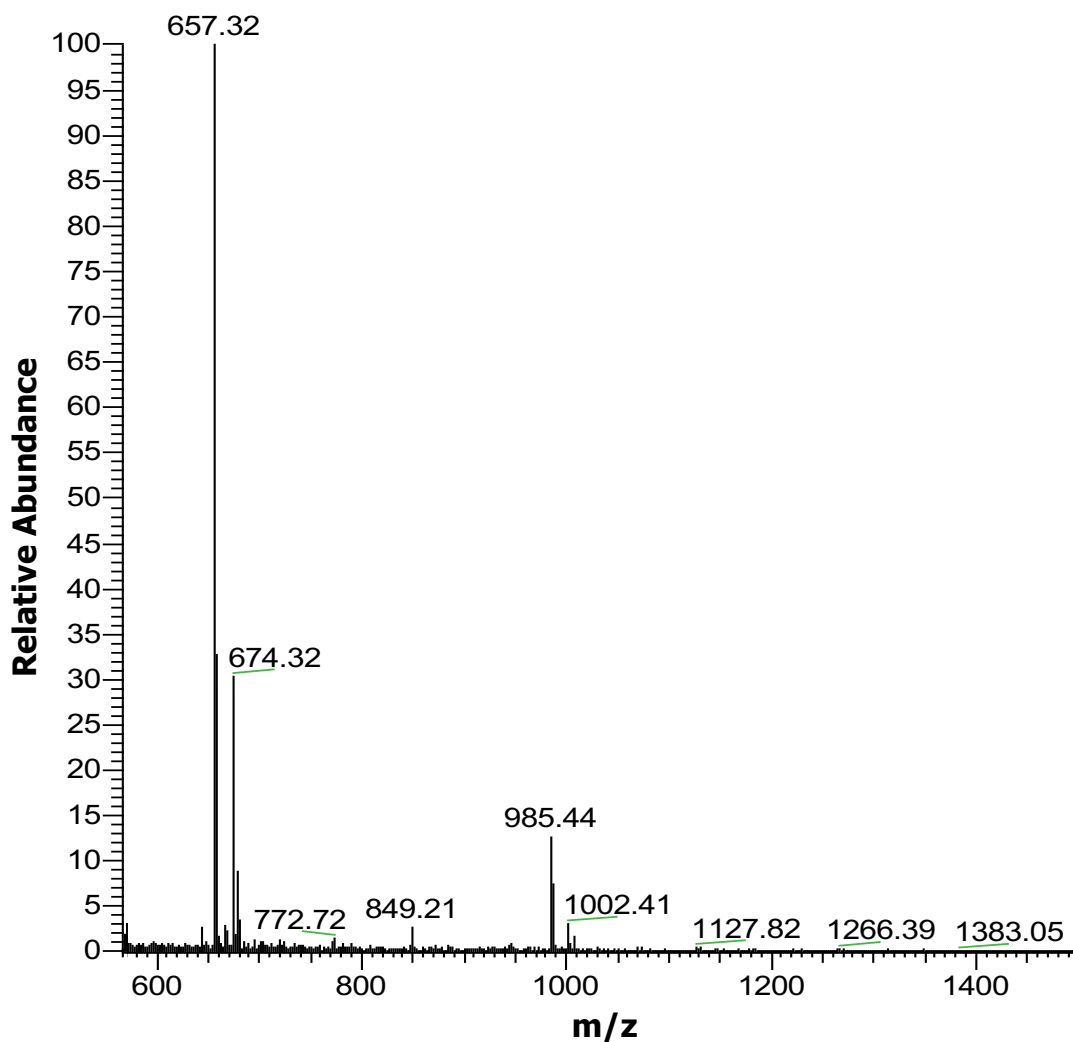


Figure S6.3. Mass spectrometry (MS) analysis of poly(hydroxyethylresorcinol₈₀-co-hydroxyethylhydroquinone₂₀ terephthalate) exhibiting m/z for dimer (657.32) and trimer (985.44) cyclic species

Chapter 7: Synthesis and Characterization of Polyetherimides (PEI)s with Functional Pendant Groups: Reactive Branching Imparts Improved Processability and Flame Resistant Properties

(Manuscript in preparation for publication)

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7.1 Abstract

Incorporation of 3,5-diaminobenzoic acid (DABA) into poly(ether imide)s (PEI) including bisphenol-A dianhydride (BPA-DA) and *meta*-phenylene diamine (MPD) enabled the synthesis of PEIs with functional pendant carboxylic acids. Room temperature reactions promoted poly(amic acid) formation and subsequent imidization studies utilizing thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) determined imidization temperatures (T_{im}). Synthesis of the DABA-incorporated PEIs utilizing the determined T_{im} afforded PEIs and thermal characterization with TGA and differential scanning calorimetry (DSC) determined DABA incorporation lowered the onset of weight loss temperatures ($T_{d,5\%}$) but increased the glass transition temperatures (T_g)s. Comparing the T_g and T_{im} revealed all compositions required 40-45 °C above the T_g to fully imidize. Dynamic mechanical analysis (DMA) probed thermomechanical responses and revealed samples with high mol % DABA exhibited a plateau post T_g ,

suggesting crosslinking. Analysis of the off-gas at elevated temperatures of DABA-containing PEI samples with TGA coupled to FTIR confirmed decarboxylation between 300 and 400 °C. CO₂ off-gas FTIR intensity and starting DABA mol % incorporation afforded a linear relationship. Exploiting the pendant carboxylic acid group on DABA, low mol % DABA PEI samples (5 & 10 mol %) enabled branching in the melt. Advanced permeation chromatography (APC) monitored molecular weight and polydispersity (PDI) changes over 60 min in the melt. The generation of complex viscosity (η^*) master curves enabled the evaluation of branching on η^* at low shear rates as well as over the shear thinning regime. The 10 mol % branched DABA PEI exhibited the highest η^* at low frequencies, while also possessing the steepest shear thinning slope. Lastly, the increased η^* of the 10 mol % branched DABA PEIs imparted improved flame resistance as evidence by a lack of dripping and after-flame, which was observed in non-branched samples.

7.2 Introduction

Polyimides (PIs), typically classified as high performance polymers, possess high thermal stability (>450 °C), thermomechanical properties, mechanical performance, and highly aromatic composition.¹ Although PIs possess numerous properties required for applications in automotive, aerospace, electronics, and consumer applications, the rigid and aromatic backbone presents processing challenges such as insolubility or limited melt flow at common processing temperatures and shear rates. Thus, these polymers require manufacturing using high energy consumption or alterations to the backbone composition to improve processability. Recently, advances in additive manufacturing (also known as 3-dimensional (3D) printing) offer new avenues to manufacture previously difficult to

process PIs.²⁻⁴ Hence, high interest remains in developing PIs with improved properties while also improving processability.

The most commonly employed method to improve PIs processability is to incorporate flexible linkages into the backbone such as an ether and/or an isopropylidene/hexafluoro-isopropylidene.⁵⁻⁷ Commonly known as polyetherimides (PEIs), these high performance thermoplastics offer processability, such as in injection molding, while maintaining desirable thermal and mechanical properties.⁸ Other methods utilized to improve processability include compositional and topological changes. Incorporation of thioether linkages increases backbone flexibility, but typically lessens thermal stability.⁹⁻¹¹ Long-chain branching imparts improved shear thinning behavior at processing shear rates, though careful consideration is required to avoid crosslinking during synthesis.¹² Decreasing chain packing and alignment through alterations in backbone regiochemistry,¹³⁻¹⁴ pendant groups,¹⁵ or bulky halogenated monomers¹⁶ all improve processability but likely increase cost and reduce mechanical properties. Lastly, latent reactive pendant groups or end-cappers offer easily processable polymers which react during or after processing to form products with the desired properties of compositions more difficult to process.

Reactive extrusion¹⁷⁻¹⁸ and post-processing treatment utilize reactive functionality, typically activated at high temperatures, to increase molecular weight or promote crosslinking during or after processing. Typically, low molecular weight oligomers are utilized to possess better processability while the final product possesses properties akin to high molecular weight polymers. The most commonly used functionality in PEIs include various phenylethynyl structures as chain end-cappers due to their high thermal stability

and tunability.¹⁹⁻²³ Chain extension/crosslinking as well as reaction rates are tuned through the end-capper structure.²⁴⁻²⁵ Reversible Diels-Alder chemistry affords “reprocessable” polymers, though careful consideration is required when processing due to thermal instability of commonly utilized functional groups.²⁶ A lesser utilized reactive functionality is a pendant carboxylic acid group, although it is typically cheaper than phenylethynyl groups.

At temperatures near and above 300 °C, carboxylic acid pendant groups on PEIs incorporated through the monomer 3,5-diaminobenzoic acid (DABA) decarboxylate and form biphenyl units or other crosslinks through radical coupling.²⁷⁻²⁸ Exploiting the production of carbon dioxide and carbon monoxide, researchers developed porous gas separation membranes based on PEIs with tunable performance based on composition and processing.^{27, 29-32} Subsequent pyrolysis afforded carbon molecular sieve membranes which also acted as gas separation membranes.³³⁻³⁶ Although current research shows promise for gas separation, limited research exists on other important PEI properties such as melt processability and flame retardance, or utilizing reactive functionality to induce branching during processing.

Long-chain branching (LCB) influences polymer melt strength and shear thinning behavior,^{12, 37-38} both contributing to the polymer’s processability. Low branching density reduces coil size altering viscosity and more rapid shear thinning at similar molecular weights and processing temperatures.³⁹ Thus PEIs incorporating LCB offer an avenue to tune rheological performance while increasing melt flow properties.¹² Processing-induced branching uses lower molecular weight starting polymer which is easier to process, but reacts to form higher molecular weight and zero-shear viscosity during or after processing.

It is suggested that higher molecular weights correspond to increased flame resistant properties due to the lower propensity of dripping imparted by the higher viscosity at low shear rates.⁴⁰ PEIs typically possess desirable flame retardance due to their highly aromatic composition, although thinner samples decrease flame resistant properties.⁴¹ Thus, improving flame retardance while improving processability is highly desirable, especially in thin films.

This report describes the synthesis and characterization of melt processable PEIs incorporating reactive pendant carboxylic acid functionality. Replacement of *meta*-phenylene diamine (MPD) with DABA in PEI synthesis utilizing a bisphenol-A dianhydride resulted in a series of PEIs with targeted compositions. Thermal analysis probed imidization temperatures (T_{im}), onset of weight loss ($T_{d,5\%}$), and glass transition temperatures (T_g). Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) confirmed decarboxylation consistent with the mol % of DABA monomer incorporated. Dynamic mechanical analysis (DMA) confirmed crosslinking at high mol % DABA incorporation. Utilizing melt rheology, simulated processing branched low mol % DABA PEIs in the melt and subsequent rheological analysis confirmed high viscosities at low shear rates as well as steeper shear thinning. Advanced permeation chromatography (APC) confirmed increases in molecular weight and polydispersity (PDI) for samples processed which included DABA. Melt pressed branched PEI samples possessed improved flame resistant properties due to the higher viscosity at low shear rates post processing.

7.3 Experimental

7.3.1 Materials. Phthalic anhydride (PA) (Sigma-Aldrich; ReagentPlus 99%) was dried in a vacuum oven at 60 °C overnight prior to use. *Meta*-phenylene diamine (MPD) (Aldrich; flakes 99%) was sublimated under reduced pressure prior to use. Bisphenol-A dianhydride (BPA-DA) was kindly supplied by SABIC in high purity. Under a N₂ blanket, BPA-DA was dried and ensured to be in the anhydride form by heating into the liquid phase and cooling to an amorphous solid. 3,5-diaminobenzoic acid (DABA) (Aldrich, 98%) was purified by recrystallization in DI H₂O prior to use. All monomers were stored under vacuum. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. All other solvents were purchased from Spectrum Chemical and used as received.

7.3.2 Analytical Methods. ¹H NMR spectroscopy was operated at 23 °C and at 400 MHz on a Varian Unity 400 in deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (DMSO-d₆). A Waters ACQUITY Advanced Permeation Chromatograph (APC) equipped with one 450 Å x 150 mm, one 200 Å x 150 mm, and one 125 Å x 150 mm XT columns and a Waters ACQUITY RI detector used a 1.0 mL min⁻¹ flow rate at 40 °C in CHCl₃ to afforded molecular weights relative to polystyrene standards. Prior to APC analysis, dynamic light scattering (DLS) at 40 °C analyzed all polymer solutions in CHCl₃ confirming no aggregation. Differential scanning calorimetry (DSC) probed thermal transitions using a TA instruments Q1000 DSC, calibrated with indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards, and utilizing a nitrogen flow of 50 mL min⁻¹ at a 10 °C min⁻¹ heating and cooling rate. Utilizing the second heating ramp, glass transition temperatures (*T*_g) were measured at the midpoint of the transition. Thermogravimetric

analysis (TGA) using a TA Instruments Q50 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 25 to 600 or $1000\text{ }^{\circ}\text{C}$ analyzed weight loss as a function of time in nitrogen or air. Stepwise isothermal analysis employed a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and an isothermal step when weight % changes were $>0.1\% \text{ min}^{-1}$ and heating resumed once weight % changes were $<0.01\% \text{ min}^{-1}$. TGA coupled to a Thermo-Fisher Nicolet iS-10 Fourier transform infrared spectrometer (TGA-FTIR) analyzed evolved gas of 20 mg samples heated at $20\text{ }^{\circ}\text{C min}^{-1}$. Isothermal steps were employed for 30 min between solvent evaporation/imidization and decarboxylation as well as between decarboxylation and backbone degradation to separate FTIR analysis of the various off-gas components. FTIR analysis of imidized films was performed on a Varian 670-IR equipped with a Diamond GladiATR attachment. Spectral data was acquired with 32 scans each at a resolution of 4 cm^{-1} . Stepwise isothermal analysis probed imidization temperatures (T_{im}). Dynamic mechanical analysis (DMA) revealed modulus *versus* temperature behavior utilizing a TA Instruments Q800 Dynamic Mechanical Analyzer in oscillatory tension mode at a 1 Hz frequency, a $15\text{ }\mu\text{m}$ oscillatory amplitude, and a 0.01 N static force with a $3\text{ }^{\circ}\text{C min}^{-1}$ heating ramp. Compression molding was performed on a Carver Model No. 3856 and utilized two stainless steel plates covered with Kapton® films coated with Rexco Partall® Power Glossy Liquid mold release agent to produce transparent and ductile films. 16 mil thick steel shims controlled film thickness.

Rheological analysis was performed under N_2 atmosphere on a TA Instruments Discovery Hybrid Rheometer (DHR)-2 using an 8 mm diameter disposable aluminum parallel-plate geometry. Strain sweep testing from 0.01-10% oscillatory strain at 1 Hz probed the linear viscoelastic region (LVR). Utilizing 1.25% oscillatory strain amplitude and an oscillatory frequency range of $1\text{-}100\text{ rad s}^{-1}$, frequency sweeps at $10\text{ }^{\circ}\text{C}$ intervals

from 340 °C to 220 °C provided complex viscosity (η^*) as well as storage (G') and loss moduli (G''). TA Instruments software (TRIOS) generated master curves by shifting viscosity and moduli. Melt flow property determination involved power law analysis of the shear thinning regime. Time sweeps at 10 rad/s and 1.0 % strain amplitude for 1 h (3600 s) monitored viscosity and modulus as a function of time and induced branching in the melt.

Flame-test-response setup and analysis used UL94-V and ASTM D3801 for guidance. A vertical flame test was performed on melt pressed films approximately 10 mm wide, 0.4 mm thick, and 100 mm tall. Films were conditioned in a vacuum desiccator for at least 48 h prior to testing. A flame was applied to the bottom of the rectangular sample and was approached from the wide side. The sample was exposed to the flame for 10 s and the time the sample remained on fire was determined as t_1 . Once the flame extinguished, the same sample was exposed to the flame for 10 s and the time the sample remained on fire was determined as t_2 . After the flame extinguished, the time of ember afterglow was recorded as t_3 . The flame testing was performed over cotton and drips were recorded as well as if the drip caused the cotton to ignite.

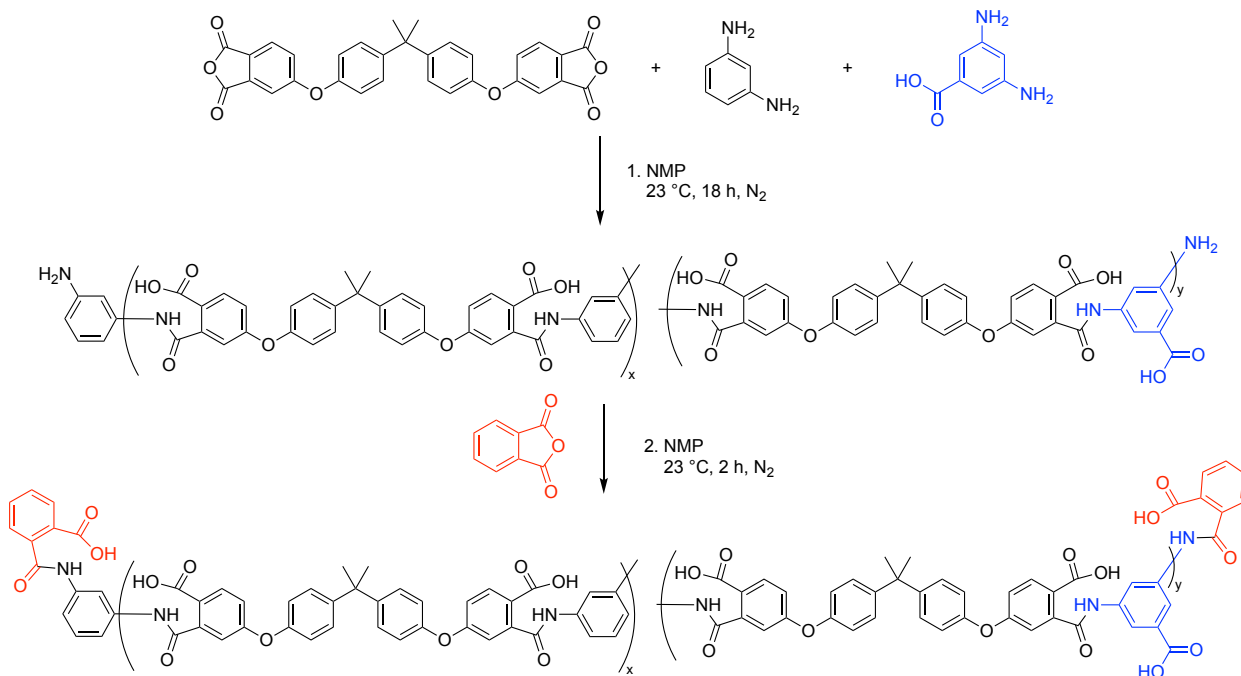
7.3.3 Synthesis of poly(ether imides) (PEIs). The synthesis of a 20 kg mol⁻¹ number average molecular weight (M_n) poly(ether imide) follows as an example targeting 50 mol % DABA. 3,5-diaminobenzoic acid (DABA) (3.02 g, 19.6 mmol), *meta*-phenylene diamine (MPD) (2.12 g, 19.6 mmol), bisphenol-A dianhydride (BPA-DA) (20.00 g, 37.8 mmol) and *n*-methyl-2-pyrrolidone (92 mL) were charged to a three-necked, 500-mL, round-bottomed flask. The flask was then equipped with a glass stir rod fitted with a Teflon stir blade, a rubber septum, and a Dean-Stark trap topped with a condenser. The contents

were purged with nitrogen for 20 minutes while slowly stirring. Imidization studies proceeded through the poly(amic acid) (PAA). To produce the PAAs, contents were stirred at 75-100 rpm at RT for 18 h once all compounds dissolved. Phthalic anhydride (PA) (0.42 g, 2.9 mmol) was then added to end-cap the polymers. PAA solutions were then either precipitated into methanol and isolated or solutions were cast immediately to produce films. The same setup as PAA synthesis was used for direct PEI synthesis but after purging with nitrogen, contents were heated to 180 °C and stirred at 75-100 rpm for 18 h. PA was then added to the reaction. Similarly, either precipitation or solution casting films followed. Both PAA and PEI films were cast onto glass plates/slides and heated to various temperatures to either partially imidize or fully imidize. Transparent, ductile, and orange/brown films resulted from melt pressing.

7.4 Results and Discussion

As seen in **Scheme 7.1**, poly(amic acid)s (PAA)s synthesized at room temperature proceeded through a one-pot, two-step reaction. First, utilizing an excess of total diamines, BPA-DA, MPD, and DABA dissolved in NMP (20 wt % solids) and stirred at RT afforded PAAs with amine end-groups. 1.1 mol equiv of PA per amine end group end-capped the PAAs in the second step. Precipitating PAAs into methanol purified and isolated the polymers as an off-white powder. ¹H NMR spectroscopy determined comonomer mol % incorporations and also confirmed targeted number average molecular weights (M_n) through end-group analysis of the shifts associated with the PA aromatic protons (Figure S7.1.). Solution casting samples directly from the reaction mixture produced free-standing films. Samples cast onto glass slides/plates and heated to 80, 150, or 200 °C enabled analysis of the imidization temperature. After removing the films from the glass substrate

and drying, FTIR and thermogravimetric analysis (TGA) determined the temperatures required for full imidization (T_{im}).



Scheme 7.1: Synthesis of poly(ether amic acid)s (PEAA)s incorporating 3,5-diaminobenzoic acid (DABA) (blue) and end-capping with phthalic anhydride (PA) (red)

TGA probed T_{im} through stepwise analysis, where a change of greater than 0.1 wt % per min prompted an isothermal step lasting until a change of less than 0.01 wt % per min occurred, with repeating heating and isothermal steps until the sample reached 600 °C. Using 50 mol % DABA-PAA as an example (Figure S7.2.), films heated to 80 and 150 °C exhibited an isothermal step around 260 °C and a second isothermal step around 480-490 °C. The first isothermal step occurs due to volatilization of the NMP solvent as well as thermal imidization. T_{im} was determined as the temperature of the isothermal step plus 10 °C. FTIR analysis of films heated to appropriate T_{im} confirmed these temperatures (Figure S7.3.).⁴² Films heated to 150 °C were chosen to analyze for all compositions, as seen in **Figure 7.1.**

All compositions displayed two isothermal steps. The first isothermal step occurred between 250-300 °C. Higher mol % DABA incorporation increased the temperature of the first step. The first isothermal step plus 10 °C determined the T_{im} of each composition. As seen in **Figure 7.2**, the T_{im} increased linearly with increased incorporation of the mol % DABA comonomer, up to 300 °C for the 100 mol % DABA-PEI. All compositions exhibited a steady weight % between T_{im} and 450 °C, where weight loss began again until the second isothermal step near 520 °C. The second isothermal step occurred due to backbone degradation, consistent with other PEIs. Weight loss between 450 °C and the second isothermal step became more noticeable for higher mol % incorporation of DABA suggesting thermal instability before backbone degradation imparted by the inclusion of the carboxylic acid pendant group. Pendant carboxylic acid groups in PEIs are known to decarboxylate at temperatures ≥ 300 °C.³⁰

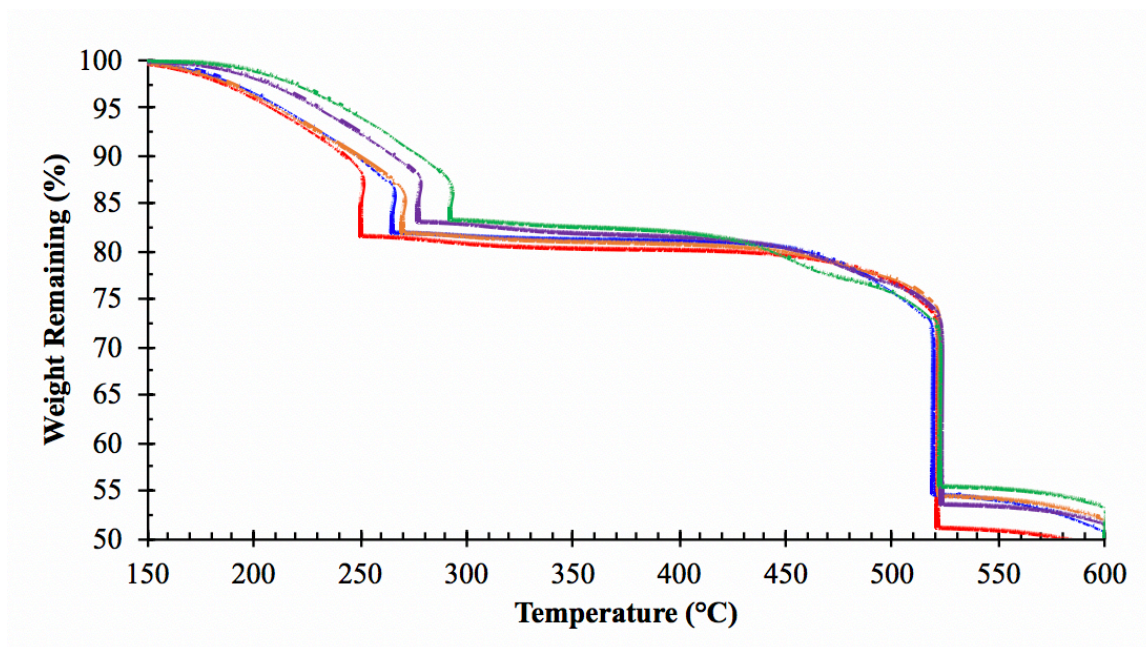


Figure 7.1. Isothermal step-wise thermogravimetric analysis (TGA) of poly(amic acid)s incorporating DABA, previously heat treated to 150 °C. Stepwise drops between 250 and 300 °C correlates to cyclo-imidization, signifying imidization temperature (T_{im}).

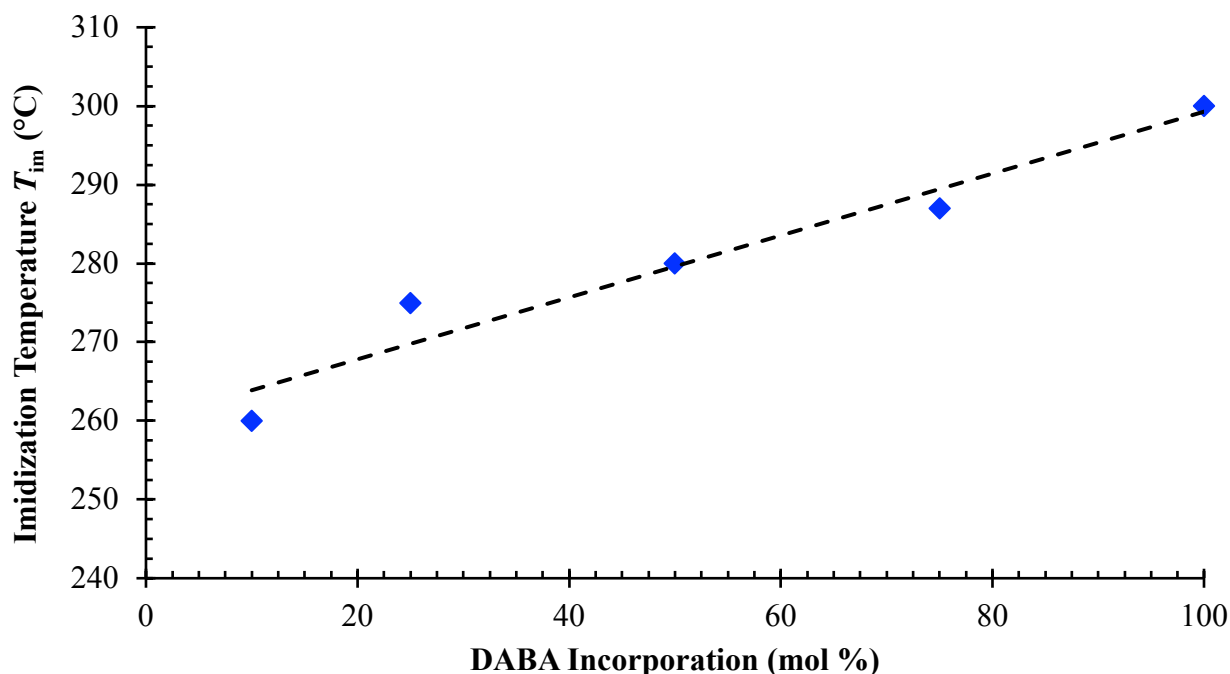


Figure 7.2. Imidization temperature (T_{im}) versus mol % DABA incorporation. T_{im} increases linearly with increasing DABA incorporation

Determining the T_{im} corresponding to the mol % DABA incorporation enabled PEI synthesis consistent with industrial practices. Reaction setup remained consistent with PAA synthesis but the reaction was heated to 180 °C (Scheme S7.2.). After completion of the synthesis, heating the reaction flask to the appropriate T_{im} removed NMP solvent as well as completed imidization. Samples re-dissolved in NMP and solution cast afforded transparent, ductile, and orange/brown films. TGA of fully imidized DABA-PEIs revealed no weight loss until around 450 °C, with earlier onset of weight loss occurring for PEIs with higher mol % DABA incorporation (Figure S7.4.), consistent with TGA analysis of DABA-PAAAs. Differential scanning calorimetry (DSC) determined glass transition temperatures (T_g)s increased with higher mol % DABA incorporation, as seen in **Figure 7.3**. The pendant carboxylic acid group hinders cooperative backbone segmental motion; thus increasing the T_g . As seen in **Figure 7.4**, normalizing the T_{im} with the T_g revealed all

compositions required similar temperatures above the T_g (~ 45 °C) to undergo full imidization. The T_g increases as imidization progresses. In order for the PAA to possess the right conformation to undergo cyclodehydration and form the imide functionality, enough chain mobility is required.⁴³ Thus, all samples required similar temperatures above the final PEIs' T_g to facilitate chain mobility and thus the proper conformation for full imidization to occur. All thermal properties are summarized in **Table 7.1**.

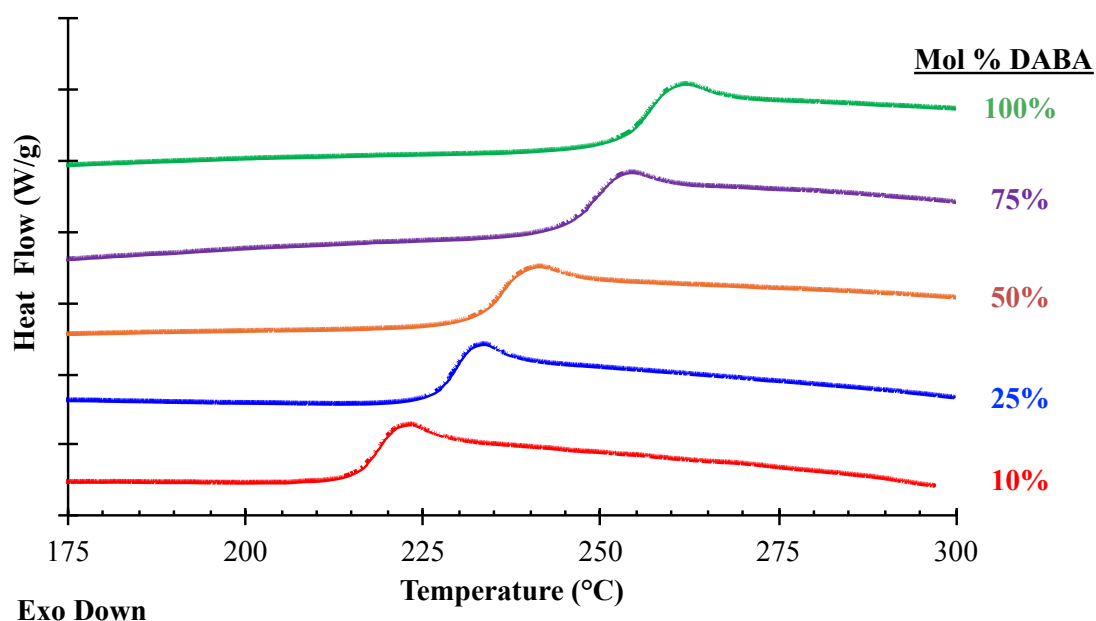


Figure 7.3. Glass transition temperature (T_g) determined utilizing differential scanning calorimetry (DSC). T_g increases with increasing DABA mol % incorporation.

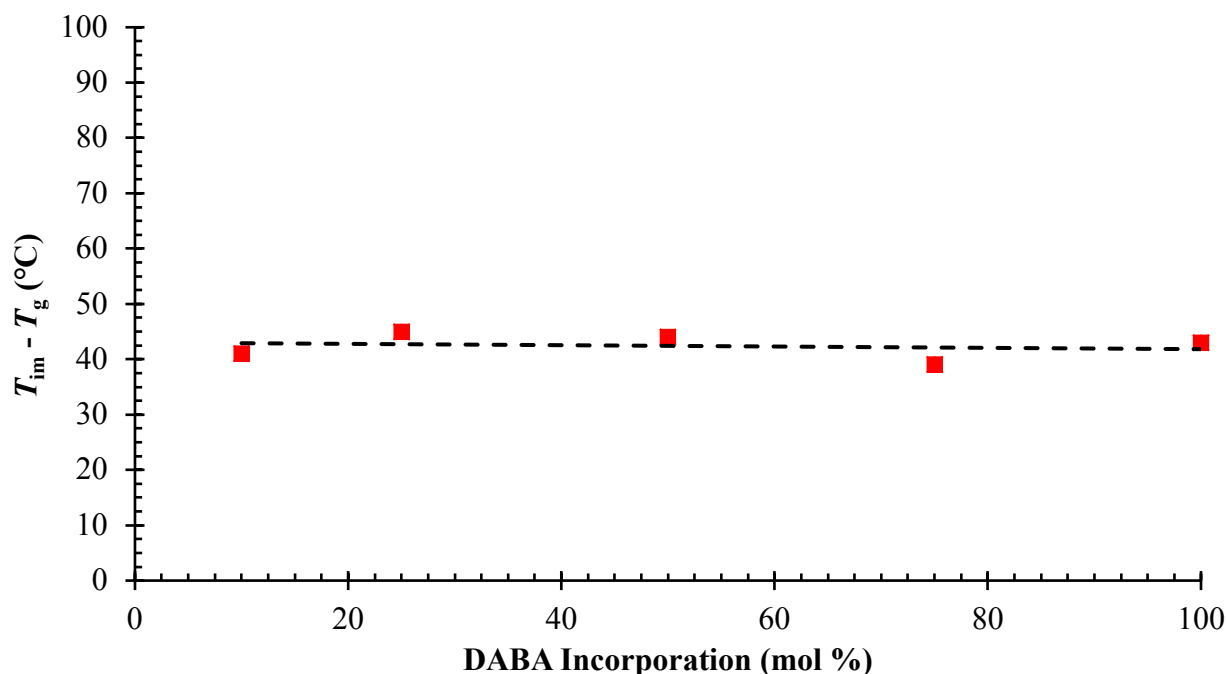


Figure 7.4. Normalizing imidization temperature (T_{im}) with the glass transition temperature (T_g) indicates similar temperatures above T_g required for thermal imidization

Table 7.1: Summary of thermal properties of DABA-PEIs

Mol % DABA (%)		$T_{d, 5\%}$ (°C)	T_g (°C)		T_{im} (°C)	$T_{im} - T_g$ (°C)
Feed	^1H NMR	TGA ^a	DSC ^b	DMA ^c	TGA ^d	TGA ^d -DSC ^b
Ultem	0	517	217	228	259	42
10	10	514	220	ND	260	41
25	25	505	228	237	275	45
50	50	501	238	239	280	44
75	75	482	248	260	287	39
100	100	451	256	278	300	43

^aTGA: 10 °C min⁻¹ heat, N₂

^bDSC: heat/cool/heat, second heat; N₂, 10 °C min⁻¹. T_g reported as inflection point of step transition.

^cDMA: tension mode, 1 Hz, 3 °C/min. T_g reported as peak maximum in tan delta curve

^dTGA: 10 °C min⁻¹ heat, isothermal if change in weight % min⁻¹ >0.1, resume heat if change in weight % min⁻¹ <0.01. T_{im} determined as isothermal step between 250 and 300 °C, imidization confirmed by FTIR

Dynamic mechanical analysis (DMA) probed thermomechanical performance over a range of temperatures (Figure S7.5.). All DABA-PEIs exhibited flow after T_g other than 100 mol % DABA-PEI, which possessed a plateau after the T_g . The plateau, extending upwards of 400 °C, indicated crosslinking, which is consistent with previous literature possessing high amounts of the pendant carboxylic acid and heat treatments near and above 300 °C.³⁰ Thus, these compositions are good candidates to be thermally crosslinkable PEI thermosets, which some applications such as gas separation have explored.^{30-32, 44}

To further understand the decarboxylation and crosslinking for this system, TGA coupled to FTIR monitored and analyzed the off-gas from the TGA furnace. Heating 20 mg films with similar size and shape probed the chemical composition of the off-gas. As seen in **Figure 7.5**, the first volatilized compound is the NMP solvent, between 10 and 20 min. This peak is followed by CO₂/CO for the 100 mol % DABA-PEI sample, with no CO₂/CO peak for the 0 mol % DABA-PEI indicating a relationship between the peak and amount of initial DABA monomer incorporated into the sample. After the CO₂/CO peak around 70 min, backbone degradation is noticed at >80 min. Similar peak wavenumbers and intensity is observed between both samples. Further analysis of the intensity of the Gram-Schmidt plot at times corresponding to the maximum removal of CO₂/CO versus mol % DABA incorporation revealed a linear relationship, allowing for quantification of decarboxylation during different processing procedures, as seen in **Figure 7.6**.

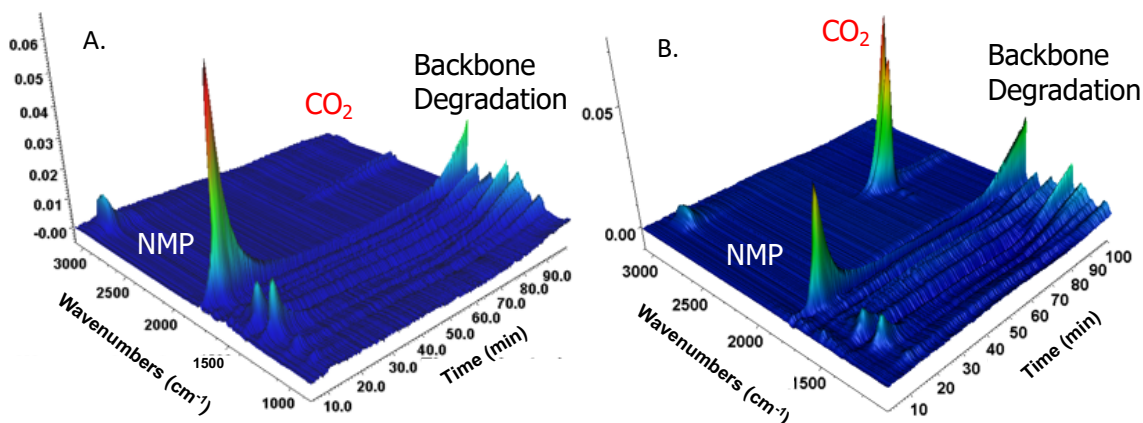


Figure 7.5: Gaseous FTIR analysis of off-gas from thermogravimetric analyzer (TGA). Graph A represents 0 mol % DABA-PEI. No CO₂ peak is observed between NMP evaporation and backbone degradation. Graph B represents 100 mol % DABA-PEI. A large CO₂ peak, due to decarboxylation, is observed between NMP evaporation and backbone degradation.

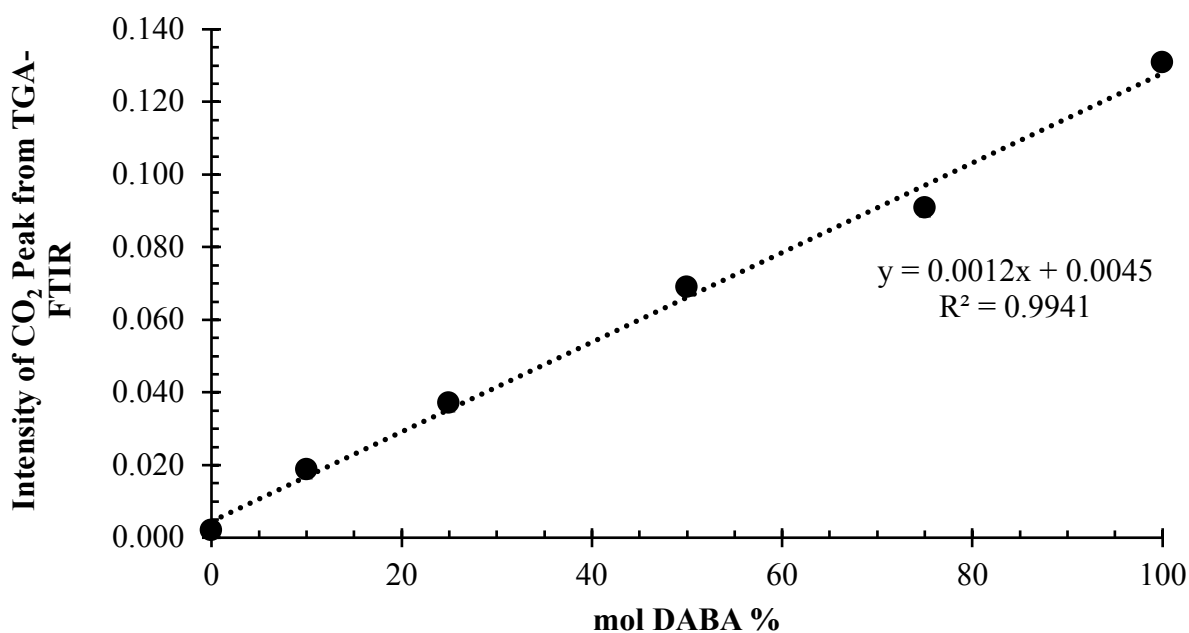


Figure 7.6. CO₂ peak max intensity from Gram-Schmidt plot of TGA-FTIR analysis versus mol % DABA incorporation.

Exploiting the reactivity of the pendant carboxylic acid groups at elevated temperatures enabled reactive branching in the melt. Utilizing a rheometer, time sweeps in

the melt at 340 °C of 0, 5, and 10 % DABA-PEIs targeted branching induced in the melt (Figure S.7.6.). All compositions targeted 20 kg mol⁻¹ M_n and exposure to 300 °C under N₂ atmosphere ensured full imidization before rheological analysis. Thus, some branching may have occurred during the initial imidization. Samples containing DABA possessed a smaller gap between the storage (G') and loss (G'') modulus over the entire time sweep compared to the control PEI. Ultem and 5 mol % DABA samples maintained a higher G'' relative to G' over the entire time, suggesting no crosslinking. 10 mol % DABA maintained a higher G' compared to G'' over the entire time due to either a higher molecular weight requiring higher temperatures to observe viscous behavior or due to the sample crosslinking. A loss in complete solubility of the 10 mol % sample after processing suggests partial crosslinking. DSC confirmed minimal shifts in the T_g for the samples after the time sweep (Figure S.7.), although a slight broadening of the transition suggests a minor change in the polymer architecture.

Advanced permeation chromatography (APC) analyzed the relative molecular weights (Figure S7.8-7.9.) and polydispersity (PDI) (Figure S7.10.) of the Ultem PEI control and the 5 mol % branched DABA-PEI. The 10 mol % branched DABA-PEI produced a heterogeneous solution, unsuitable for APC analysis. As seen in **Figure 7**, the Ultem control PEI maintained a similar relative weight average molecular weight (M_w) while the 5 mol % DABA-PEI sample increased linearly with time. A corresponding increase in PDI to >2.0 along with solubility in CHCl₃ suggests branching for step-growth polymers.⁴⁵ Thus, a change in viscoelastic behavior and rheological performance is expected after processing and samples processed for 60 min were further analyzed with melt rheology.⁴⁶

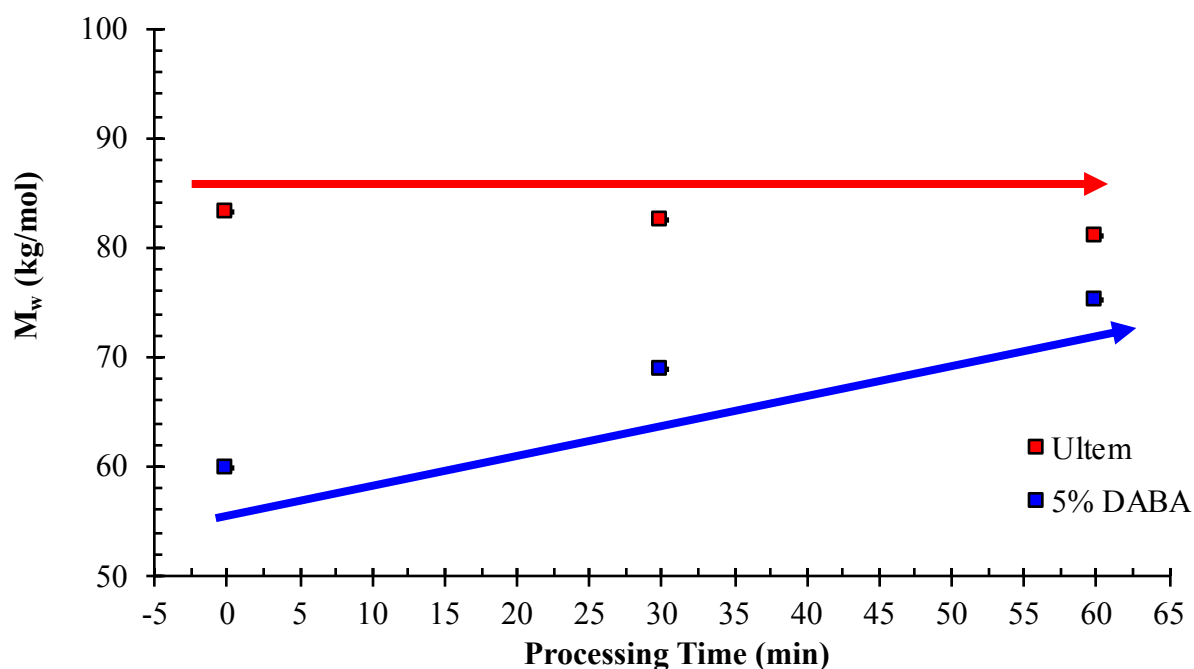


Figure 7.7. Increase in weight average molecular weight (M_w) after branching through processing. Ultem samples maintain similar M_w s while DABA-PEI samples increase M_w consistent with branching.

Frequency sweeps at 10 °C increments between 340 and 220 °C probed viscoelastic responses. Shifting the resulting G' and G'' (Figure S7.12.) and complex viscosity (η^*) resulted in master curves. As seen in **Figure 7.8**, η^* master curves revealed a Newtonian plateau for the control PEI Ultem sample, while no plateau is discernible for both 5 and 10 mol % DABA-PEIs. The 10 mol % DABA-PEI sample exhibited the highest η^* at the lowest frequencies, suggesting the highest amount of branching and potential M_w . The 5 mol % branched PEI possessed a higher η^* at low frequencies even though it has a slightly lower M_w . It is suggested that low branching density results in an increase in entanglements per chain, which dominates flow behavior at low shear rates over the usual reduction in coil size which commonly reduces η^* .^{12, 39, 47-48} Upon reaching higher frequencies, noticeable shear thinning begins and proceeds over 2-3 decades of frequencies, most of

which are commonly utilized in processing such as injection molding.⁴⁹ Shear thinning is desirable in processing due to the lower viscosity at high shear rates making processing easier. Long chain branching is known to improve shear thinning;¹² thus, power law index determination quantifies the effect of branching on the shear thinning behavior (Figure S7.13.). As seen in **Figure 7.9**, the power law index decreases as mol % DABA and branching increases. A smaller power law index value indicates a steeper shear thinning slope and a lower η^* at processing frequencies.

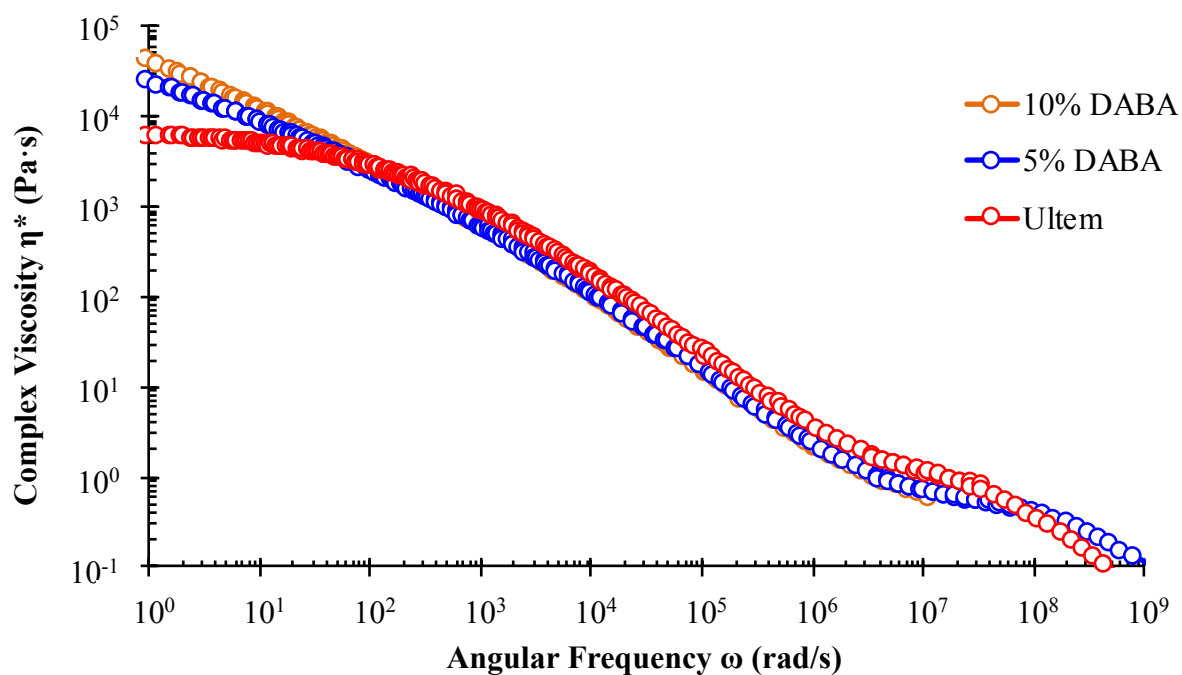


Figure 7.8. Complex viscosity (η^*) versus angular frequency, ω (rad/s) for branched DABA-PEIs

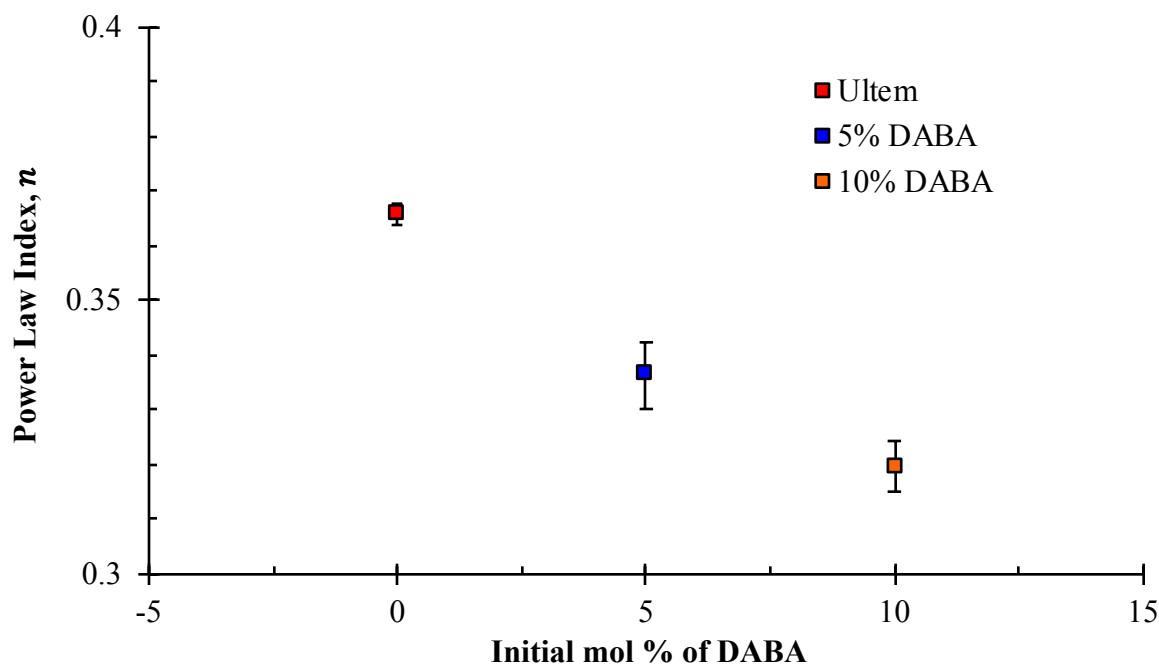


Figure 7.9. Power law index, n , versus mol % DABA-PEI indicates higher branched PEI's improve shear thinning behavior.

$$\eta = k\dot{\gamma}^{n-1} \quad \text{Eq. 1}$$

PEIs high incorporation of aromatic character impart high flame resistance, although higher molecular weight polymers are believed to possess better flame resistance.⁴⁰ As previously mentioned, processing high molecular weight PEIs is difficult due to the rigid nature of the backbone and thus high viscosity. PEI samples branched through the pendant carboxylic acid group enable processing of similar molecular weight PEIs, with in melt branching increasing the final molecular weight of the polymer. Thus, a vertical flame test evaluated the DABA branched PEIs' flame resistance performance. As seen in **Table 7.1**, the control PEI sample (0.4 mm thick) exhibited dripping for all samples and ignited the cotton on 6 of 7 tests, consistent with the UL Recognized, 94V-2 Flame Class Rating for commercial PEI samples at 0.4 mm thickness.⁴¹ 5 and 10 mol % DABA branched PEIs possessed low t_1 and t_2 after-flame times while possessing no afterglow. No

samples dripped or ignited the cotton; thus, the closest rating for these samples would be a 94V-0 rating. TGA determined the char yield at 900 °C, summarized in **Table 7.1**. Increased char yields for higher branched samples correlates well with the increase in flame resistance and further helps to explain the lack of dripping. This improvement, imparted by the branching and high viscosity at low frequencies, is desirable for applications in automotive, aerospace, energy, and microelectronic industries.

Table 7.1: Summary of Thermal and Flame Retardancy Properties of Branched DABA-PEIs

Initial Mol % DABA	Thermal Properties			UL94-V/ASTM D3801 Flame Testing				
	T_g (°C)	CTE (m/m/°C) $\times 10^5$	Char Yield at 900 °C (%)	t_1	t_2	t_3	Drip	Ignite Cotton
Feed	DSC ^a	TMA ^b	TGA ^c				Y or N	Y or N
0	217	5.7 ± 0.8	49.4 ± 1.3	ND	ND	ND	Y (7/7)	Y (6/7)
5	217	6.9 ± 1.4	51.5 ± 0.8	2.7 ± 1.1	2.1 ± 0.2	0.0 ± 0.0	N (7/7)	N (7/7)
10	220	7.0 ± 1.5	52.3 ± 0.8	4.6 ± 1.8	5.0 ± 2.5	0.0 ± 0.0	N (5/5)	N (5/5)

^aDSC: heat/cool/heat, second heat; N₂, 10 °C min⁻¹. T_g reported as inflection point of step transition.

^bTMA: 3 °C min⁻¹ heating rate

^cTGA: 10 °C min⁻¹ heating rate to 1000 °C under N₂ atmosphere

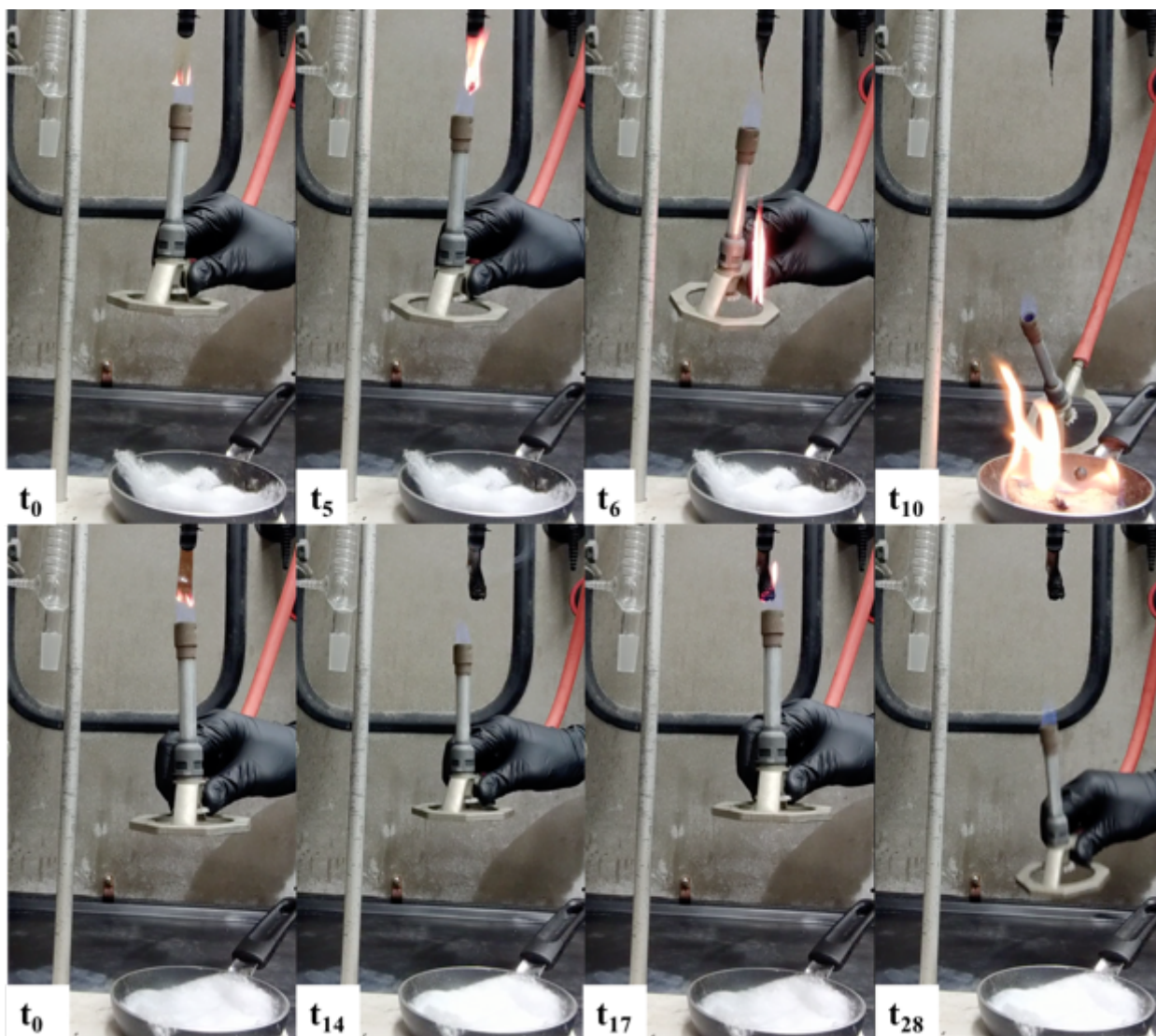


Figure 7.10. Vertical flame testing of control PEI (top) and 10 mol % branched DABA-PEI (Bottom). Control PEI catches on fire and drips after 6 s, igniting the cotton below. The 10 mol % branched DABA-PEI catches on fire after 10 s of exposure and is extinguished after 4 s (t_{14}). During the second exposure, the sample catches on fire again, but extinguished in <5 s, with no afterburn noticed. The 10 mol % branched DABA-PEI sample lacked dripping and resulted in no igniting of the cotton. Time points t_5 , t_{10} , t_{22} , and t_{26} (Figure S.14.) show intermittent time points.

7.5 Conclusions

Lower molecular weight PEIs typically offer the easiest processability, although properties such as flame resistance worsen. The inherent trade-off between processability and properties of high performance polymers continues to challenge scientists in

developing new and improved polymers. Thus, innovation is required to overcome these through functional polymers and processing. Incorporating reactive functional groups installed a handle to branch PEIs during melt processing, thus improving their shear thinning behavior as well as flame resistance. Commonly utilized reactive functionality such as phenylethynyl groups are expensive and synthetic challenges hinder control of the onset temperatures and chain-extension versus crosslinking balance. A pendant carboxylic acid incorporated through DABA offers a cheap and controllable method to branch or crosslink during or after melt processing. Understanding the imidization behavior as well as properties enables the design of processable PEIs with reactive methods to tune properties in applications including conducting devices through pyrolysis into carbon, additive manufacturing (3D printing), and PEI foams through the decarboxylation.

First, a thorough understanding of the pendant carboxylic acid's influence on imidization temperature (T_{im}) allowed for optimized processing conditions and a relationship to other thermal properties such as the glass transition temperature (T_g). Evaluation of the off-gassing at elevated temperatures confirmed the decarboxylation induced crosslinking, and provided a means to characterize the extent of decarboxylation. Exploiting this reactivity to produce long-chain branched PEIs enabled a way to process lower molecular weight PEIs and obtain desirable properties more consistent with higher molecular weights. Long-chain branched (LCB) PEI thin films exhibited improved flame resistance with no dripping and short after-flame times, improved over commercial control PEI samples.

Supporting Information.

¹H NMR spectra, DSC & TGA thermograms, TTS master curves of η^* and G'/G'' , APC chromatographs, DMA storage modulus and $\tan \delta$ graphs, rheological time sweeps, PDI versus processing time, and shear thinning single rheological frequency sweeps.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

7.6 Acknowledgements

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7.7 References

1. Hergenrother, P. M., The use, design, synthesis, and properties of high performance/high temperature polymers: an overview. *High Perform. Polym.* **2003**, *15* (1), 3-45.
2. Hegde, M.; Meenakshisundaram, V.; Chartrain, N.; Sekhar, S.; Tafti, D.; Williams, C. B.; Long, T. E., 3D Printing All-Aromatic Polyimides using Mask-Projection Stereolithography: Processing the Nonprocessable. *Adv. Mater.* **2017**, *29* (31).
3. Herzberger, J.; Meenakshisundaram, V.; Williams, C. B.; Long, T. E., 3D Printing All-Aromatic Polyimides Using Stereolithographic 3D Printing of Polyamic Acid Salts. *Acs Macro Lett* **2018**, *7* (4), 493-497.
4. Rau, D. A.; Herzberger, J.; Long, T. E.; Williams, C. B., Ultraviolet-Assisted Direct Ink Write to Additively Manufacture All-Aromatic Polyimides. *ACS Appl Mater Interfaces* **2018**.
5. *Polyimides: Synthesis, Characterization, and Applications*. Plenum Press: New York, 1984; Vol. 1.
6. Floryan, D. E.; Serfaty, I. W., Polyetherimide - More Information on a New High-Performance Resin. *Mod Plast* **1982**, *59* (6), 146-&.
7. Dingemans, T. J.; Mendes, E.; Hinkley, J. J.; Weiser, E. S.; StClair, T. L., Poly(ether imide)s from Diamines with Para-, Meta-, and Ortho-Arylene Substitutions: Synthesis, Characterization, and Liquid Crystalline Properties. *Macromolecules* **2008**, *41* (7), 2474-2483.
8. Johnson, R. O.; Burlhis, H. S., Polyetherimide - a New High-Performance Thermoplastic Resin. *J Polym Sci Pol Sym* **1983**, (70), 129-143.
9. Grabiec, E.; Schab-Balcerzak, E.; Wolinska-Grabczyk, A.; Jankowski, A.; Jarzabek, B.; Kozuch-Krawczyk, J.; Kurcok, M., Physical, optical and gas transport properties of new processable polyimides and poly(amideimide)s obtained from 4,4' -[oxybis(4,1-phenylenethio)]dianiline and aromatic dianhydrides. *Polym. J.* **2011**, *43* (7), 621-629.
10. Mushtaq, N.; Chen, G. F.; Sidra, L. R.; Liu, Y.; Fang, X. Z., Synthesis and crosslinking study of isomeric poly(thioether ether imide)s containing pendant nitrile and terminal phthalonitrile groups. *Polymer Chemistry* **2016**, *7* (48), 7427-7435.
11. Burks, H. D.; Stclair, T. L., Processable Aromatic Polyimides. *J. Appl. Polym. Sci.* **1985**, *30* (6), 2401-2411.
12. Dennis, J. M.; Mondschein, R. J.; Hegde, M.; Odle, R.; Long, T. E., Synthesis and Characterization of Long-chain Branched Poly(ether imide)s. *In Press* **2018**.
13. Ding, M., Isomeric polyimides. *Prog. Polym. Sci.* **2007**, *32* (6), 623-668.
14. Moore, J. S.; Thompson, D. S.; Markoski, L. J. Branched and hyperbranched polyetherimides. 2001.
15. Yi, L.; Huang, W.; Yan, D., Polyimides with side groups: Synthesis and effects of side groups on their properties. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (4), 533-559.
16. Vora, R. H.; Goh, S. H.; Chung, T. S., Synthesis and properties of fluoro-polyetherimides. *Polym. Eng. Sci.* **2000**, *40* (6), 1318-1329.
17. Tzoganakis, C., Reactive Extrusion of Polymers: A Review. *Adv. Polym. Tech.* **1989**, *9* (4), 321-330.

18. Graebbling, D., Synthesis of branched polypropylene by a reactive extrusion process. *Macromolecules* **2002**, *35* (12), 4602-4610.
19. Holland, T. V.; Glass, T. E.; McGrath, J. E., Investigation of the thermal curing chemistry of the phenylethynyl group using a model aryl ether imide. *Polymer* **2000**, *41* (13), 4965-4990.
20. Jayaraman, S.; Srinivasan, R.; McGrath, J. E., Synthesis and Characterization of 3-Phenylethynyl Endcapped Matrix Resins. *J Polym Sci Pol Chem* **1995**, *33* (10), 1551-1563.
21. Hergenrother, P. M.; Bryant, R. G.; Jensen, B. J.; Havens, S. J., Phenylethynyl-terminated imide oligomers and polymers therefrom. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32* (16), 3061-3067.
22. Bryant, R. G.; Jensen, B. J.; Hergenrother, P. M., Chemistry and properties of a phenylethynyl-terminated polyimide. *J. Appl. Polym. Sci.* **1996**, *59* (8), 1249-1254.
23. Guan, Q.; Norder, B.; Chu, L.; Besseling, N. A. M.; Picken, S. J.; Dingemans, T. J., All-Aromatic (AB)_n-Multiblock Copolymers via Simple One-Step Melt Condensation Chemistry. *Macromolecules* **2016**.
24. Bullions, T. A.; Stoykovich, M. P.; McGrath, J. E.; Loos, A. C., Monitoring the reaction progress of a high-performance phenylethynyl-terminated poly(etherimide). Part II: Advancement of glass transition temperature. *Polym. Compos.* **2002**, *23* (4), 479-494.
25. Bullions, T. A.; McGrath, J. E.; Loos, A. C., Monitoring the reaction progress of a high-performance phenylethynyl-terminated poly(etherimide). Part I: Cure kinetics modeling. *Polym. Eng. Sci.* **2002**, *42* (5), 1056-1069.
26. Yang, K.; Grant, J. C.; Lamey, P.; Joshi-Imre, A.; Lund, B. R.; Smaldone, R. A.; Voit, W., Diels-Alder Reversible Thermoset 3D Printing: Isotropic Thermoset Polymers via Fused Filament Fabrication. *Adv. Funct. Mater.* **2017**, *27* (24).
27. Kratochvil, A. M.; Koros, W. J., Decarboxylation-Induced Cross-Linking of a Polyimide for Enhanced CO₂ Plasticization Resistance. *Macromolecules* **2008**, *41* (21), 7920-7927.
28. Koros, W. J. K., A. M. Thermally Crosslinked Polymeric Compositions and methods of making the same. 8664335 B2, 2014.
29. Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J., The effects of crosslinking chemistry on CO₂ plasticization of polyimide gas separation membranes. *Industrial & Engineering Chemistry Research* **2002**, *41* (24), 6139-6148.
30. Qiu, W. L.; Chen, C. C.; Xu, L. R.; Cui, L. L.; Paul, D. R.; Koros, W. J., Sub-T-g Cross-Linking of a Polyimide Membrane for Enhanced CO₂ Plasticization Resistance for Natural Gas Separation. *Macromolecules* **2011**, *44* (15), 6046-6056.
31. Qiu, W. L.; Xu, L. R.; Chen, C. C.; Paul, D. R.; Koros, W. J., Gas separation performance of 6FDA-based polyimides with different chemical structures. *Polymer* **2013**, *54* (22), 6226-6235.
32. Xu, S.; Wang, Y., Novel thermally cross-linked polyimide membranes for ethanol dehydration via pervaporation. *Journal of Membrane Science* **2015**, *496*, 142-155.
33. Qiu, W.; Zhang, K.; Li, F. S.; Zhang, K.; Koros, W. J., Gas separation performance of carbon molecular sieve membranes based on 6FDA-mPDA/DABA (3:2) polyimide. *ChemSusChem* **2014**, *7* (4), 1186-94.

34. Fu, S. L.; Sanders, E. S.; Kulkarni, S. S.; Koros, W. J., Carbon molecular sieve membrane structure-property relationships for four novel 6FDA based polyimide precursors. *Journal of Membrane Science* **2015**, *487*, 60-73.
35. Fu, S.; Sanders, E. S.; Kulkarni, S. S.; Wenz, G. B.; Koros, W. J., Temperature dependence of gas transport and sorption in carbon molecular sieve membranes derived from four 6FDA based polyimides: Entropic selectivity evaluation. *Carbon* **2015**, *95*, 995-1006.
36. Fu, S. L.; Wenz, G. B.; Sanders, E. S.; Kulkarni, S. S.; Qiu, W. L.; Ma, C. H.; Koros, W. J., Effects of pyrolysis conditions on gas separation properties of 6FDA/DETDA:DABA(3:2) derived carbon molecular sieve membranes. *Journal of Membrane Science* **2016**, *520*, 699-711.
37. Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; Garcia-Franco, C. A.; Lyon, M. K., Well-defined, model long chain branched polyethylene. 2. Melt rheological behavior. *Macromolecules* **2002**, *35* (8), 3066-3075.
38. Mannion, A. M.; Bates, F. S.; Macosko, C. W., Synthesis and Rheology of Branched Multiblock Polymers Based on Polylactide. *Macromolecules* **2016**, *49* (12), 4587-4598.
39. Yan, D.; Wang, W. J.; Zhu, S., Effect of long chain branching on rheological properties of metallocene polyethylene. *Polymer* **1999**, *40* (7), 1737-1744.
40. Lee, K.; Yoon, K.; Kim, J.; Bae, J.; Yang, J.; Hong, S., Effect of novolac phenol and oligomeric aryl phosphate mixtures on flame retardance enhancement of ABS. *Polym. Degrad. Stab.* **2003**, *81* (1), 173-179.
41. ULTEM(TM) RESIN 1000. SABIC Innovative Plastics: <https://www.sabic.com/en/products/specialties/ultem-resins/ultem-resin>, 2018.
42. Hegde, M.; Lafont, U.; Norder, B.; Samulski, E. T.; Rubinstein, M.; Dingemans, T. J., SWCNT induced crystallization in amorphous and semi-crystalline poly(etherimide)s: Morphology and thermo-mechanical properties. *Polymer* **2014**, *55* (16), 3746-3757.
43. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., *Polyimides*. Springer Science+Business Media: New York, 1990.
44. Calle, M.; Jo, H. J.; Doherty, C. M.; Hill, A. J.; Lee, Y. M., Cross-Linked Thermally Rearranged Poly(benzoxazole-co-imide) Membranes Prepared from ortho-Hydroxycopolyimides Containing Pendant Carboxyl Groups and Gas Separation Properties. *Macromolecules* **2015**, *48* (8), 2603-2613.
45. Odian, G., *Principles of Polymerization*. 4th ed.; Wiley-Interscience: 2004.
46. Rubinstein, M.; Colby, R. H., *Polymer Physics*. Oxford University Press Inc.: New York, 2003.
47. Wild, L.; Ranganath, R.; Knobloch, D. C., Influence of Long-Chain Branching on Viscoelastic Properties of Low-Density Polyethylenes. *Polym. Eng. Sci.* **1976**, *16* (12), 811-816.
48. McKee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E., Branched polyesters: recent advances in synthesis and performance. *Prog. Polym. Sci.* **2005**, *30* (5), 507-539.
49. Franck, A. *Understanding Rheology of Thermoplastic Polymers*; TA Instruments.

7.8 Supporting Information

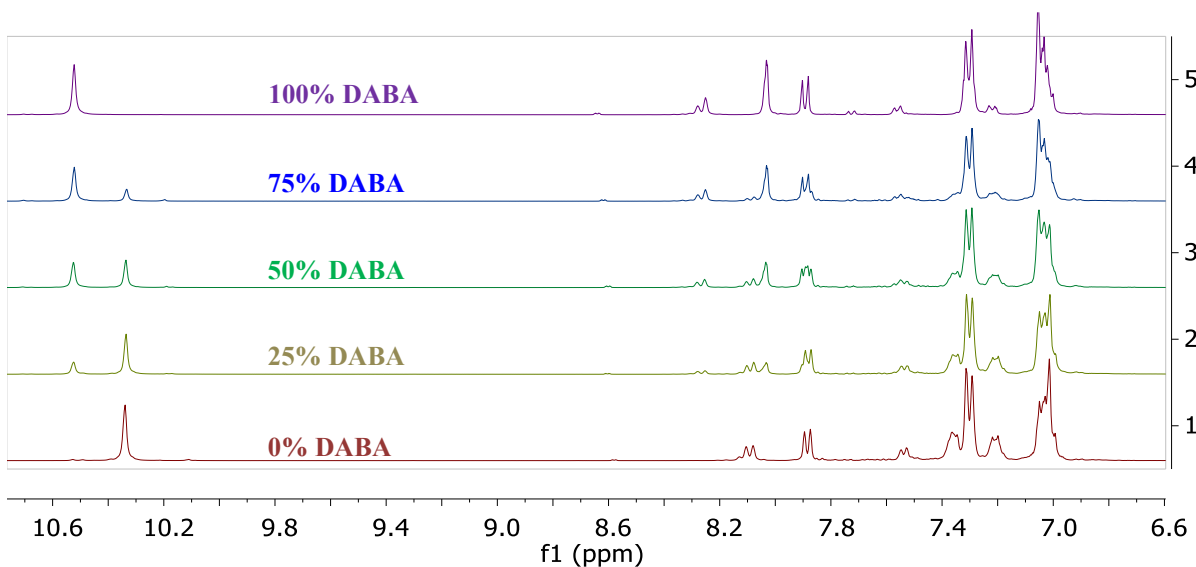


Figure S7.1. NMR spectra of varying PEAA-DABA (co)polymers. PA end-groups around 8.6 ppm determined M_n consistent with targets.

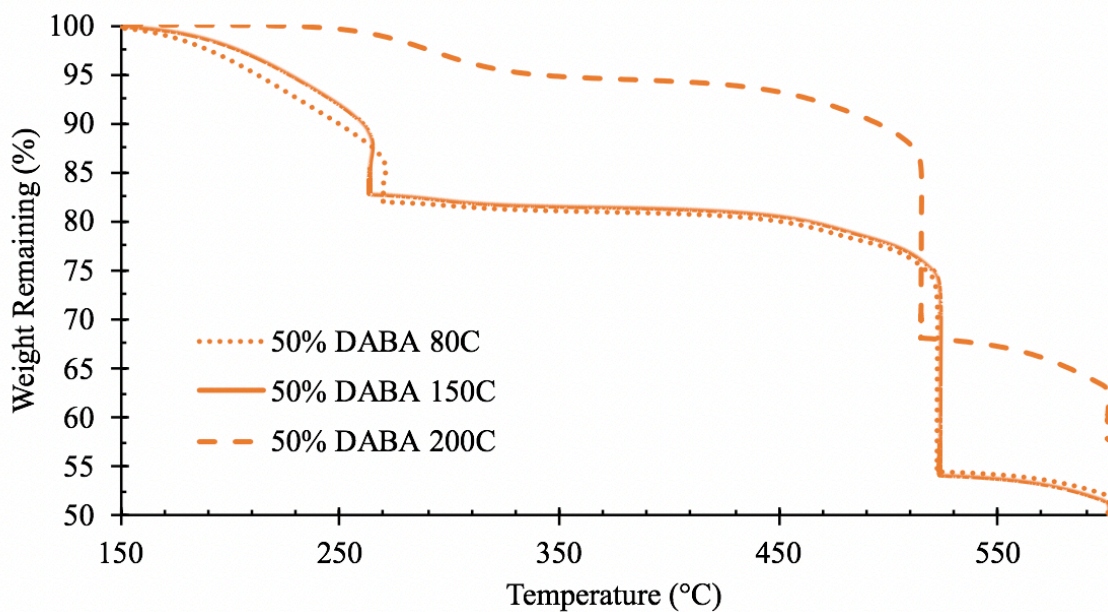


Figure S7.2. Isothermal step-wise thermogravimetric analysis (TGA) of poly(amic acid)s incorporating 50 mol % DABA, previously heat treated to 80, 150, or 200 °C. Stepwise drops around 250 °C correlates to cyclo-imidization, signifying imidization temperature (T_{im}).

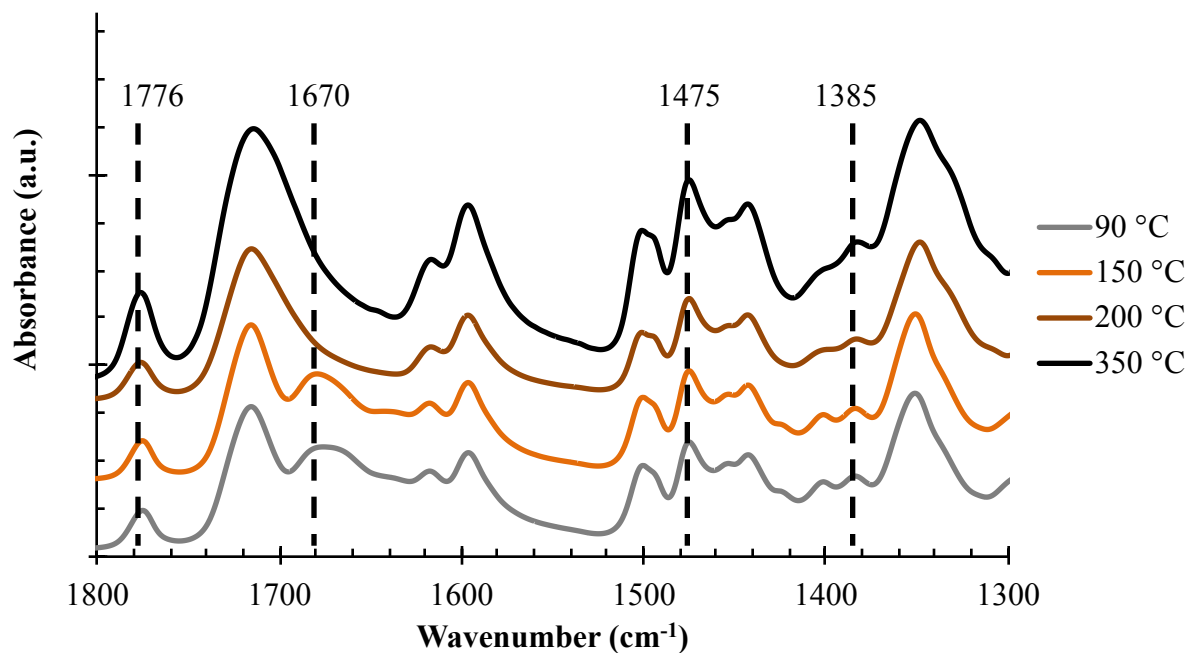
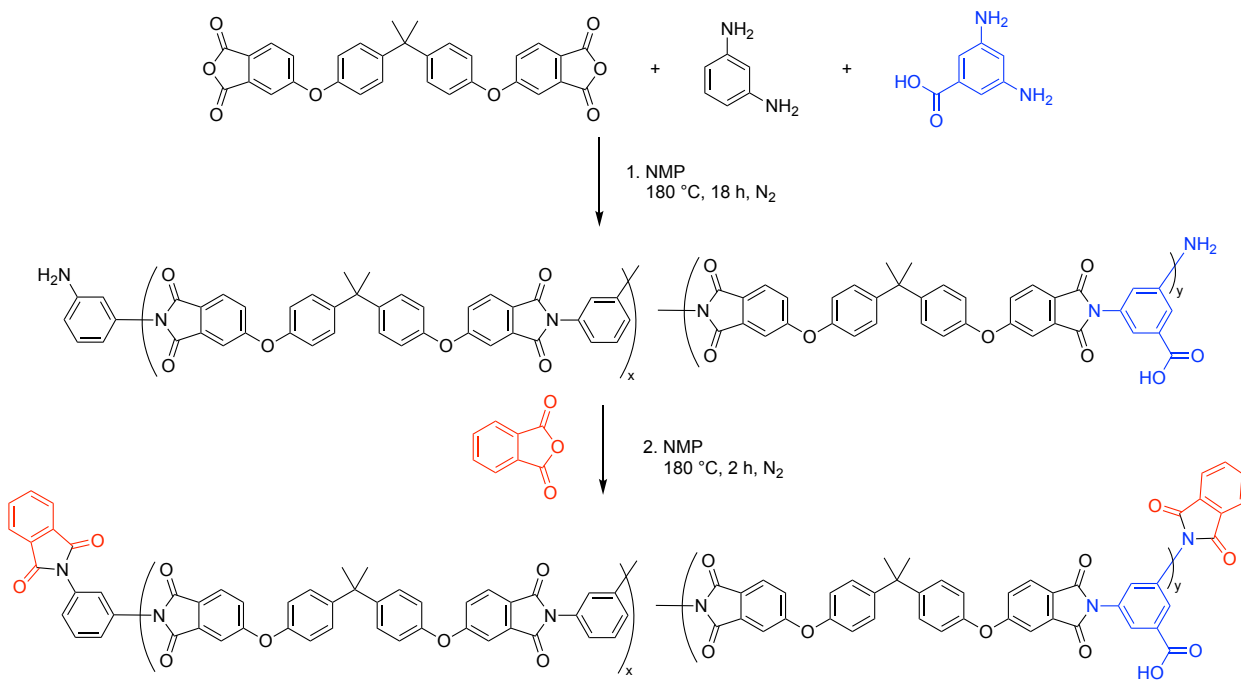


Figure S7.3. FTIR analysis of imidization based on final imidization temperature of PEI-DABA₅₀



Scheme S7.1: Synthesis of poly(ether imide)s (PEIs) incorporating 3,5-diaminobenzoic acid (DABA) (blue) and end-capping with phthalic anhydride (PA) (red)

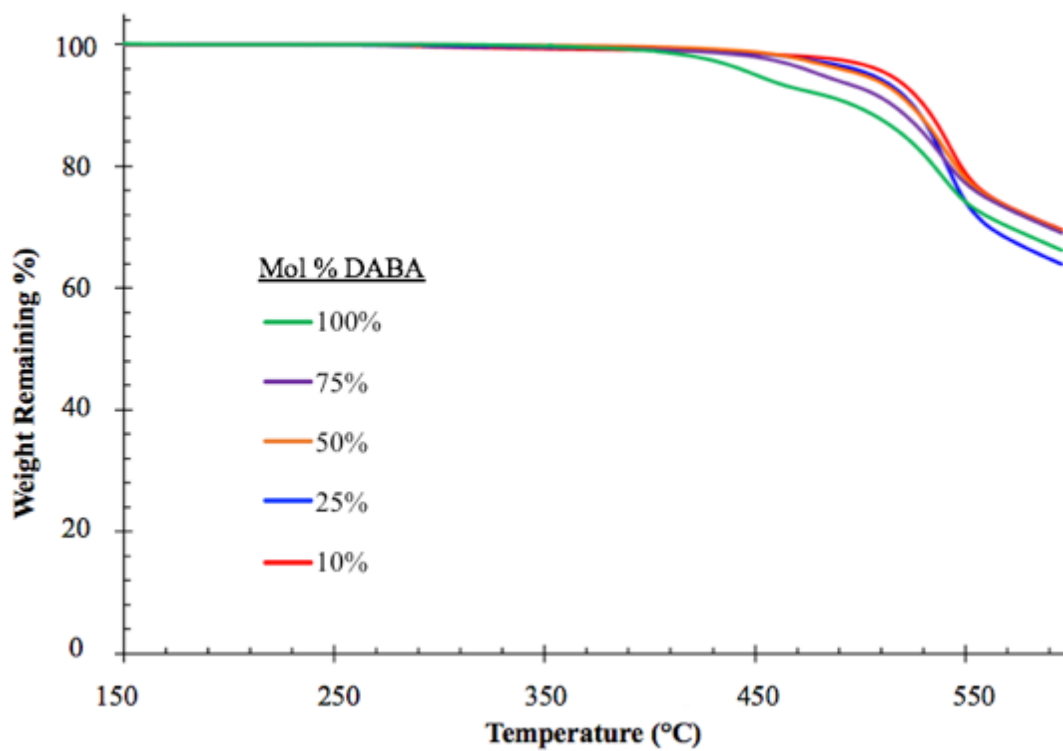


Figure S7.4. TGA of DABA-PEIs

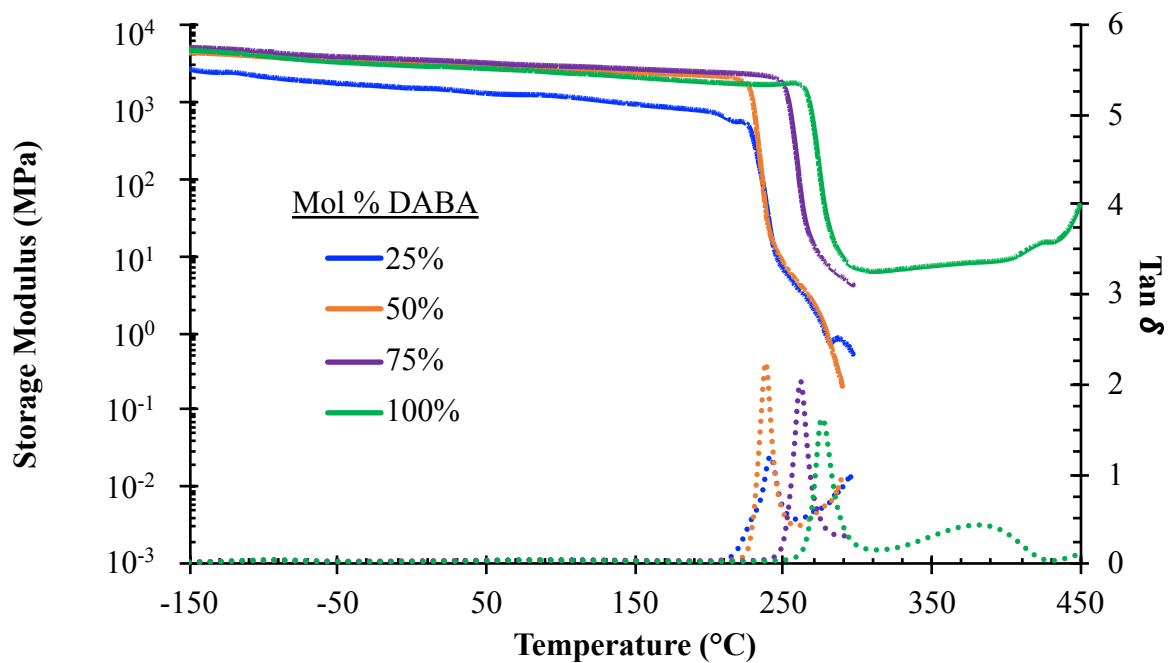


Figure S7.5. DMA analysis of DABA-PEIs.

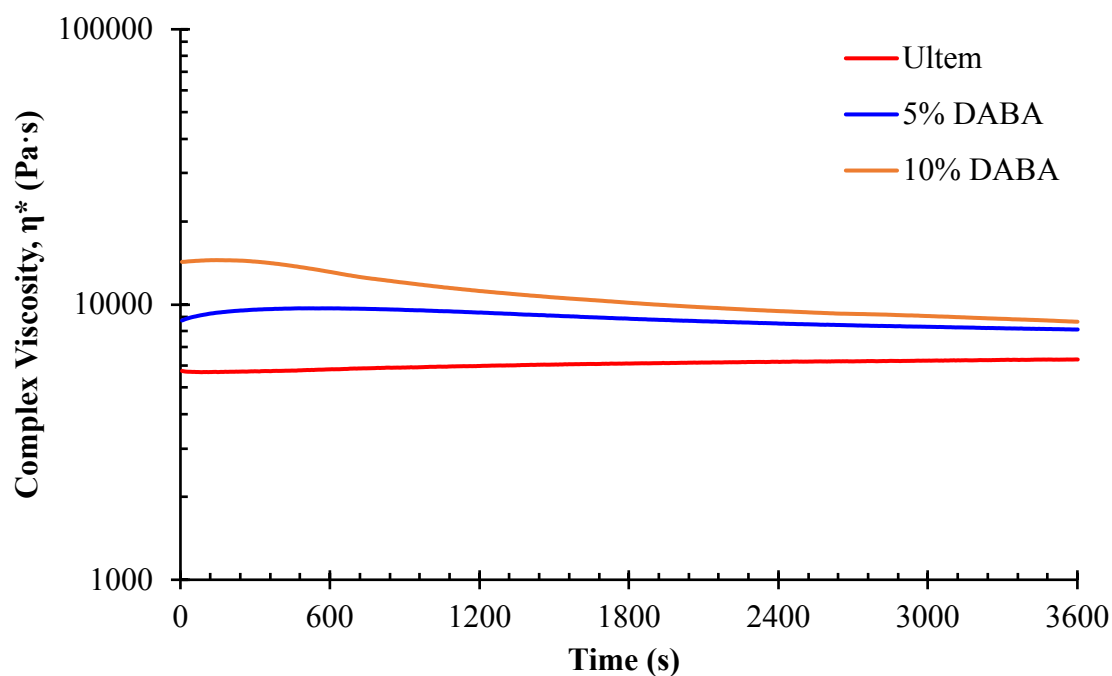


Figure S7.6. Time sweeps utilizing 10 rad/s and 1.0 % strain at 340 °C induced branching in the melt. 5 and 10 mol % DABA samples undergo shear thinning at 10 rad/s as evident by TTS master curves, thus little change in η^* over 3600 s.

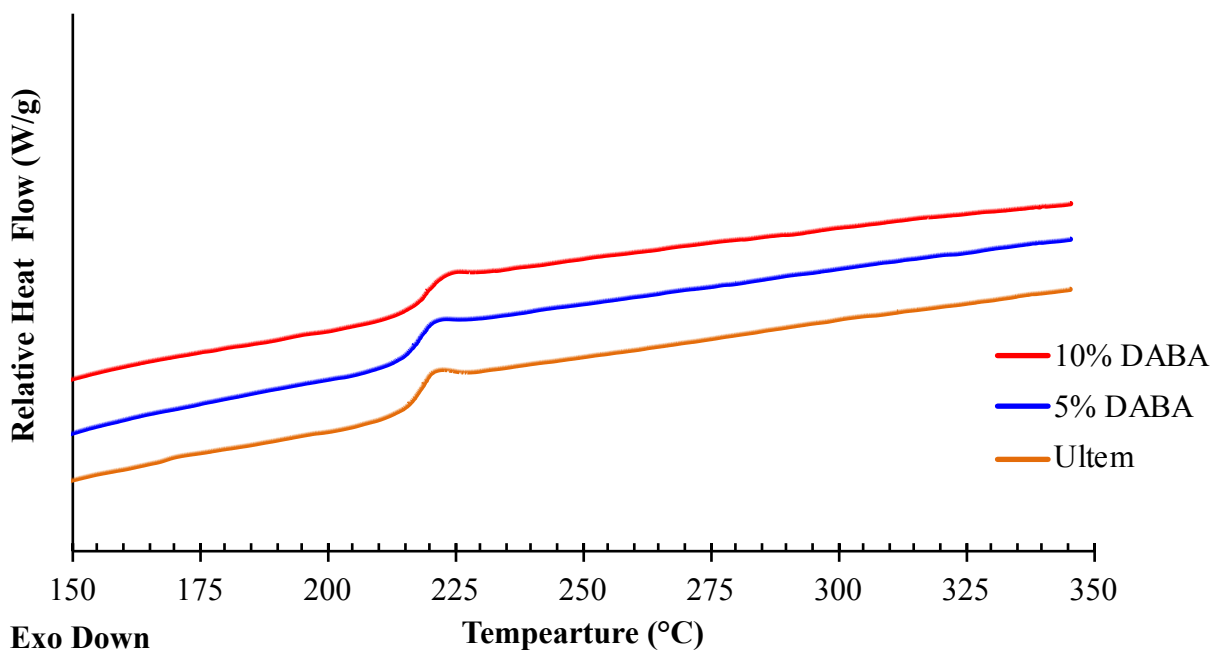


Figure S7.7. Differential scanning calorimetry (DSC) elucidated glass transition temperatures (T_g s) for branched samples. No change in T_g suggests limited influence from architecture on thermal transitions.

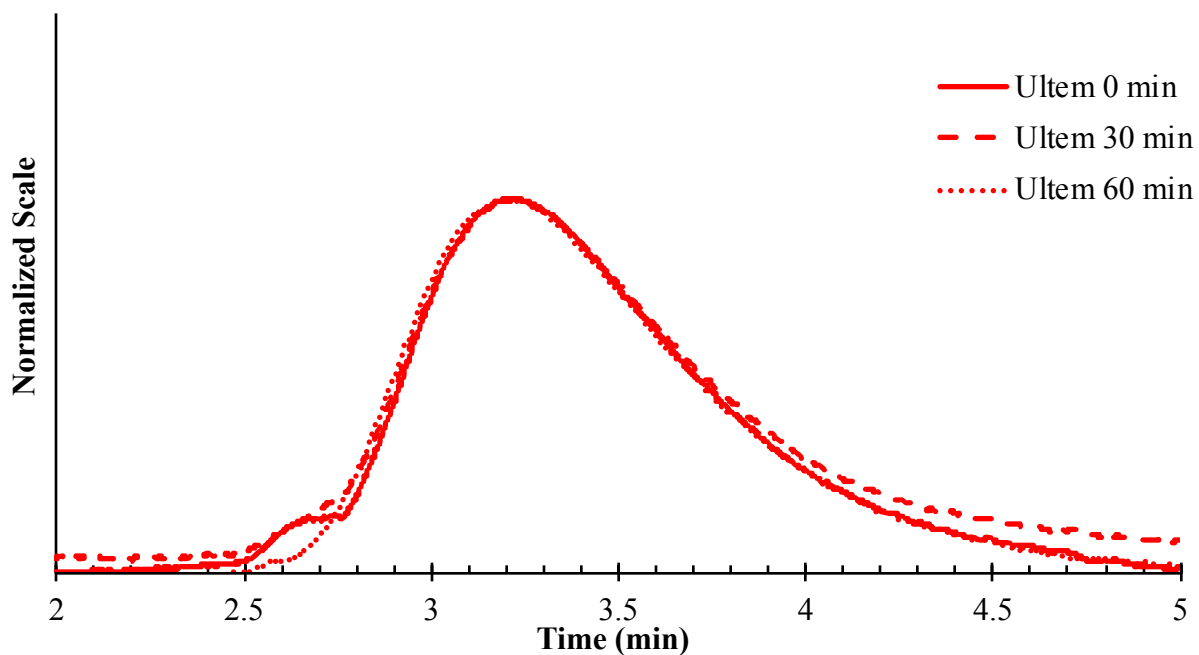


Figure S7.8. Molecular weight of Ultem PEI after simulated processing over 0, 30, and 60 min of processing.

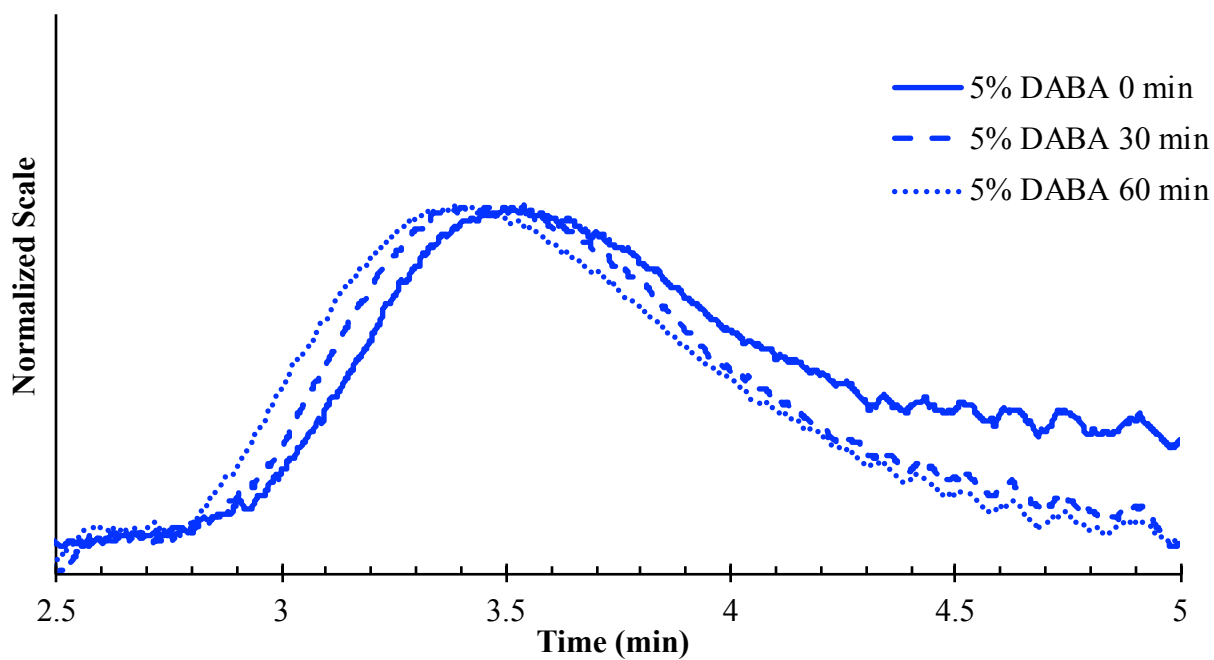


Figure S7.9. Molecular weight of 5% DABA-PEI after simulated processing over 0, 30, and 60 min of processing. Increasing time induces branching and thus shifts in peaks to lower retention times, higher molecular weight.

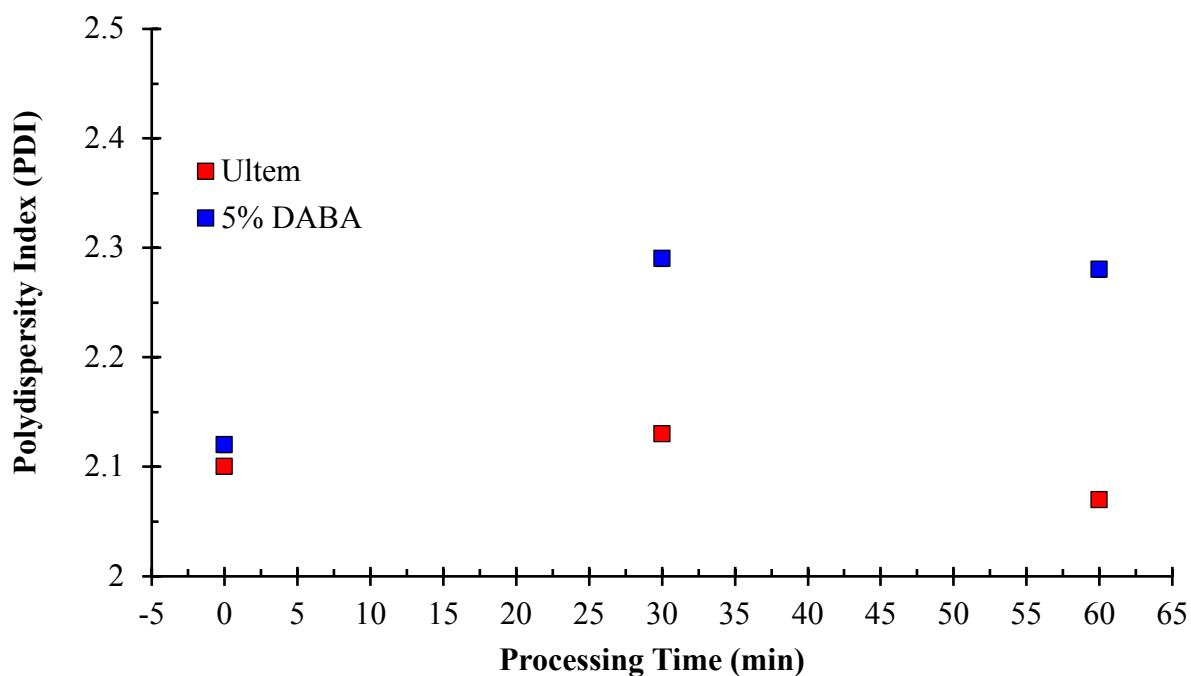


Figure S7.10. Increase in polydispersity (PDI) when increasing branching through reactive branching of DABA-PEIs.

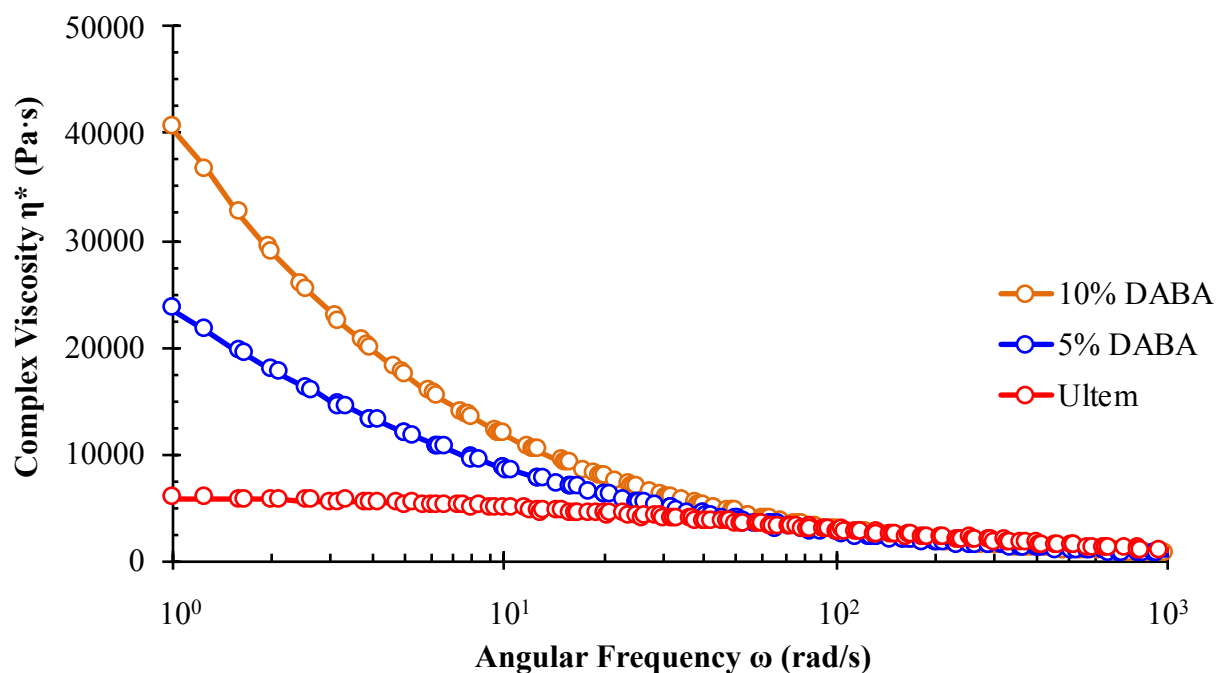


Figure S7.11. Complex viscosity (η^*) versus angular frequency ω (rad/s) highlighting changes in viscosity at low frequencies for branched samples compared to linear, non-branched Ultem control.

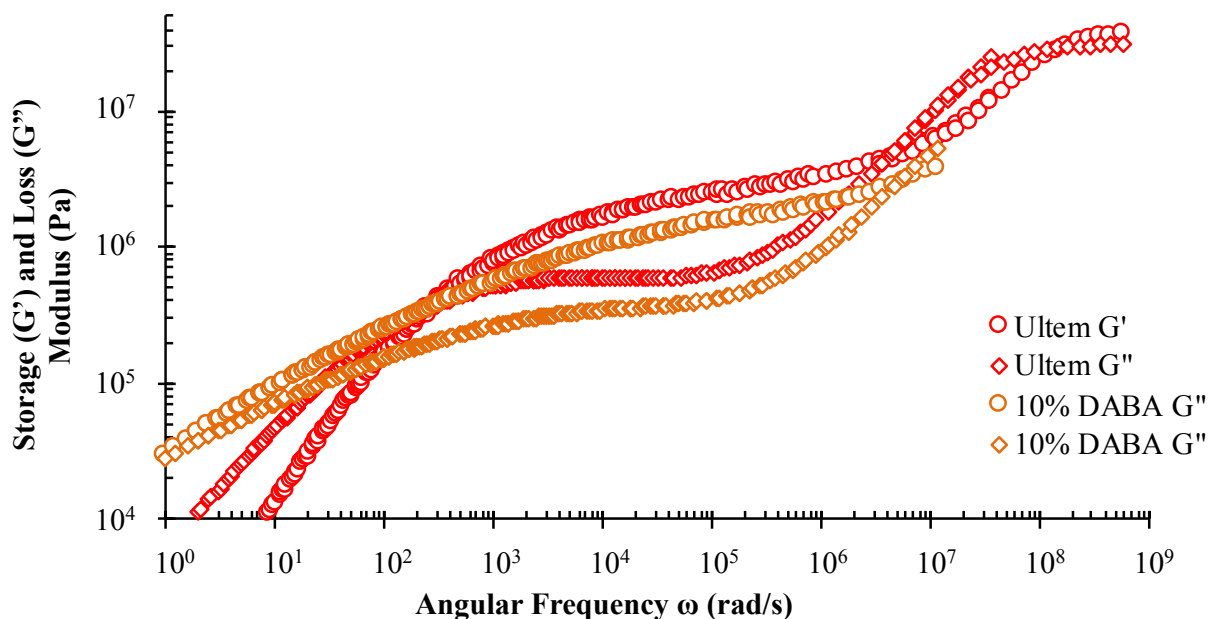


Figure S7.12. Storage (G') and Loss (G'') modulus versus angular frequency, ω (rad/s) for Ultem and 10% DABA-PEI. No change in the frequency is noticed related to the relaxation of an entangled strand ($1/\tau_e$) though the relaxation associated with reptation ($1/\tau_{rep}$) shifts to much lower frequencies, indicating much longer relaxation times, thus branching.

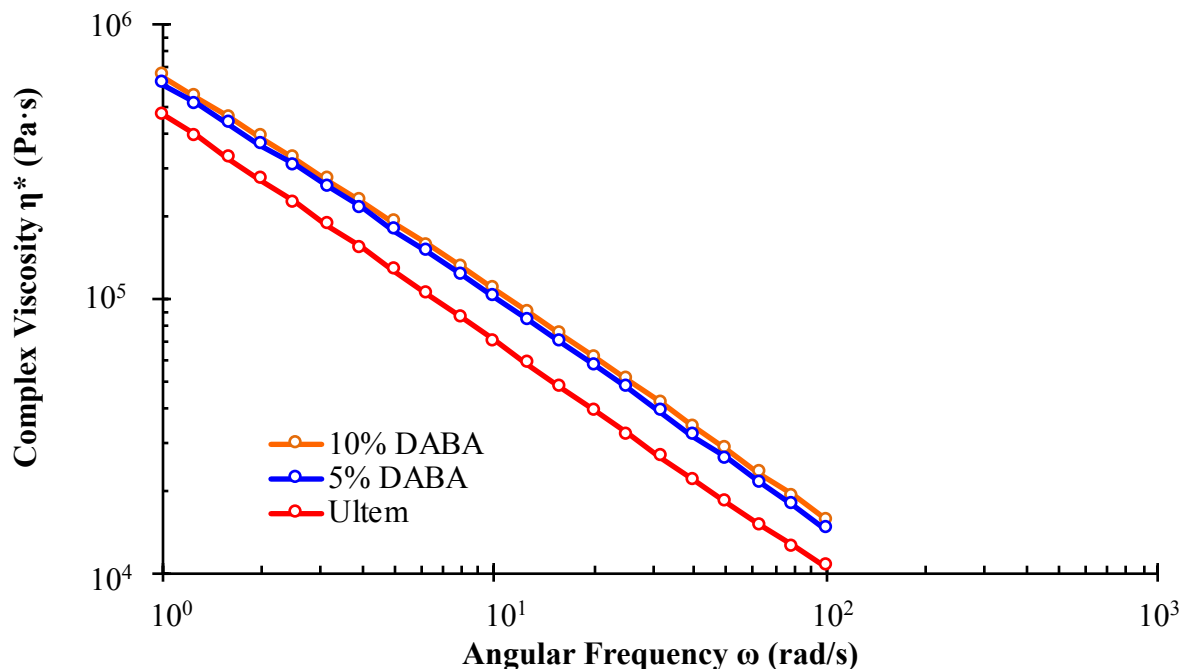


Figure S7.13. Shear thinning behavior of branched DABA-PEIs from complex viscosity (η^*) versus angular frequency, ω (rad/s) indicates greater shear thinning for higher branched PEIs.

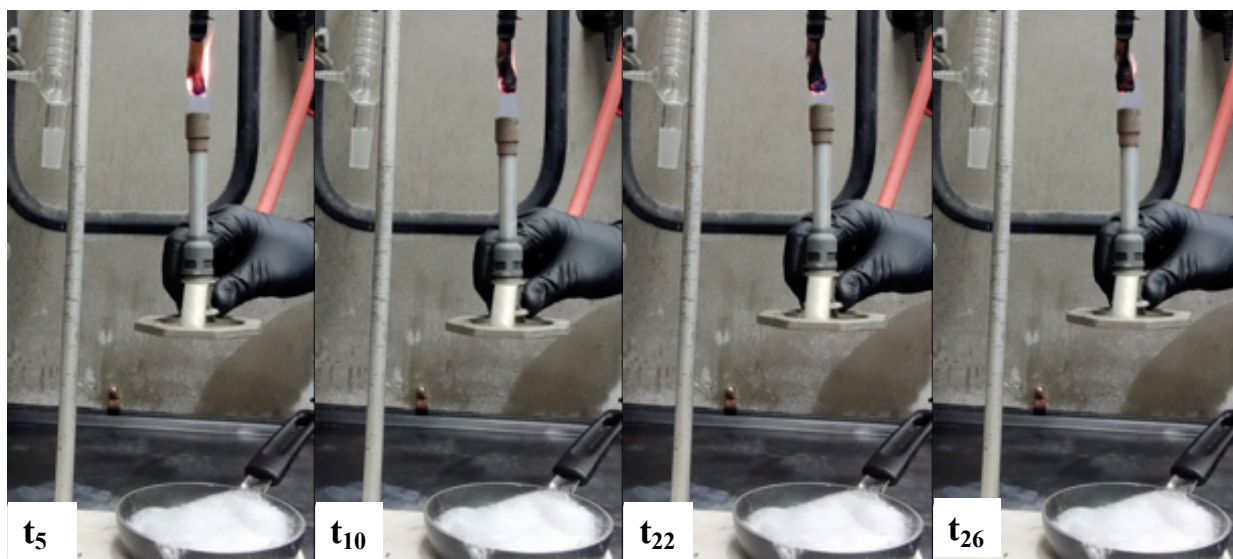


Figure S7.14. Time points t_5 , t_{10} , t_{22} , and t_{26} for 10 mol % branched DABA-PEIs.

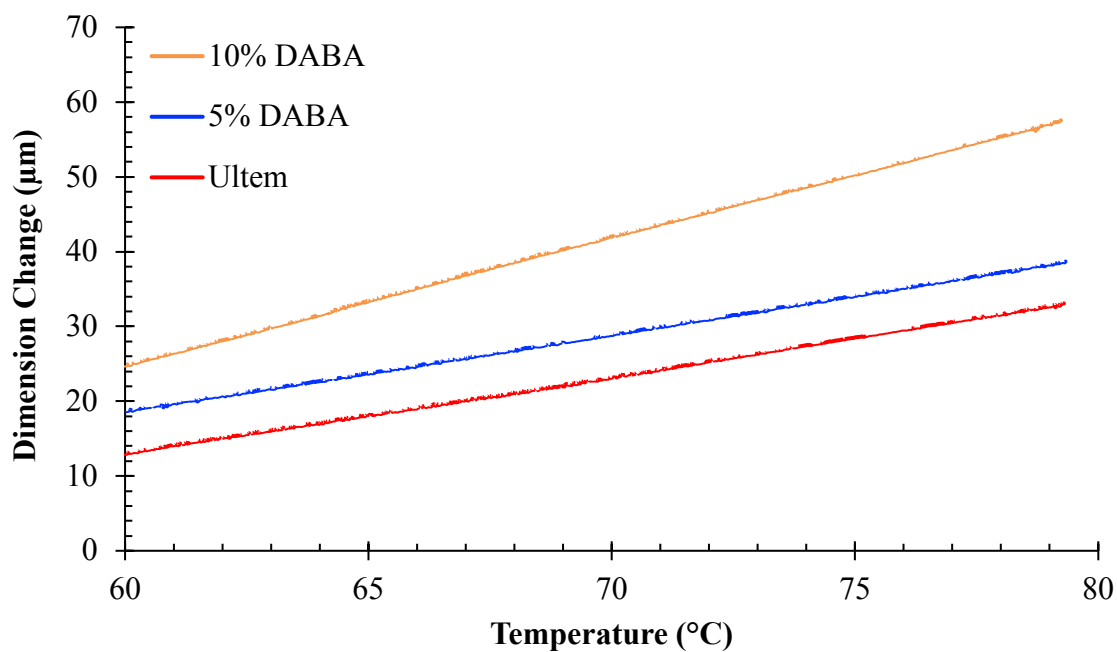


Figure S7.15. Displacement *versus* temperature of DABA-branched PEIs used to determine coefficient of thermal expansion (CTE).

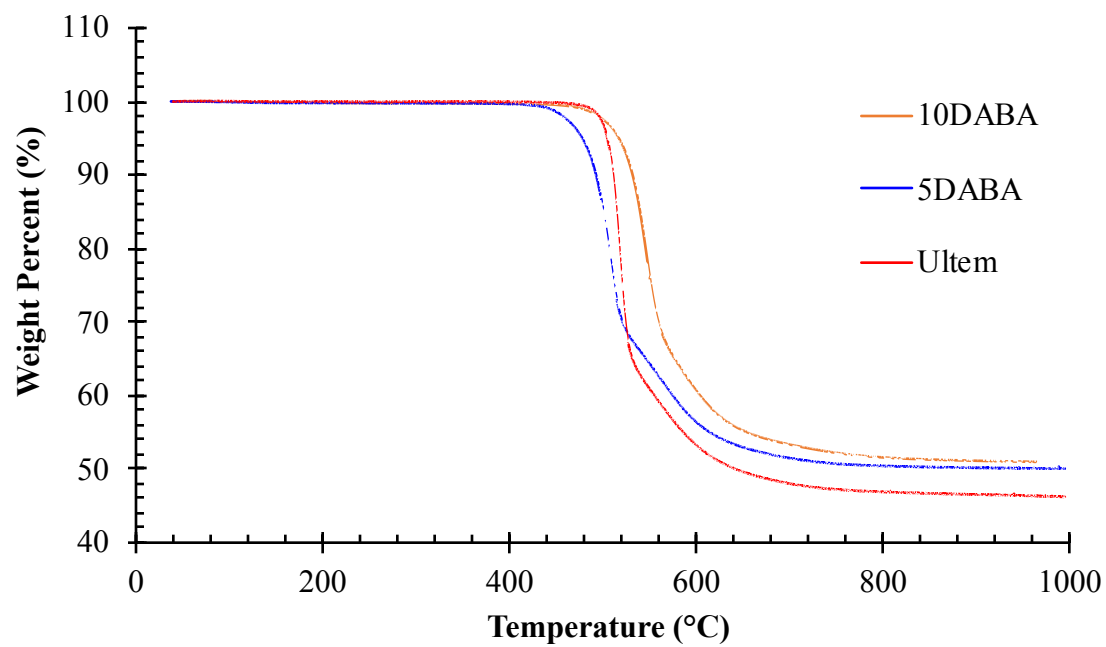


Figure S7.16. Thermogravimetric analysis (TGA) of DABA-branched PEIs to determine char yield % at 900 °C.

Chapter 8: Synthesis and Characterization of Polyetherimides (PEI)s with Ester/Amide-based Pendant Groups

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Keywords: Polyetherimide, Pendant Groups, High Performance, Benzamide

8.1 Abstract

Various aromatic diamine monomers incorporating amide or ester pendant groups enabled the synthesis of novel poly(ether imide)s (PEIs) with pendant functionality. Synthesis of 3,5-diamino phenyl benzoate (DAPB) and 3,5-diamino phenyl benzamide (DAPBam) enabled the synthesis of PEIs possessing phenyl pendant groups, with either a ester or amide linkage. Similarly, utilizing methyl 3,5-diaminobenzoate (MDAB) afforded a methyl ester pendant group on PEIs. Lastly, 3,5-diaminobenzamide (DABAm) installed a hydrogen bonding pendant functionality. ¹H NMR spectroscopy and mass spectrometry (MS) confirmed monomer structure. Size exclusion chromatography (SEC) and ¹H NMR spectroscopy confirmed PEI structure as well as molecular weights. Fourier transform infrared spectroscopy (FTIR) confirmed imidization of PEIs. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) evaluated thermal properties. Phenyl pendant group incorporation increased the glass transition temperature (T_g) up to 245 °C, regardless of ester or amide linkage. Similarly, methyl ester and amide incorporation raised the T_g as well. All pendant functional groups decreased the onset of weight loss temperature ($T_{d,5\%}$).

8.2 Introduction

Poly(ether imide) (PEI), commercially known as Ultem™, is a high performance polymer which possesses high thermal stability ($>500\text{ }^{\circ}\text{C}$), a high glass transition temperature (T_g) ($217\text{ }^{\circ}\text{C}$), and melt processability, commonly difficult with highly aromatic polyimides.¹⁻⁵ PEI processing requires high temperatures or other high energy manufacturing. Thus, interest remains in either developing new processing methods or more easily processable PEI structures. Recent advances in additive manufacturing (3D printing) offers advanced ways of processing.^{2, 6-9} although intricate synthesis/compositions or equipment is required. Even with these advanced processing techniques and methods, improving melt processability while maintaining thermal and mechanical properties is desired in aerospace and automotive applications.

Common ways to improve PEI processability include altering backbone regiochemistry,¹⁰⁻¹¹ branching,¹²⁻¹⁷ and pendant groups.¹⁸ Incorporating pendant groups pushes chains away, hindering chain packing, and improving melt flow. Once pendant groups get too large, melt processability is worsened, as bulky pendant groups hinder chain reptation. Decreasing chain packing too much also negatively effects mechanical properties as well as chemical resistance. Lastly, many functional pendant groups impart desirable properties, but are thermally unstable, thus decreasing the potential application temperature range. Thus, determining the pendant group composition as well as preferred linkage is key to balancing properties and processability.

This report describes the synthesis of various aromatic diamines with pendant groups, consisting of either ester or amide linkages. Commercially available methyl ester and amide pendant group aromatic diamines enabled the synthesis of PEIs with simple

amide or ester pendant functionality. Alternatively, synthesis of aromatic diamines with pendant phenyl groups systematically studied the influence of ester and amide linkage on thermal properties. All compositions were confirmed with ^1H NMR spectroscopy and soluble compositions molecular weights were determined using size exclusion chromatography (SEC). All PEIs with pendant groups possessed increased T_g s, but lower onset of weight loss temperatures ($T_{d,5\%}$)

8.3 Experimental

8.3.1 Materials. Phthalic anhydride (PA) (Sigma-Aldrich; ReagentPlus 99%) was dried for 16 h at 60 °C under vacuum prior to using. *Meta*-phenylene diamine (MPD) (Aldrich; flakes 99%) was purified by sublimation under vacuum prior to using. Bisphenol-A dianhydride (BPA-DA) and Ultem U1000/U1010 was supplied in high purity by SABIC Innovative Plastics. BPA-DA was dried under a nitrogen gas blanket and by heating into the liquid phase and cooling to an amorphous solid. This ensured anhydride form. 3,5-dinitrobenzamide (DABAm) (Sigma-Aldrich), 3,5-dinitrobenzoyl chloride (Sigma-Aldrich), methyl 3,5-diaminobenzoate (MDAB) (Alfa Aesar), phenol (Sigma-Aldrich), pyridine (Sigma-Aldrich), and aniline (Sigma-Aldrich) were used as received. All solid monomers were kept under vacuum prior to use. All deuterated solvents were purchased (Cambridge Isotope Laboratories, Inc) and used as received. All other solvents (Spectrum Chemical) were used as received.

8.3.2 Analytical Methods. ^1H NMR spectroscopy (^1H NMR) was performed (23 °C, 400 MHz) on a Varian Unity 400 utilizing deuterated chloroform (CDCl_3). Differential scanning calorimetry (DSC; TA instruments Q1000 DSC) characterized thermal transitions. DSC was calibrated with zinc (mp = 419.47 °C) and indium (mp = 156.60 °C)

standards. Run settings included a nitrogen flow (50 mL min⁻¹) and a heating and cooling profile (a 10 °C min⁻¹). Utilizing the heating ramp (second), glass transition temperatures (T_g) were determined over the midpoint of the step change. Thermogravimetric analysis (TGA; TA Instruments Q50) ran from 25 to 600 °C using a linear heating rate (10 °C min⁻¹) to probe weight loss over time/temperature. FTIR analysis (Varian 670-IR equipped with a Diamond GladiATR attachment) of imidized PEIs was acquired with 32 scans each at a 4 cm⁻¹ resolution. Mass spectrometry (MS; Agilent 6220 liquid chromatograph with mass spectrometry) utilized a TOF analyzer and positive mode ESI to measure accurate molecular weights.

8.3.3 Synthesis of 3,5-dinitro(phenyl benzoate/benzamide). 3,5-dinitrobenzoyl chloride (80 g, 0.347 mol) and 200 mL toluene was added to a 250 mL round-bottomed flask and stirred until completely dissolved. Phenol (39.19 g, 0.416 mol) or aniline (38.78 g, 0.416 mol), pyridine (49.4 g, 0.624 mol), and 300 mL of toluene were added to a 3-necked, 1000 mL round-bottomed flask equipped with an addition funnel, condenser, and overhead stirrer. The contents were mixed under a nitrogen gas purge. The 3,5-dinitrobenzoyl chloride solution was added to the addition funnel and purged for 20 min. This solution was then added dropwise and a white precipitate (pyridinium chloride) formed. After all the solution was added, the reaction was stirred for 1 h and then heated to reflux for 3 h. The reaction was cooled to RT and the precipitate was filtered off. Washing the precipitate with 5% sodium bicarbonate solution removed the pyridinium salt and isolated the product (90% yield). ¹H NMR spectroscopy and MS confirmed the products.

8.3.4 Reduction of 3,5-dinitro(phenyl benzoate/benzamide) and 3,5-dinitrobenzamide to 3,5-diamino(phenyl benzoate/benzamide) and 3,5-diaminobenzamide. All dinitro

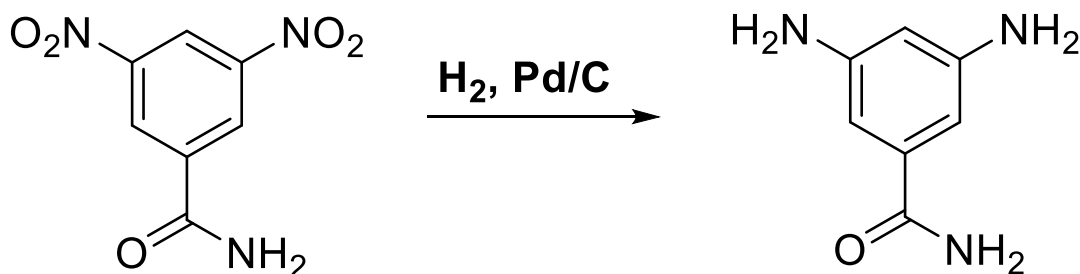
compounds were reduced using similar synthetic procedures. The reduction of 3,5-dinitro(phenyl benzoate) follows as a representative example. 3,5-dinitro(phenyl benzoate) (100 g, 0.438 mol) and tetrahydrofuran (450 mL) were added to a 3 L Parr reactor. The contents were purged with nitrogen gas for 20 min and 10 wt % palladium over carbon (Pd/C) (10 g) was charged to the reactor. The contents were again purged with nitrogen gas for 20 min before three cycles of pressurizing the reactor with hydrogen gas to 100 psi. The increased pressure ensured hydrogen saturation in the solution. The reactor maintained 100 psi throughout the reaction and proceeded at 25 °C for 18 h. The pressure was subsequently released and nitrogen was purged through the reactor. A heterogeneous and black solution was recovered and filtered through Celite to obtain a light brown, homogeneous solution. Solvent evaporation isolated the target compound as an off white/brown powder (98% yield). ¹H NMR spectroscopy and MS confirmed the products.

8.3.5 Synthesis of poly(ether imides) (PEIs). The synthesis of PEIs with pendant groups targeting 20 kg mol⁻¹ number average molecular weight (M_n) follows as an example. All PEI synthesis followed the same procedure and targeting 50 mol % of 3,5-diamino(phenyl benzoate) represents the reaction setup and conditions. 3,5-diamino(phenyl benzoate) (DAPB) (2.258 g, 9.795 mmol), *meta*-phenylene diamine (MPD) (1.059 g, 9.795 mmol), bisphenol-A dianhydride (BPA-DA) (10.00 g, 19.1 mmol) and n-methyl-2-pyrrolidone (NMP) (50 mL) were added to a three-necked, 500-mL, round-bottomed flask equipped with a glass stir rod using a Teflon stir blade, a Dean-Stark trap with a condenser, and a septum. The flask was purged with nitrogen gas for 20 minutes while stirring (~25 rpm). The contents were subsequently stirred at 100 rpm at 180 °C for 18 h. Phthalic anhydride (PA) (0.42 g, 2.9 mmol) was then introduced to the flask to end-cap the PEIs. Samples

were then heated to 380 °C for 30 min in a metal (bismuth/tin alloy) bath under nitrogen gas purge to remove all solvent and thermally imidize the PEIs. A condenser was added and a cold round-bottomed flask collected the condensate. After removal of solvent and imidization, samples were dissolved in CHCl₃ or NMP and precipitated into methanol (MeOH) to afford an off-white powder.

8.4 Results and Discussion

Reduction of the commercially available 3,5-dinitrobenzamide to the diamino analogue, 3,5-diaminobenzamide (DABAm), enabled the synthesis of poly(ether imide)s (PEI)s with pendant amide functionality. As seen in **Scheme 8.1**, reduction utilizing hydrogen gas at elevated pressures (100 psi) in THF, produced the diamino compound in a Parr reactor. ¹H NMR spectroscopy confirmed the structure, as seen in **Figure 8.1**, and mass spectrometry (MS) confirmed the molecular weight. The presence of 4 protons at ~4.75 ppm ensured complete reduction of the nitro groups to amines



Scheme 8.1: Reduction of 3,5-dinitrobenzamide to 3,5-diaminobenzamide (DABAm)

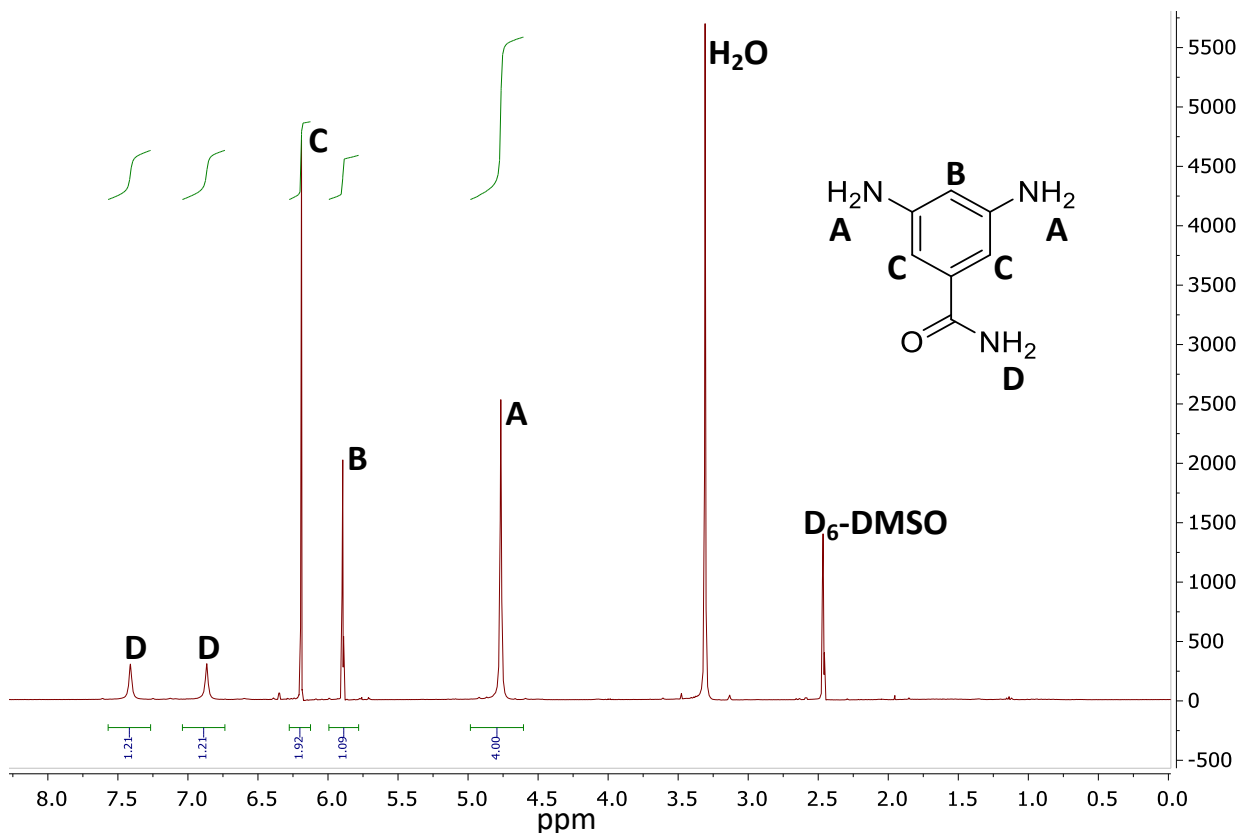
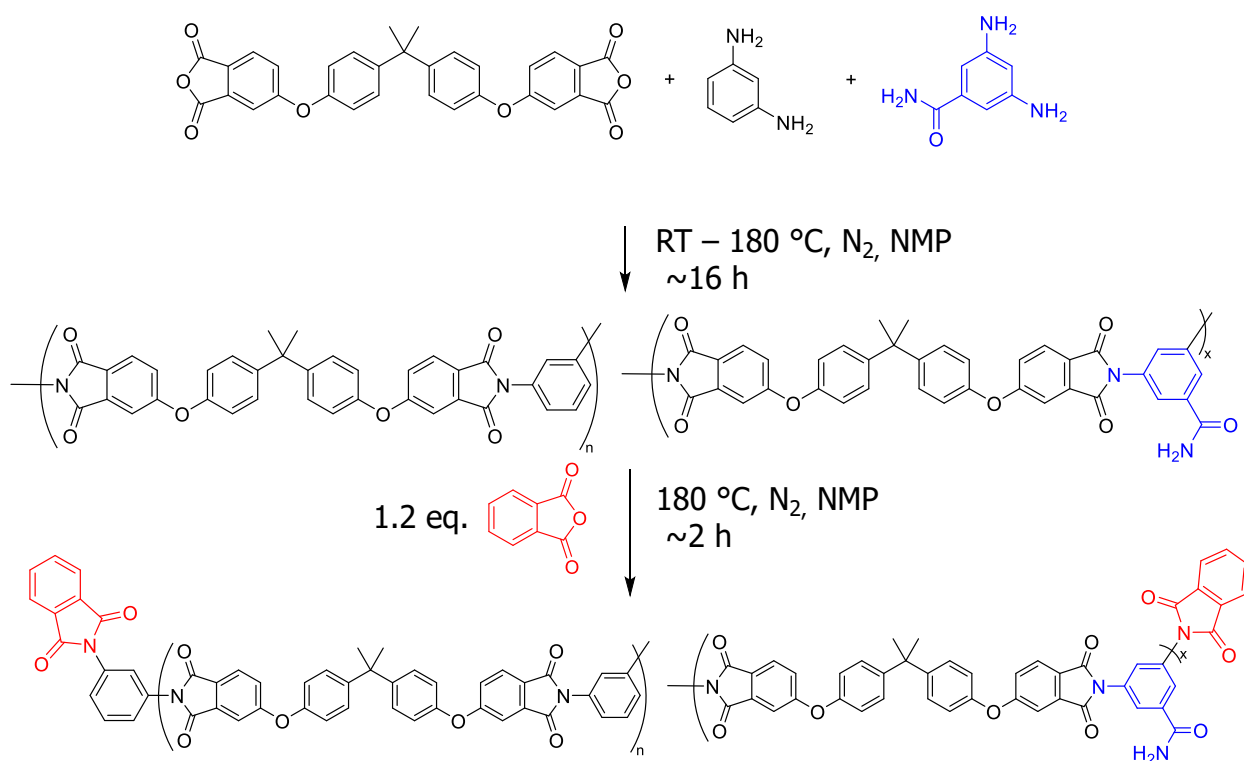


Figure 8.1. ^1H NMR spectra of 3,5-diaminobenzamide

Utilizing the DABAm, synthesis of benzamide-containing PEIs followed standard PEI synthesis, as seen in **Scheme 8.2**. First, bisphenol-A dianhydride (BPA-DA), *meta*-phenylene diamine (MPD), and DABAm dissolved in NMP and reacted at 180 °C to produce partially imidized PEI (co)polymers. An excess of diamine controlled targeted molecular weight using the Carother's equation and resulted in PEIs with amine end groups. Addition of a slight molar excess of phthalic anhydride (PA) end-capped the PEIs. Once the reaction finished, thermal imidization at 380 °C in a metal bath ensured complete imidization, adapted from commonly used industrial methods. Dissolving the imidized PEI product and precipitating into methanol (MeOH) afforded an off-white/light-brown precipitate. All compositions dissolved, except for the 100 mol % DABAm PEI. The 100 mol % DABAm PEI most likely crosslinked during the elevated temperature imidization

step, consistent with similar PEIs incorporating 3,5-diaminobenzoic acid (DABA).¹⁹⁻²⁰ DABA-based PEIs are known to crosslink at temperatures $>300\text{ }^{\circ}\text{C}$, thus a similar reaction is expected for the amide functional group. Small molecule aromatic benzamides at elevated temperatures reacted to form benzonitriles, which could further react in the presence of water to form benzoic acid derivatives.²¹⁻²² Water is the condensate of the cyclcoimidization ring closure at elevated temperatures, thus small amounts of water are present at the elevated temperatures required to undergo these reactions. The swollen gel of the 100 mol % could not be isolated and was not further analyzed. Excess PA is purified out either during the $380\text{ }^{\circ}\text{C}$ imidization step (PA bp = $295\text{ }^{\circ}\text{C}$) or during the precipitation into methanol.



Scheme 8.2: Synthesis of PEIs incorporating a pendant amide. PEIs are end-capped with PA.

As seen in **Figure 8.2**, ^1H NMR spectroscopy confirmed the chemical composition and incorporation of DABAm into PEI. Protons *ortho* to the imide linkages (d & e) shift to higher ppm due to the deshielding of the amide linkage (protons a & b). The ratio of these protons (e & a) determined the mol % incorporation of DABAm into the PEI. All composition agreed well with charged monomer amounts. Similarly, analysis of the PA end-groups by ^1H NMR spectroscopy enabled quantification of the PEIs' number average molecular weight (M_n). As seen in **Figure 8.3**, protons (1) next to the imide ring on the PA end-cap is resolved at a ppm shift of 7.75-7.80. Comparing the integral of this peak to the protons *meta* to the isopropylidene linkage in the backbone of both repeat units (proton 2) afforded the degree of polymerization (X_n). Utilizing the mol % of each repeat unit and the X_n determined each of the compositions M_n . All DABAm-PEIs achieved M_n s consistent with commercial PEI M_n s.

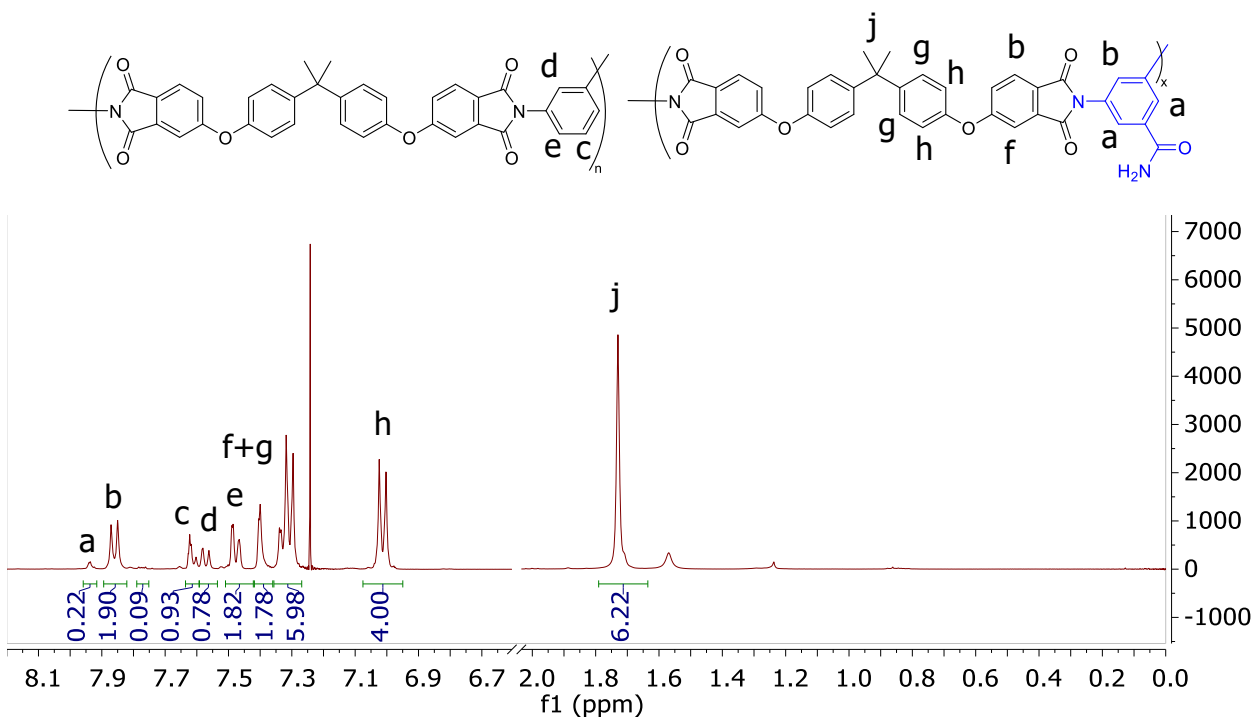


Figure 8.2. ^1H NMR spectra of 10 mol % DABAm-PEI

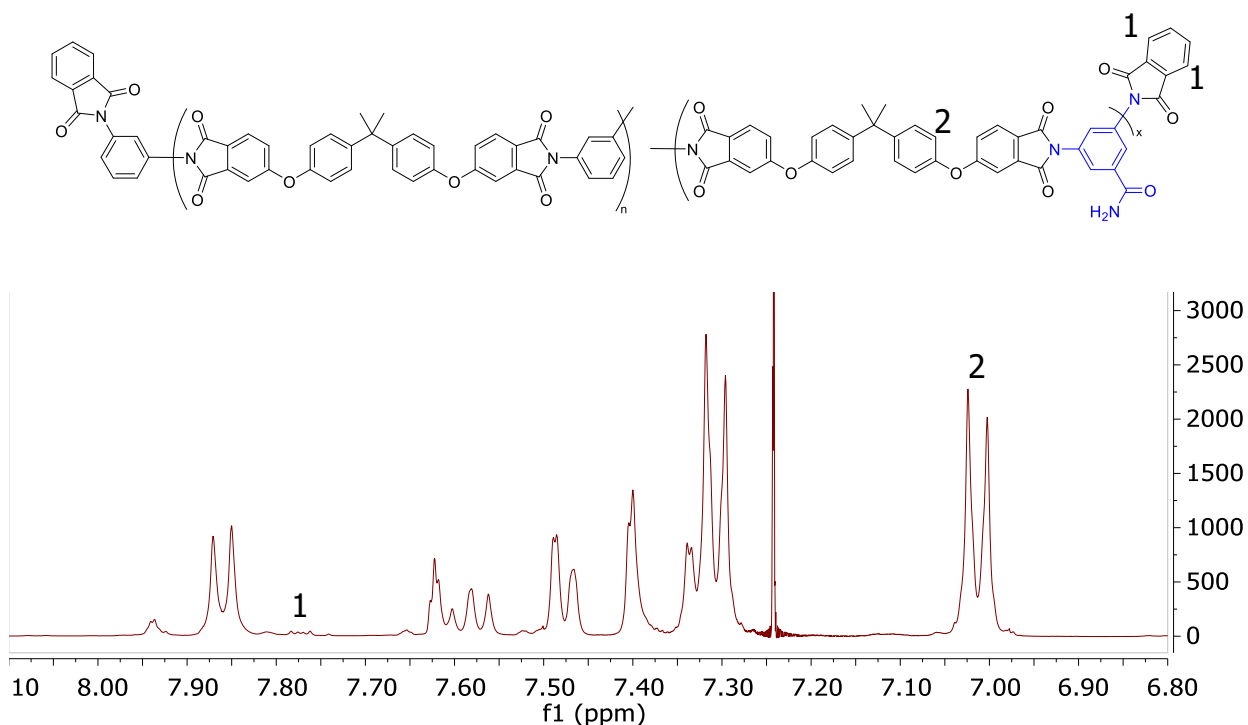


Figure 8.3. End-group analysis confirms DAPBam-PEI molecular weight consistent with commercial PEI

The potential crosslinking through the amide pendant group suggested decreased thermal stability of the DABAm-PEIs. Thus, thermogravimetric analysis is required to understand the onset of weight loss temperature ($T_{d,5\%}$) as a function of PEI composition. As seen in **Figure 8.4**, incorporating higher levels of the DABAm reduced the $T_{d,5\%}$ by 50-60 °C, although most of the wt % remains above 450 °C. Further analysis of the thermal properties required differential scanning calorimetry to determine the glass transition temperatures (T_g)s. The T_g systematically increased with increased levels of DAPAm, as seen in **Figure 8.5**. The incorporation of DABAm increased the T_g up to 240 °C at 75 mol %. A slight broadening of the T_g for the 75 mol % suggests a change in polymer architecture, most likely a result from the high temperature imidization step.

Further analysis of these PEIs requires chemical imidization to eliminate the risk of thermal degradation of the amide pendant functionality. Chemical imidization followed by

solution casting films will produce PEI compositions with hydrogen bonding potential. These PEIs should possess better ductility due to the supramolecular nature of the polymer as well as improved tensile performance. Surface property changes such as water contact angle is of interest as well due to the potential of the amide groups to migrate to the surface of the PEI and influence the wettability. Improved wettability and surface interactions could be interesting in high temperature adhesive applications where PEIs are commonly used for construction and architectural adhesives.

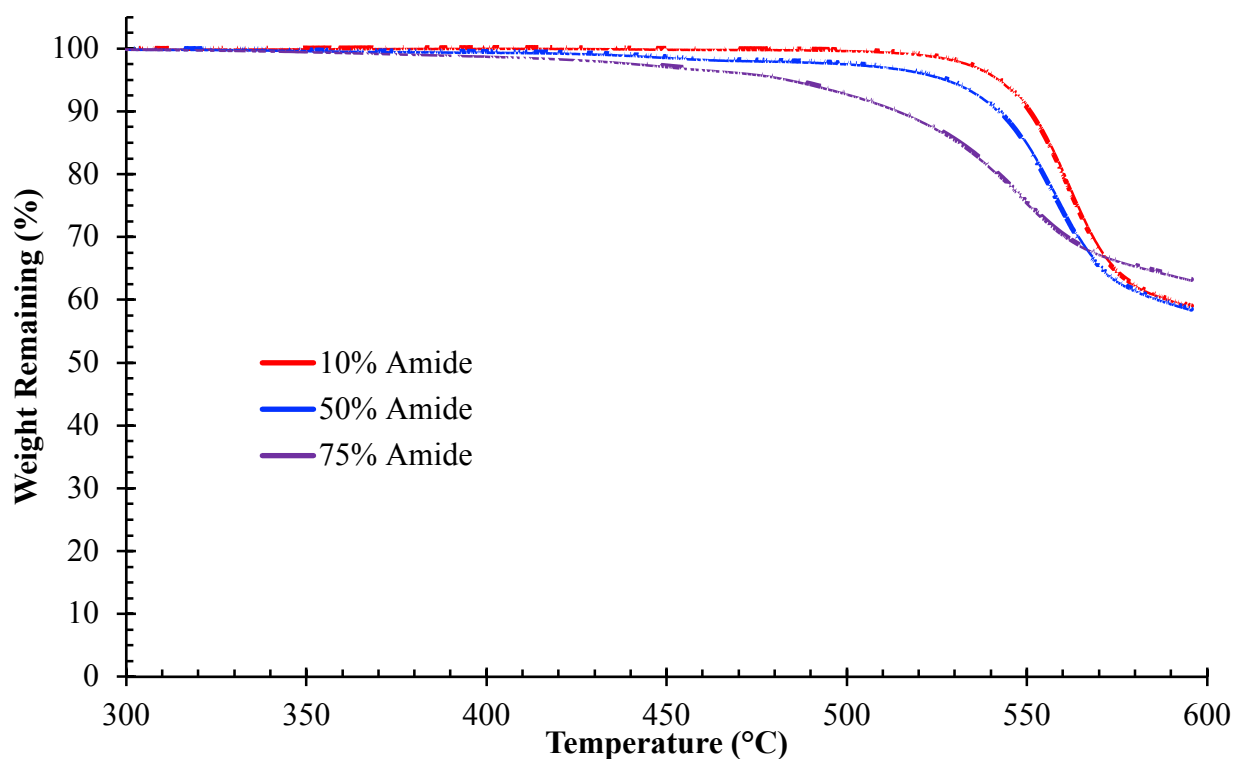


Figure 8.4. Thermogravimetric analysis (TGA) of DABAm-PEIs.

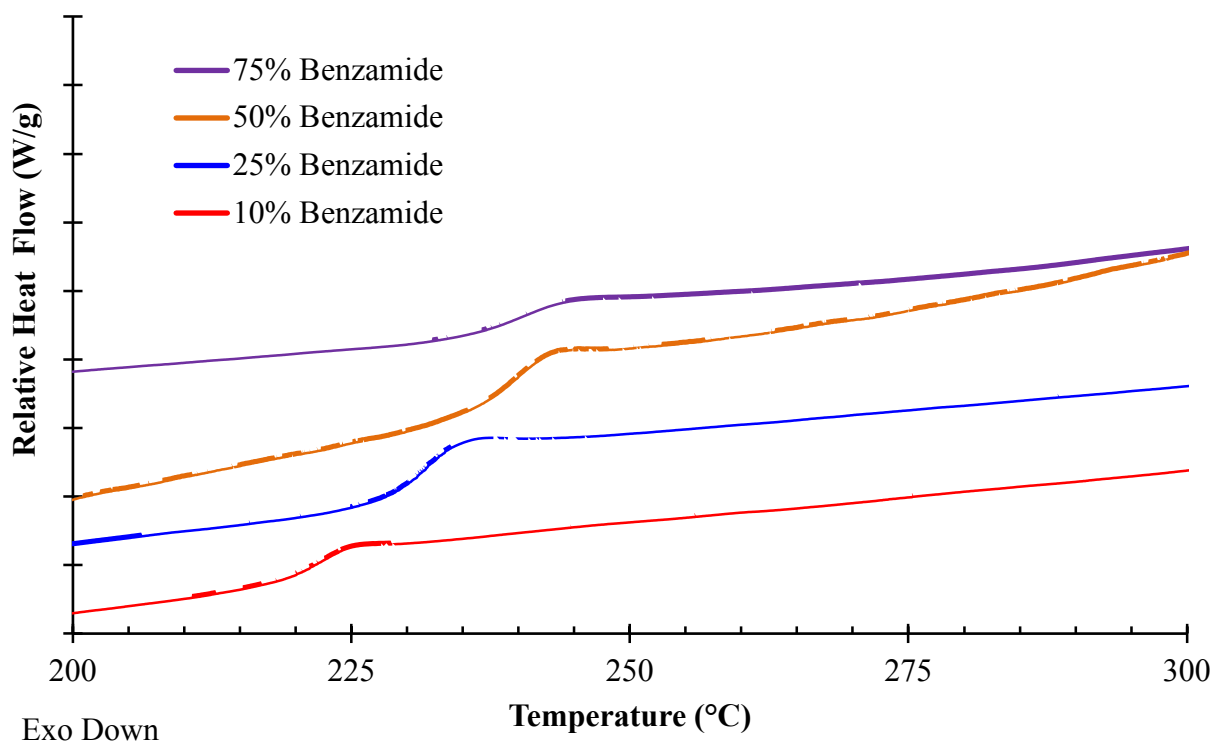
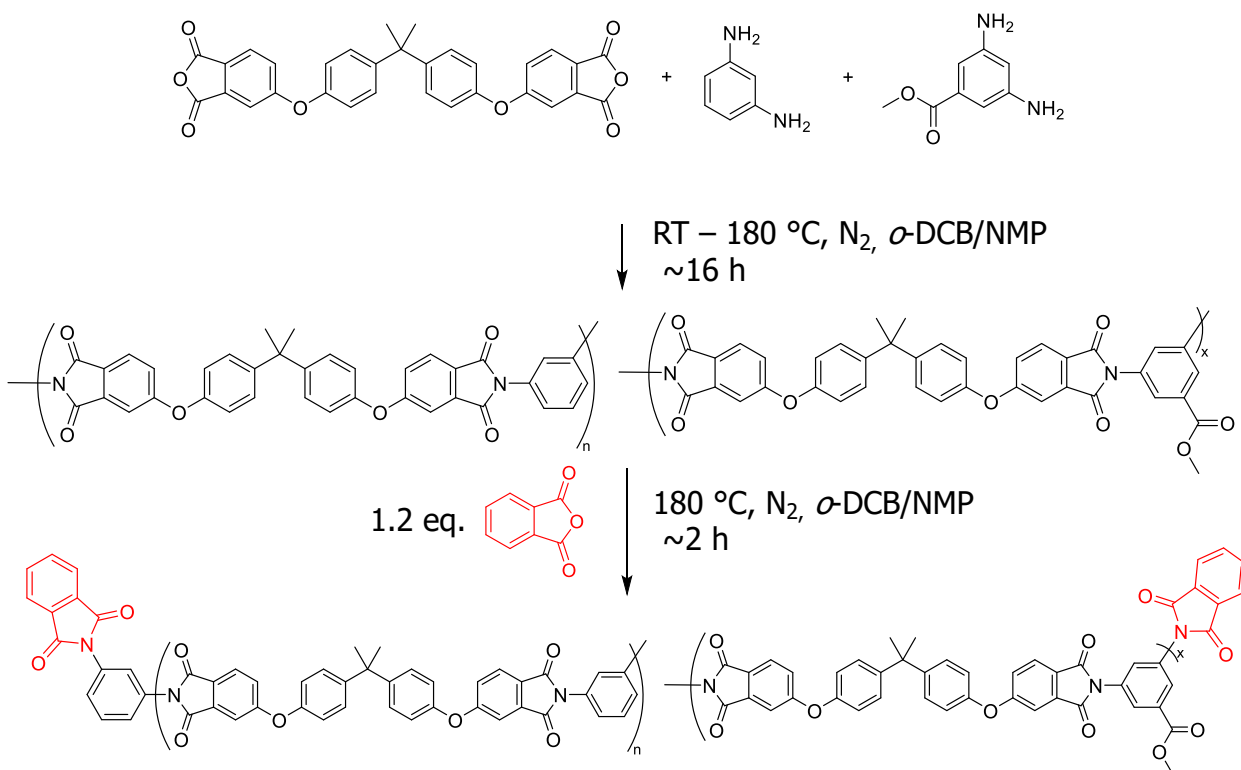


Figure 8.5. Differential scanning calorimetry (DSC) of DABAm-PEIs.

One method to improve processability is to incorporate pendant functionality that act similarly to plasticizers by pushing chains apart and increasing chain mobility. Whereas hydrogen bonding functionality like pendant carboxylic acids or amides introduce supramolecular interactions, pendant aliphatic esters act like short chain branches, altering rheological behavior.²³ Replacement of MPD with the commercially available methyl 3,5-diaminobenzoate (MDAB) enable the synthesis of PEIs containing pendant ester groups. PEI synthesis followed a similar procedure to the DABAm-PEI synthesis. Various diamine ratios were used to target mol % incorporation and an excess of diamine controlled molecular weight and ensured amine end-caps. The end-caps were reacted subsequently with PA.



Scheme 8.3: Synthesis of PEIs incorporating a pendant methyl ester, methyl 3,5-diaminobenzoate (MDAB). PEIs are end-capped with PA.

As seen in **Figure 8.6**, ^1H NMR spectroscopy confirmed MDAB incorporation. The methyl ester singlet peak at 3.9 ppm (i) represented the pendant methyl group of the ester, while peaks between 6.9 and 8.3 represented the aromatic protons on the PEI backbone. Quantifying the ratio between the methyl ester peak (i) and the proton *meta* to the imide (c) determined mol % incorporation of MDAB. All MDAB-PEIs agreed well with targeted compositions. Fourier transform infrared spectroscopy (FTIR) confirmed complete imidization of the MDAB-PEIs after the thermal imidization step. As seen in **Figure 8.7**, the lack of a peak at 1660 cm^{-1} , assigned to the carbonyl ($\text{C}=\text{O}$) stretch of the amic acid intermediate, confirmed full backbone imidization.²⁴ Size exclusion chromatography (SEC) analyzed molecular weights. As seen in **Figure 8.8**, elution peaks as well as distributions are consistent with commercial Ultem U1000/U1010 PEIs. All PEIs possess

a monomodal distribution with some individual populations appearing at high retention time, signifying low molecular weight species. These population are most likely cyclics, which are commonly produced in step growth polymerizations.²⁵

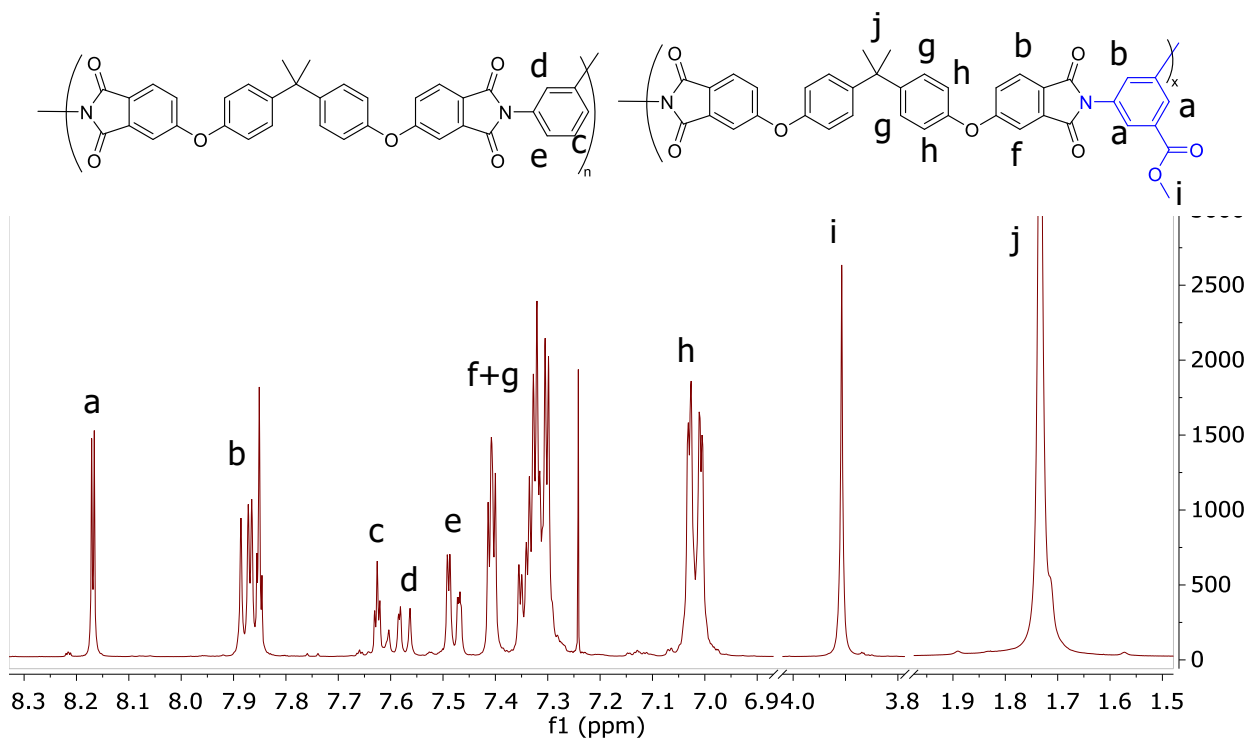


Figure 8.6. ¹H NMR spectroscopy of MDAB-PEIs.

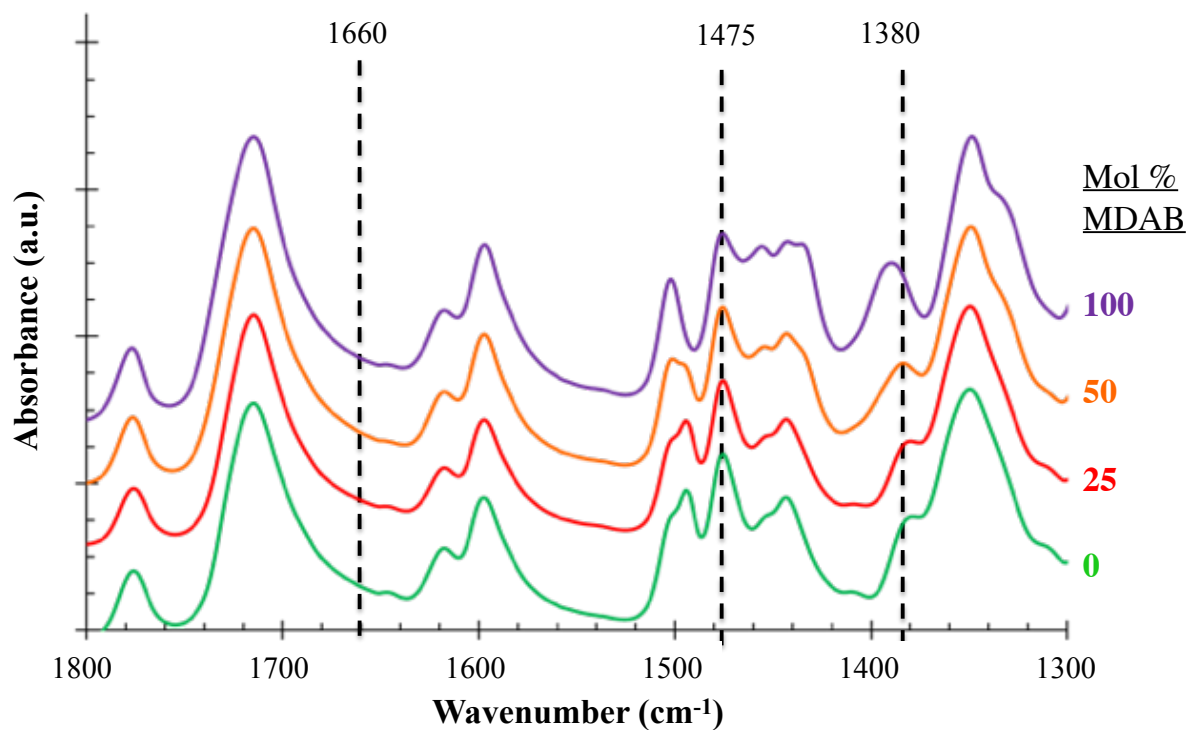


Figure 8.7. FTIR analysis of MDAB-PEIs. C-C stretch at 1475 cm^{-1} is used as standard and C-N stretch from imide (1380 cm^{-1}) and C=O stretch from amide acid (1660 cm^{-1}) used to determine imidization.

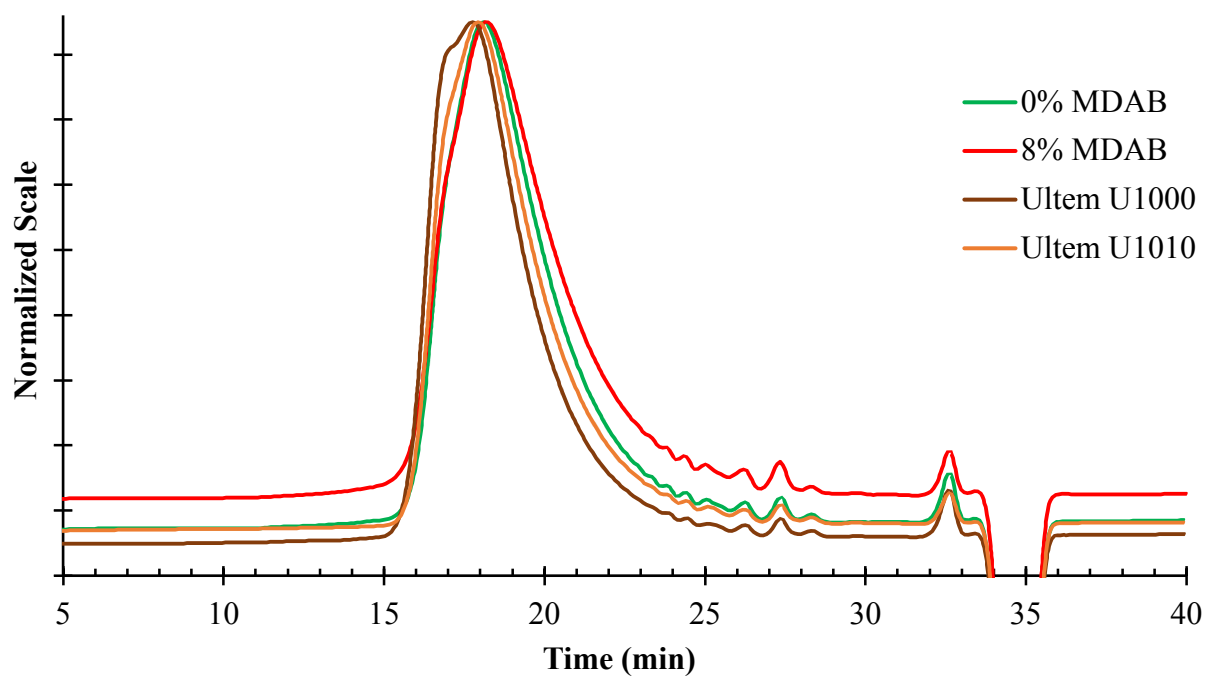


Figure 8.8. Size exclusion chromatography (SEC) of low mol % MDAB-PEIs.

Similar to the DABAm pendant functionality, MDAB-PEIs possess lower $T_{d,5\%}$ when incorporating higher levels of the methyl ester pendant group. 100 mol % MDAB incorporation reduced the $T_{d,5\%}$ down to 463 °C, as seen in **Figure 8.9**. As seen in **Figure 8.10**, the T_g slightly increases when incorporating higher levels of MDAB into the PEI. 100 mol % MDAB raises the T_g to 228 °C. Thus, the methyl ester pendant functionality hinders long-range segmental motion less than the pendant amide functionality. The mild improvement of T_g is desirable if the PEIs remain melt processable and ideally show improved melt processability. Unfortunately, even though the $T_{d,5\%}$ is above 400 °C, melt rheological analysis at 340 °C suggested crosslinking, as the storage modulus (G') increased and crossed over the loss modulus (G'') over time, indicating thermal instability and crosslinking is taking place. Thus, the methyl ester is unsuitable for melt processing.

Further analysis of the methyl ester PEIs requires chemical imidization to eliminate the thermal degradation. Similar to the DABAm functional groups, surface property changes are of interest with the methyl ester pendant groups. Incorporating the methyl group (or longer alkyl chains) pendant to the backbone introduces hydrophobic character, thus changing the surface properties of the PEIs. PEIs typically pick up some moisture, which can lead to hydrolysis of the imide linkage at elevated temperatures, thus increasing the hydrophobicity and water uptake is desirable for longer shelf life and resistance to potential hydrolysis.

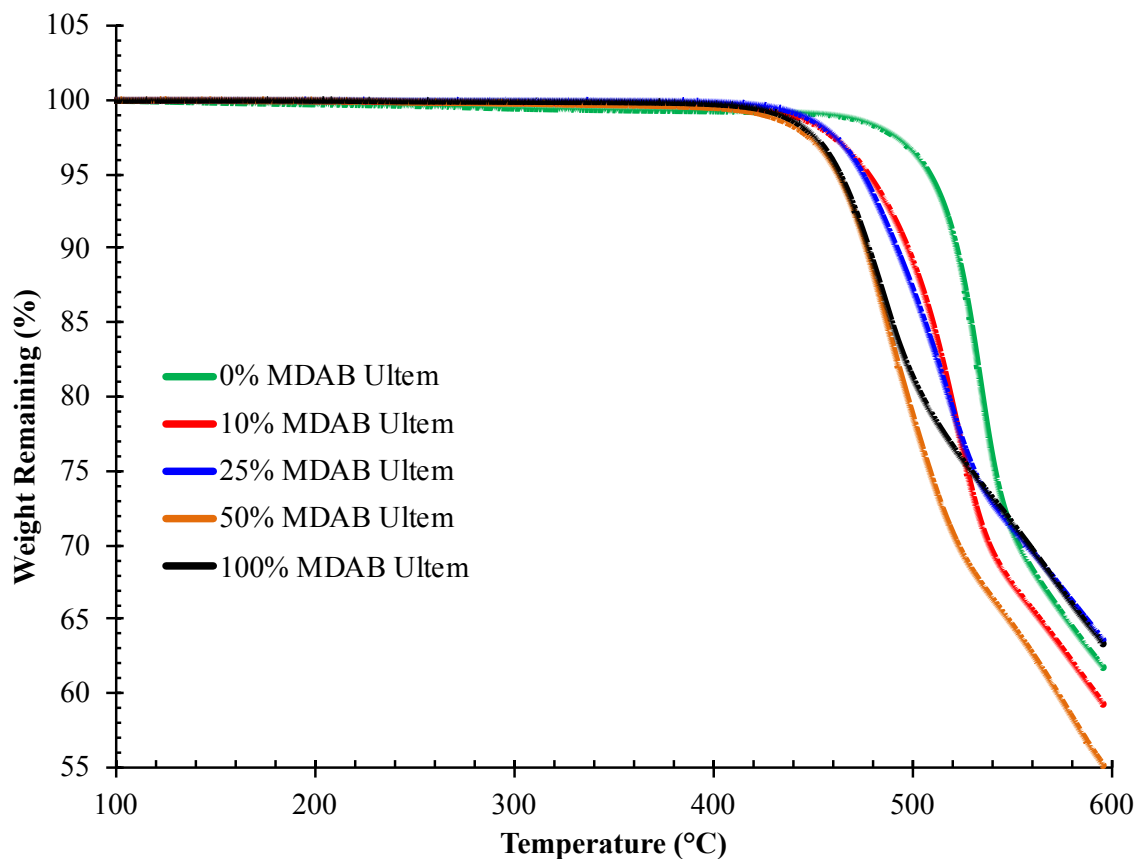


Figure 8.9. Thermogravimetric analysis (TGA) of MDAB-PEIs.

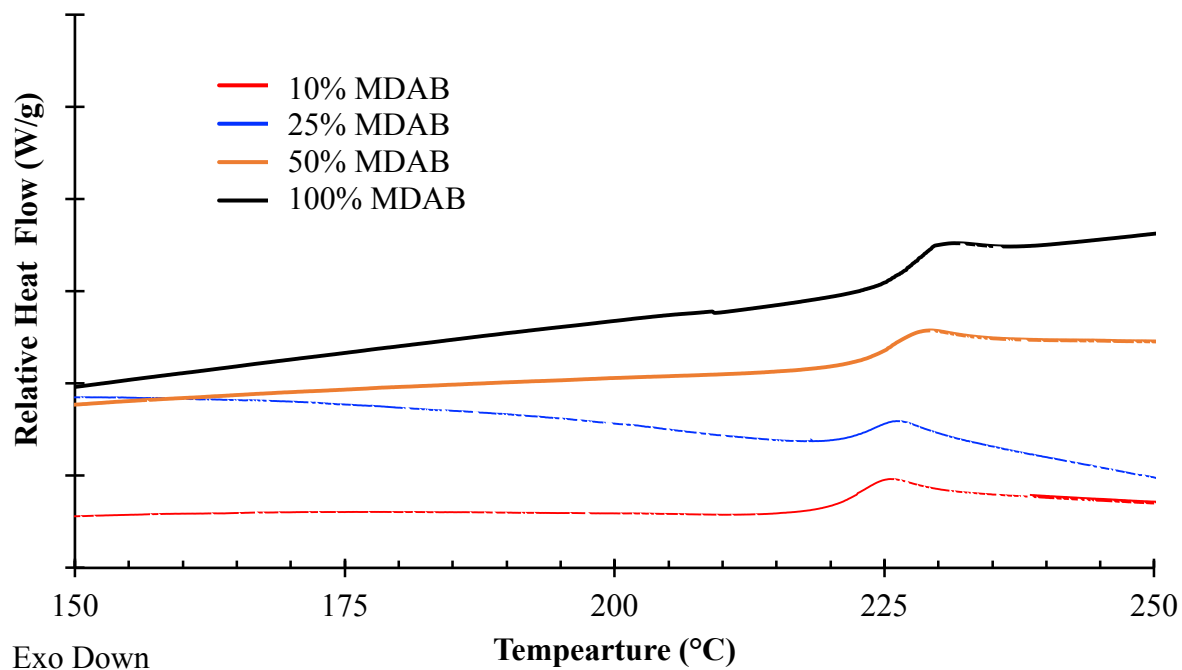
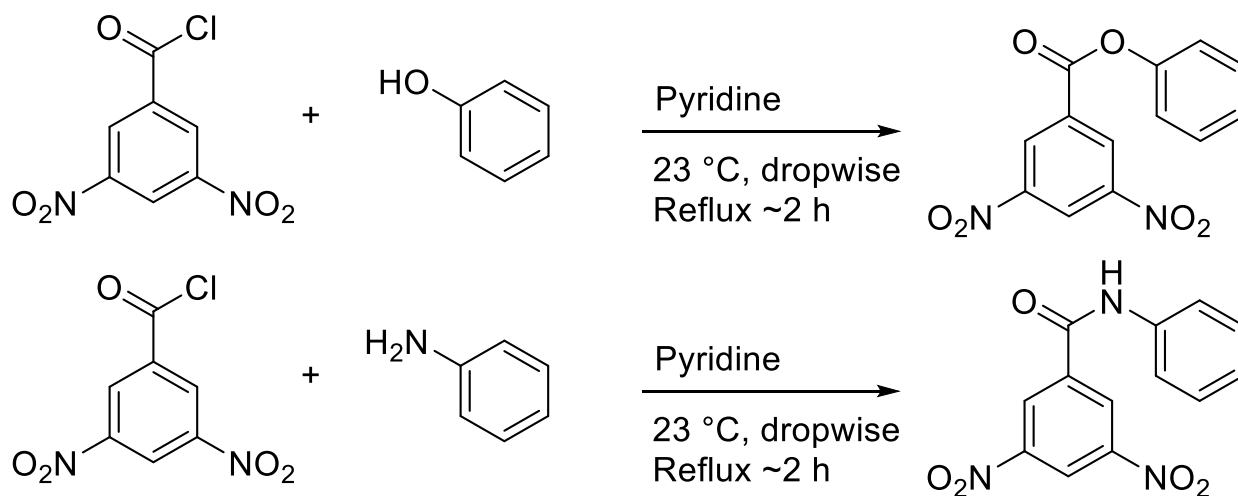
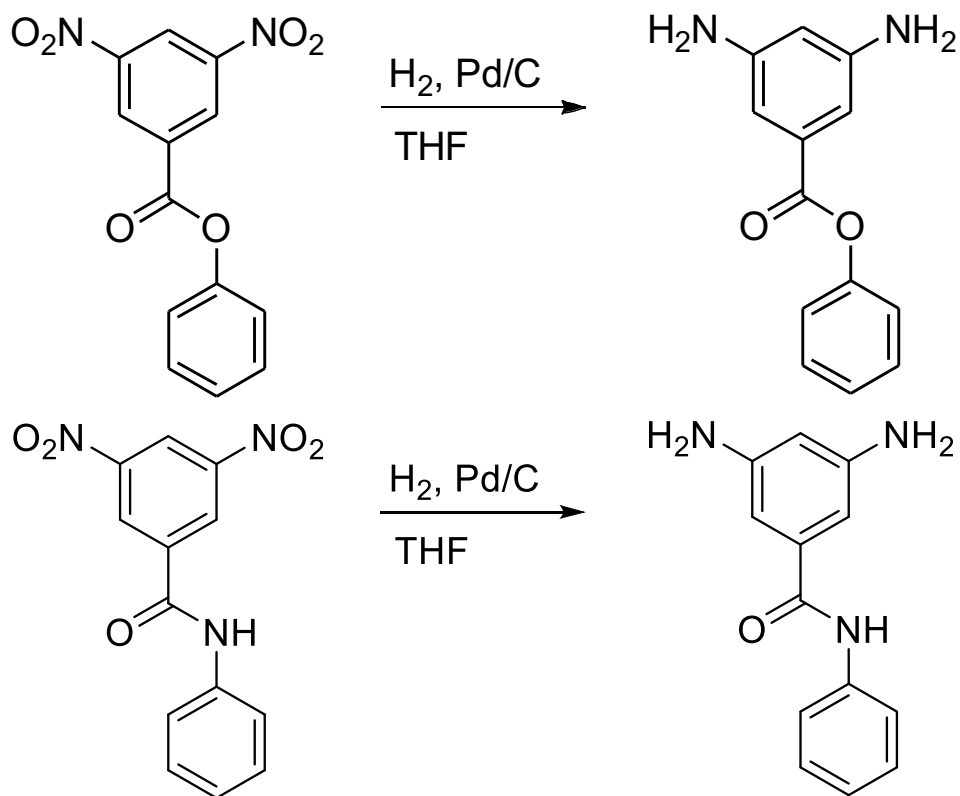


Figure 8.10. Differential scanning calorimetry (DSC) of MDAB-PEIs

The methyl ester decreased thermal stability as evident by the lower $T_{d,5\%}$ and melt rheological instability. Typically, aromatic structures possess the higher thermal stability than aliphatic structures; thus, synthesis of phenyl ester and phenyl amide monomers enabled the synthesis of PEIs with phenyl pendant groups utilizing various linkages off the backbone. As seen in **Scheme 8.4**, utilizing 3,5-dinitrobenzoyl chloride enable the synthesis of 3,5-dinitro(phenyl benzoate) and 3,5-dinitro(phenyl benzamide) through esterification with phenol or amidification with aniline, respectively. Subsequent reduction utilizing hydrogen gas and Pd/C at 100 PSI afforded the diamino monomers 3,5-diamino(phenyl benzoate) (DAPB) and 3,5-diamino(phenyl benzamide) (DAPBam). ^1H NMR spectroscopy confirmed the structures through the upfield shift of the proton in between the nitro groups (A) from 9.3 ppm to 6.2 ppm (D) between the amino groups, as seen in **Figure 8.11** and **Figure 8.12**. MS also confirmed the diamino structures, as seen in **Figure 8.13** and **Figure 8.14**.



Scheme 8.4: Synthesis of 3,5-dinitro(phenyl benzoate) and 3,5-dinitro(phenyl benzamide).



Scheme 8.5: Reduction of 3,5-dinitro(phenyl benzoate) to 3,5-diamino(phenyl benzoate) (DAPBam) and 3,5-dinitro(phenyl benzamide) to 3,5-diamino(phenyl benzamide).

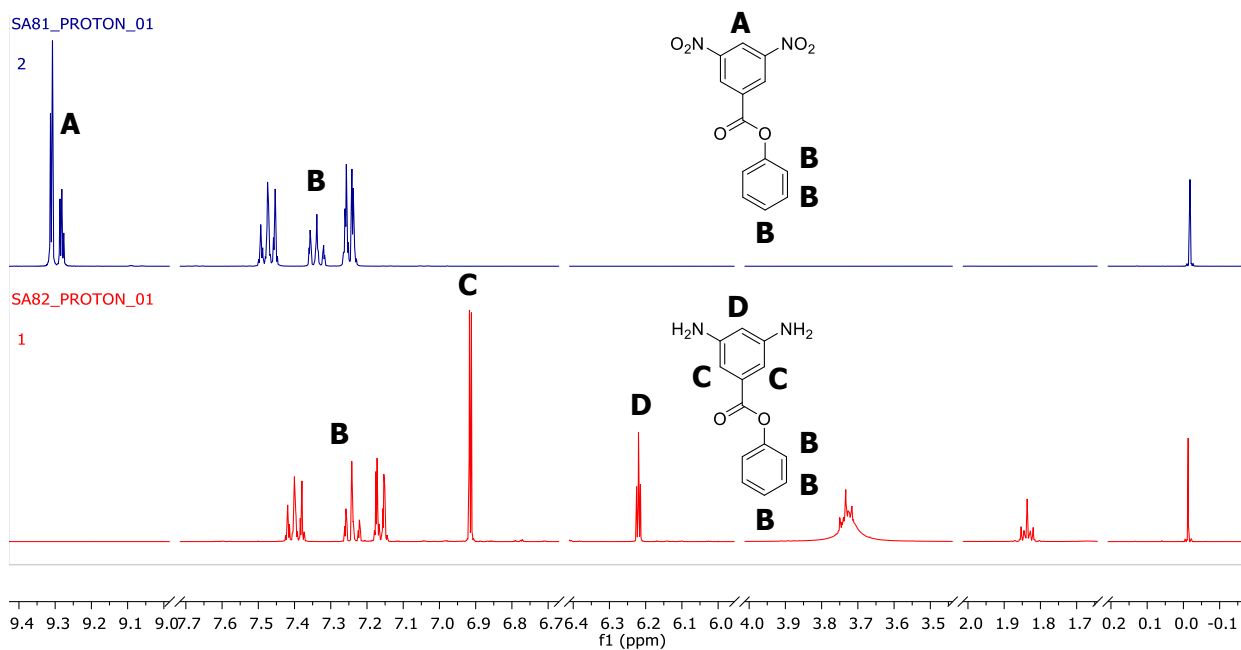


Figure 8.11. ^1H NMR spectra of 3,5-dinitro(phenyl benzoate) (top; blue) and 3,5-diamino(phenyl benzoate) (bottom; red)

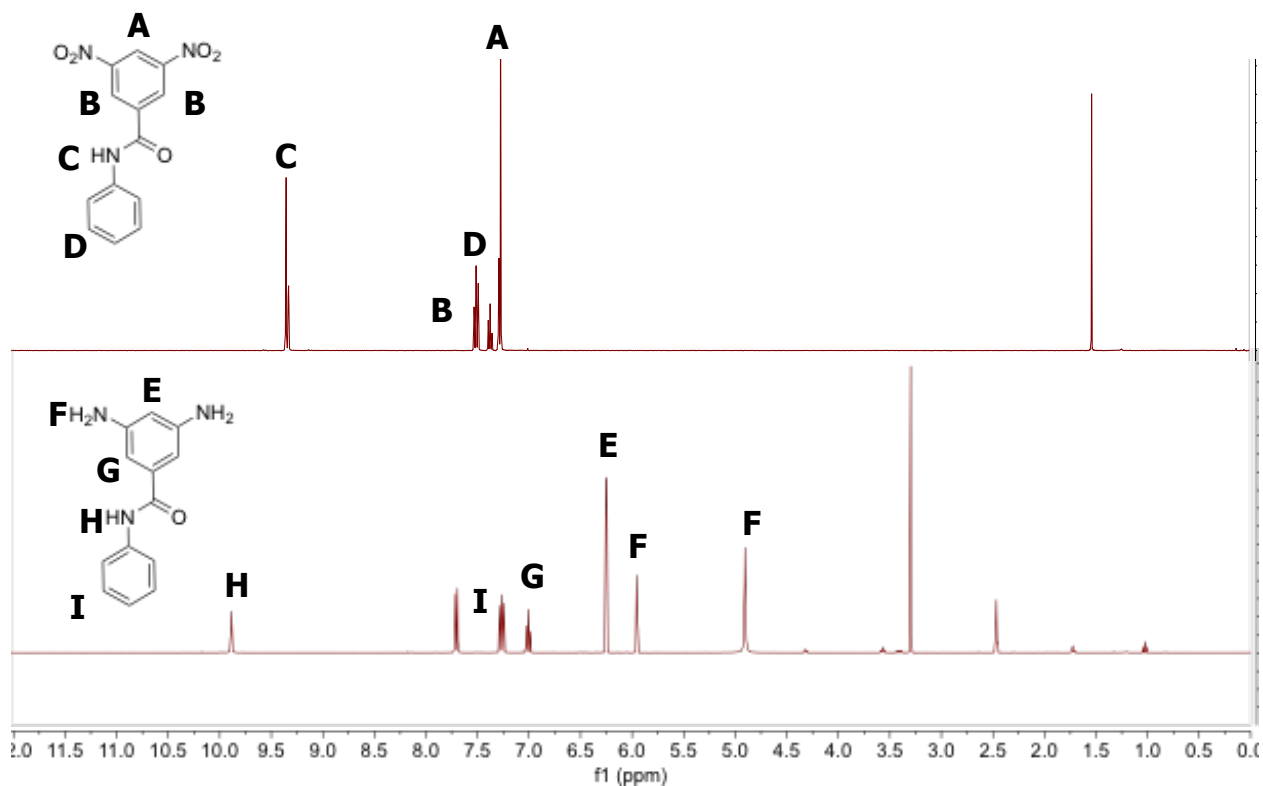


Figure 8.12. ^1H NMR spectra of 3,5-dinitro(phenyl benzamide) (top) and 3,5-diamino(phenyl benzamide) (bottom)

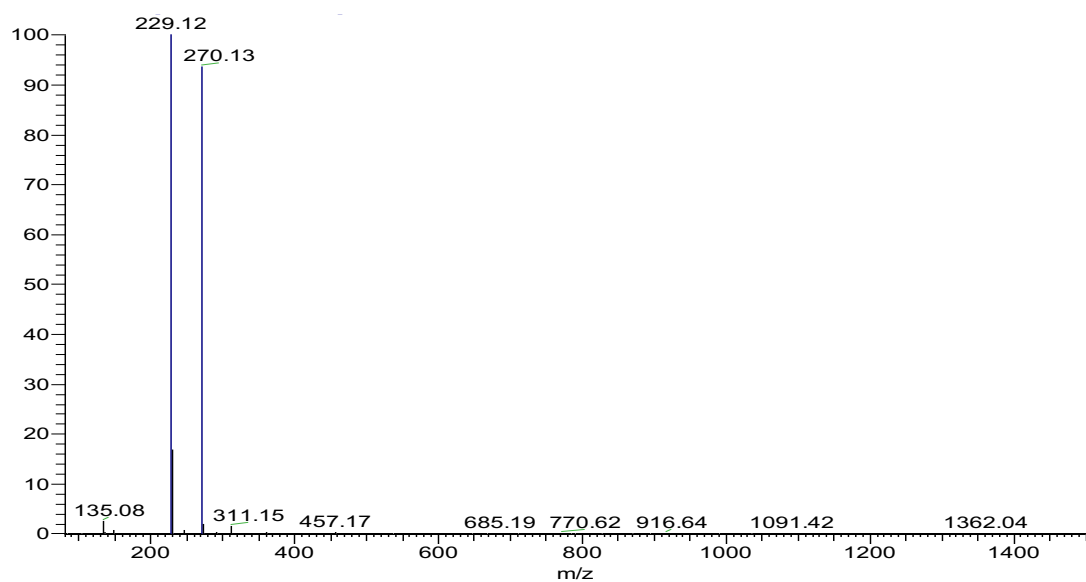


Figure 8.13. MS spectrum of 3,5-diamino(phenyl benzoate) in positive mode.

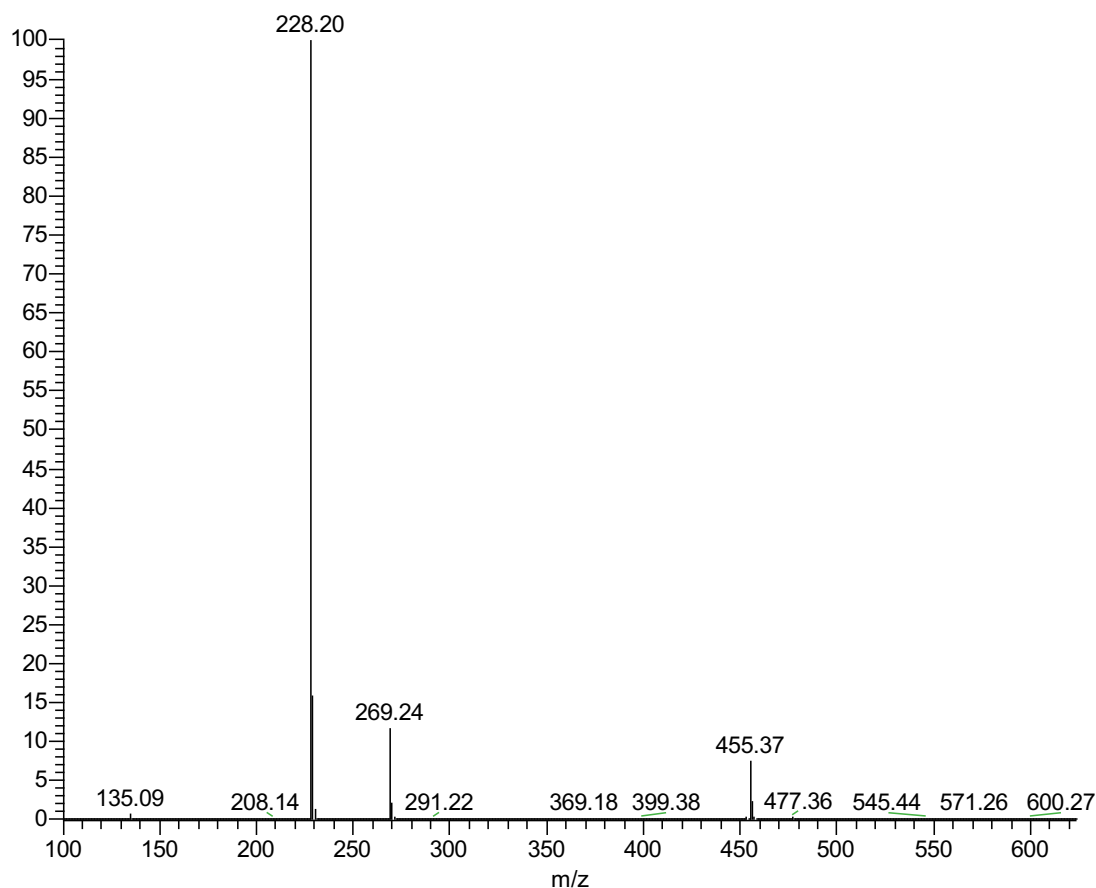
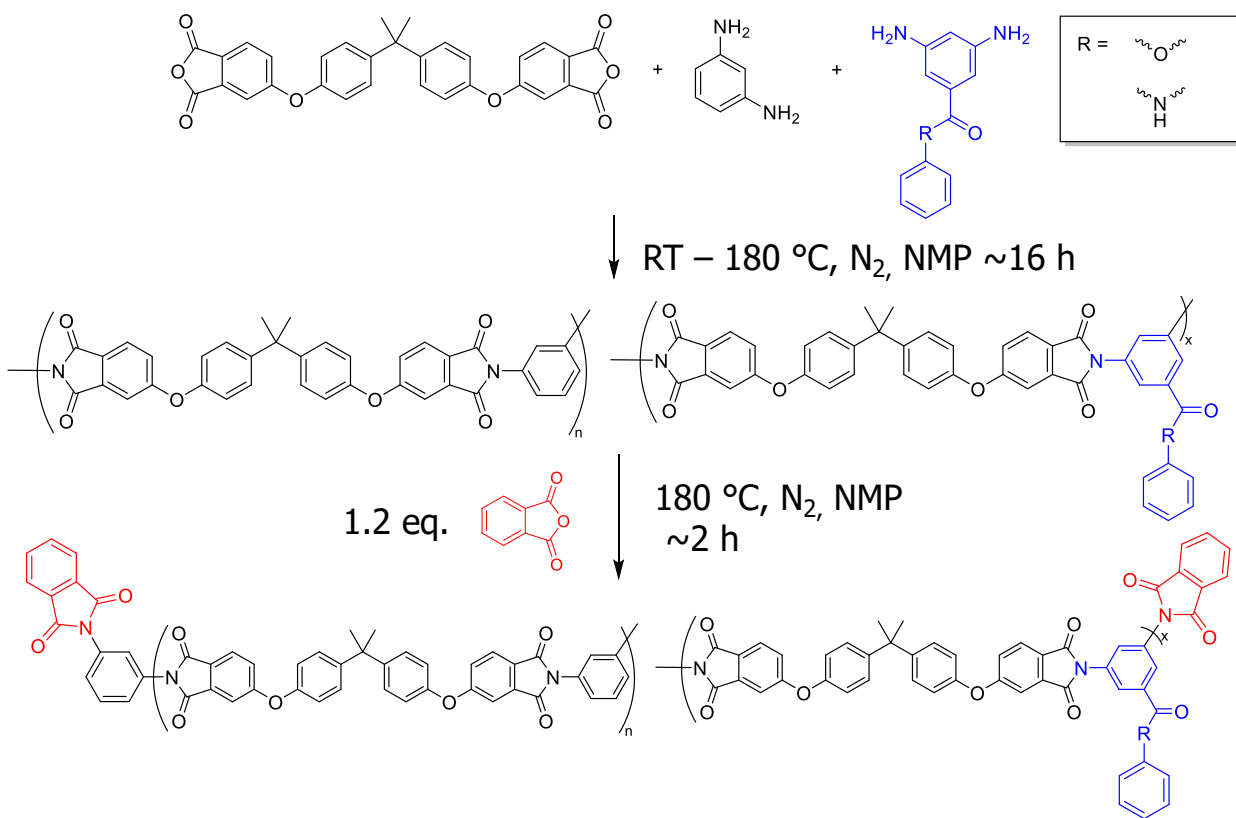


Figure 8.14. MS spectrum of 3,5-diamino(phenyl benzamide) in positive mode.

Typical PEI synthesis, as previously described and as seen in **Figure 8.6**, produced a series of PEIs with phenyl pendant groups with both ester and amide linkages off of the backbone. Systematic composition targets enabled direct comparison of phenyl pendant PEIs with the different linkages. An excess of charged diamines targeted molecular weight, while also facilitating amine end groups. PA end-capped the PEIs. Thermal imidization by heating the resulting solution in a metal bath at 380 °C ensured complete backbone imidization. All samples dissolved in NMP after imidization. Thus, no crosslinking is suspected for PEIs with phenyl ester or phenyl amide pendant groups. Precipitation in MeOH afforded off-white, light brown polymer. ^1H NMR spectroscopy confirmed the PEI compositions, as seen in **Figure 8.13** and **Figure 8.14**.



Scheme 8.6. Synthesis of phenyl ester/amide PEIs.

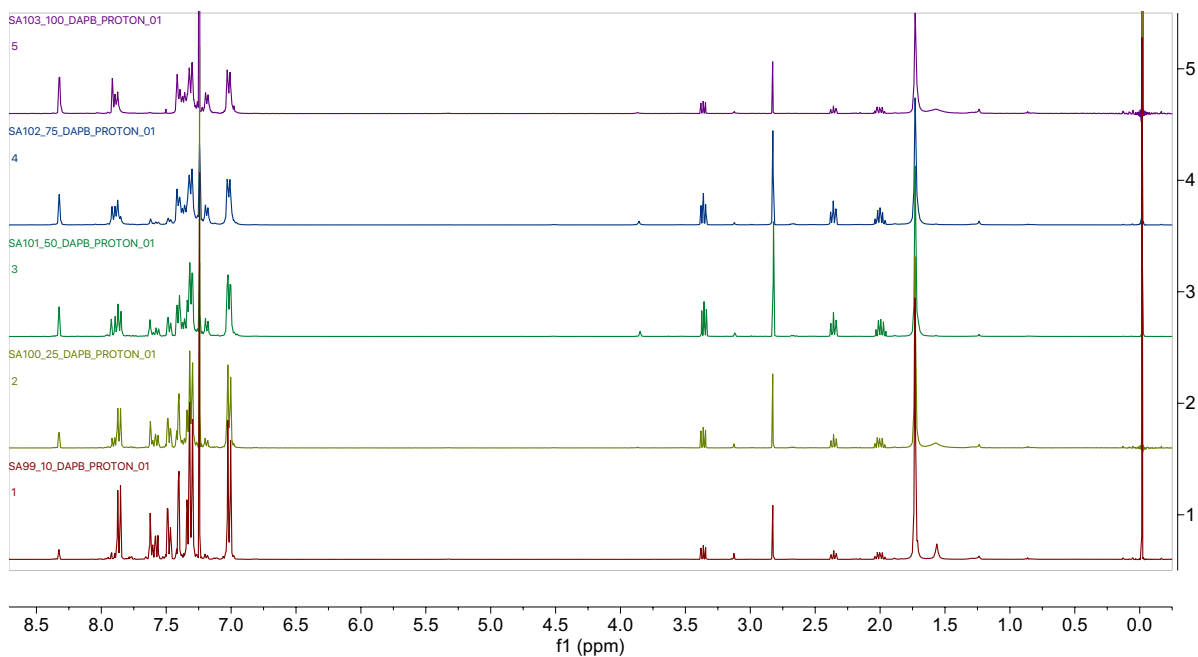


Figure 8.13. ^1H NMR spectra of DAPB-PEI copolymers

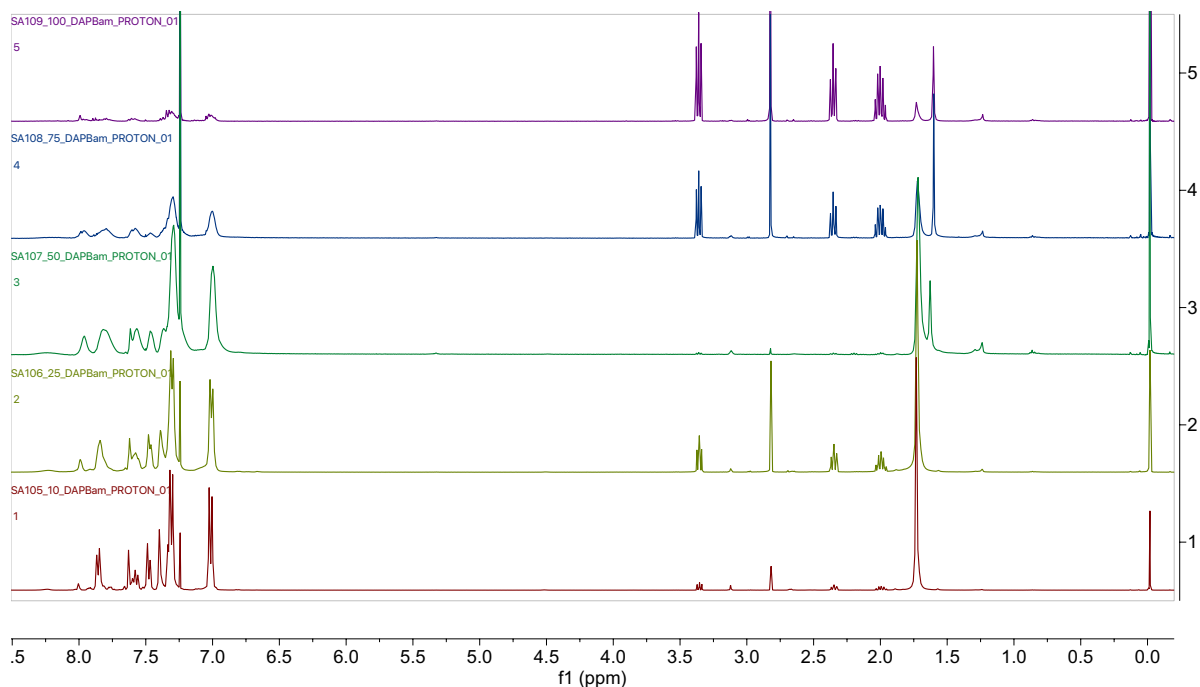


Figure 8.14. ^1H NMR spectra of DAPBam-PEI copolymers

As seen in **Figure 8.15**, phenyl ester pendant groups decrease the $T_{d,5\%}$ similarly to the methyl ester and amide pendant groups. Increasing the mol % of DAPB lowered the $T_{d,5\%}$ systematically. Incorporating either the ester or amide pendant off the backbone imparts a thermally unstable linkage compared to the typical aromatic ether and imide linkages in PEIs. Both DAPB and DAPBam incorporation increased the T_g s to 242-245 $^{\circ}\text{C}$, as seen in **Figure 8.15** and **Figure 8.16**. The T_g systematically increased with increasing mol % of either phenyl pendant group. As seen in **Figure 8.17**, the T_g trend followed the Fox equation fit well, suggesting a random distribution of repeat units. These PEIs with pendant aromatic groups are interesting candidates to probe the rheological behavior and viscoelastic properties with similar pendant groups but slightly different linkages.

All thermal properties are summarized in **Table 8.1**. In general, all pendant groups decreased the $T_{d,5\%}$ similarly but increased the T_g . The methyl ester pendant functionality

increased the T_g the least, while the amide, and both phenyl groups (ester and amide) increased the T_g by up to 30 °C.

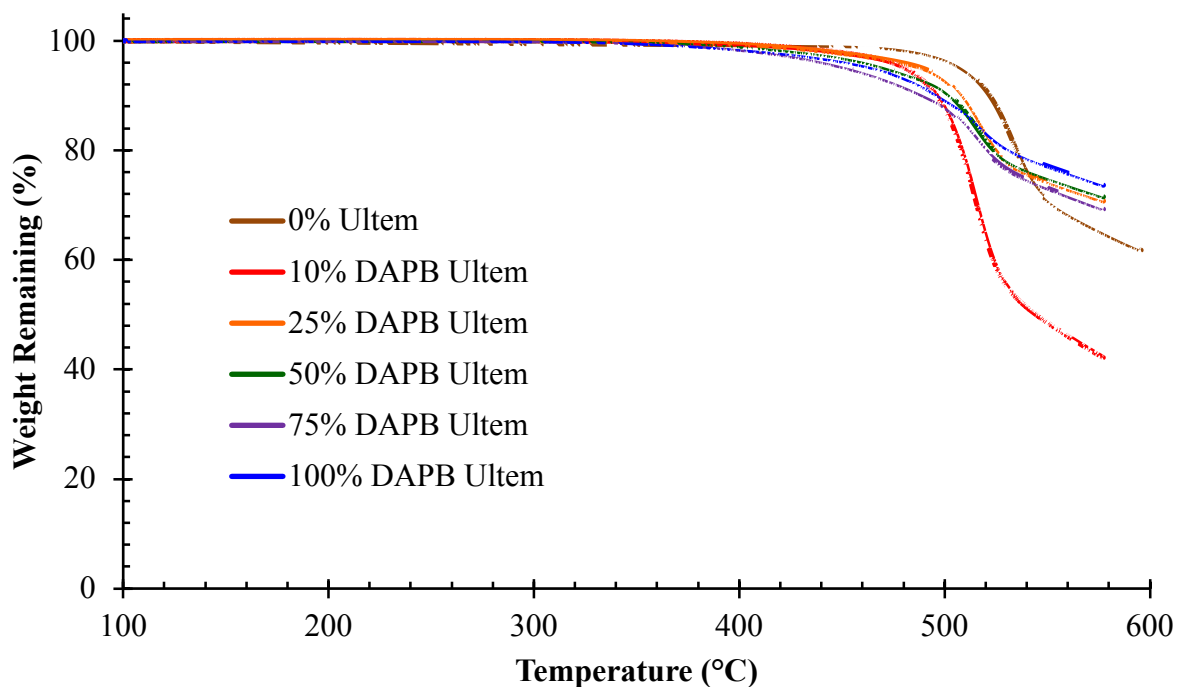


Figure 8.15. Thermogravimetric analysis (TGA) of DAPB-PEIs.

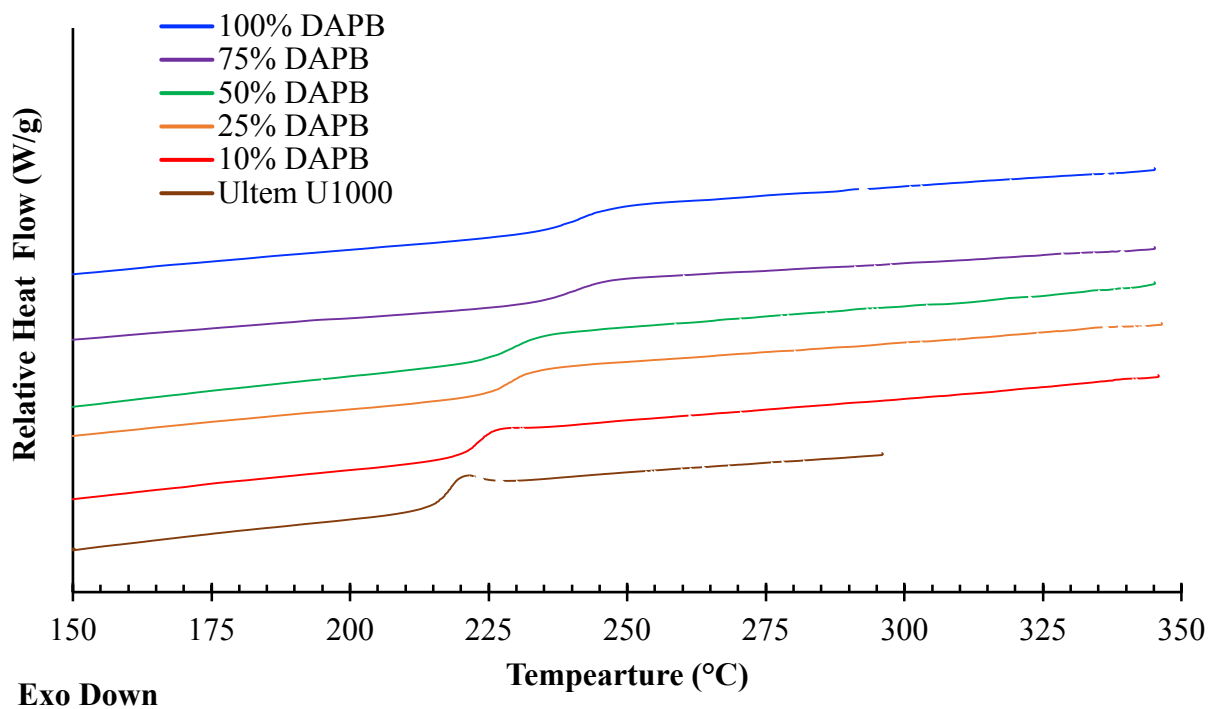


Figure 8.16. Differential scanning calorimetry (DSC) of DAPB-PEIs.

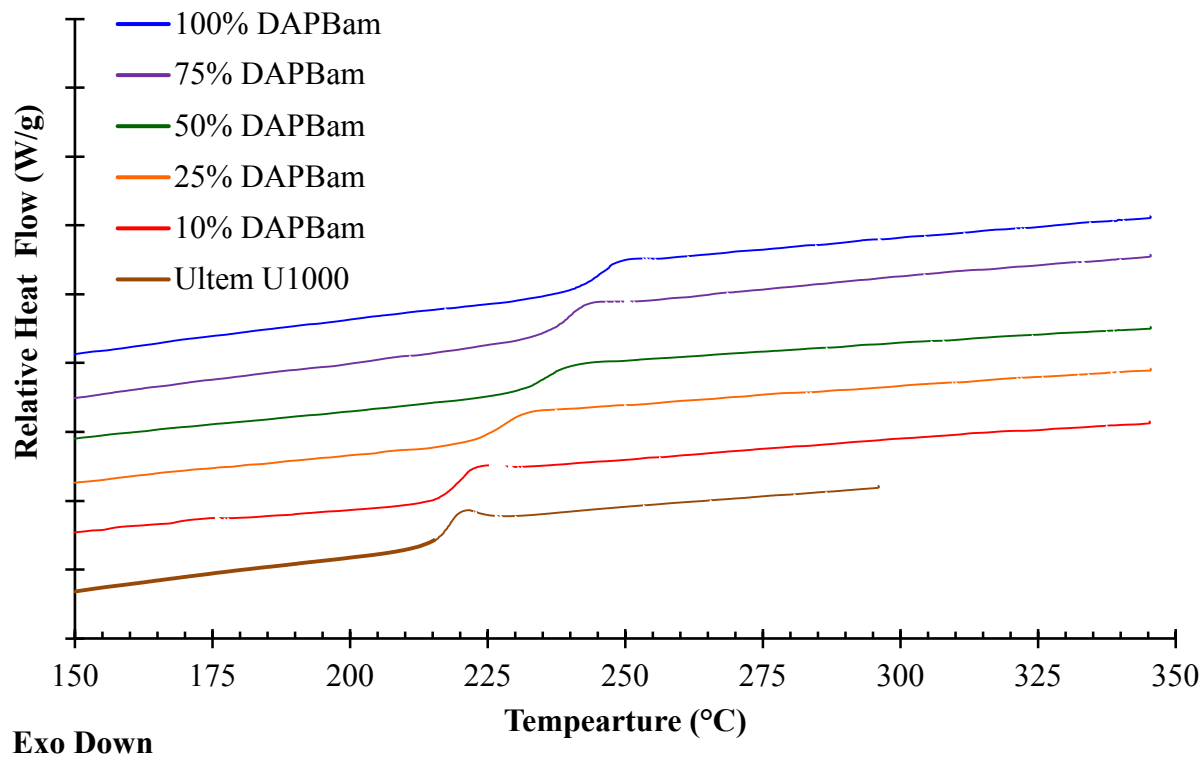


Figure 8.17. Differential scanning calorimetry (DSC) of DAPBam-PEIs.

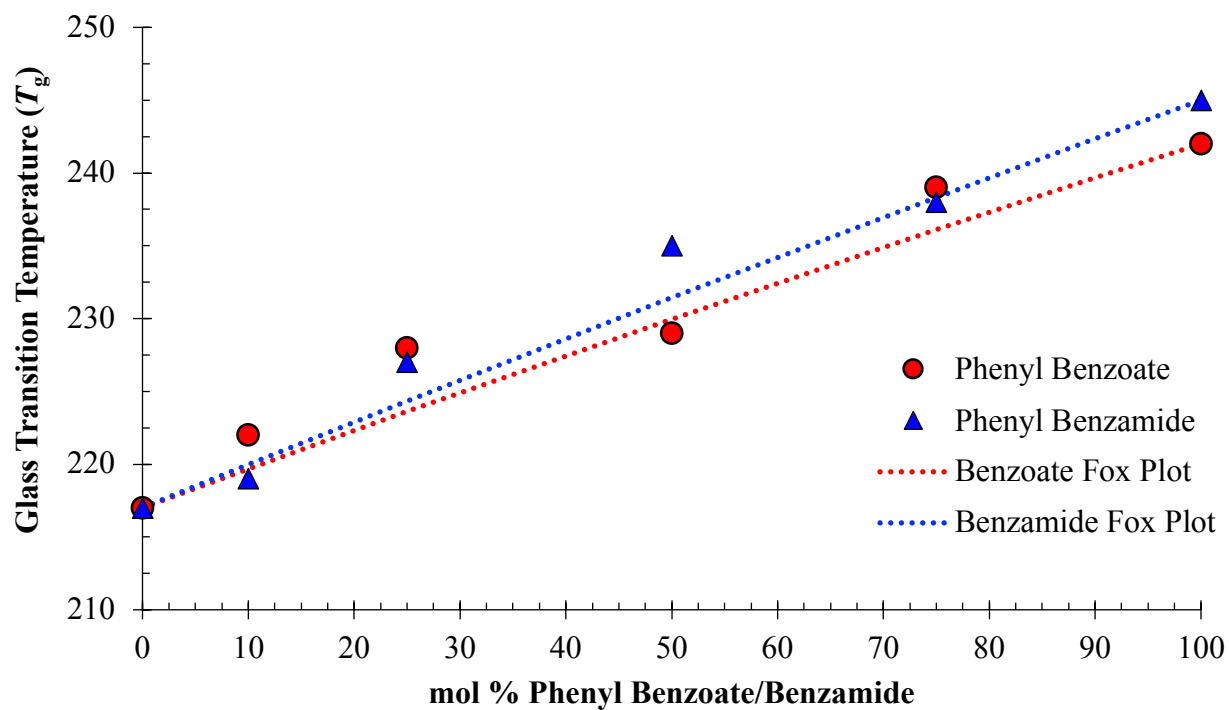


Figure 8.18. Glass transition temperature (T_g) for various mol % of DAPB- and DAPBam-based PEIs. Fox fit (dotted lines) confirms increase in T_g as expected.

Table 8.1: Summary of thermal properties of Pendant-PEIs

Comonomer	Mol % Comonomer	$T_{d, 5\%}$ (°C)	T_g (°C)
	Feed	TGA ^a	DSC ^b
	Ultem	517	217
MDAB	10	477	222
	25	475	224
	50	462	226
	100	463	228
DABAm	10	542	222
	25	528	231
	50	ND	237
	75	485	240
DAPB	10	481	222
	25	489	228
	50	472	229
	75	453	239
	100	466	242
DAPBam	10	ND	219
	25	ND	227
	50	ND	235
	75	ND	238
	100	ND	245

^aTGA: 10 °C min⁻¹ heat, N₂^bDSC: heat/cool/heat, second heat; N₂, 10 °C min⁻¹. T_g reported as inflection point of step transition.

ND: not determined

8.5 Conclusions

Incorporation of pendant functionality into PEIs is commonly used to tune bulk polymer properties, usually solubility. Pendant groups hinder chain packing and push chains apart, making them more likely to dissolve in common organic solvents used in processing. The chemical structure and size of the pendant groups determines the impact on thermal properties. Aliphatic and carbonyl based pendant groups typically decrease the thermal stability, while ether linkages and aromatic pendant groups typically maintain desired thermal stability. Similarly, the T_g is influenced by the same factors. Limited understanding exists comparing pendant functionality of PEIs with rheological behavior and viscoelastic properties. First, finding thermally melt stable PEIs which maintain the desired thermal stability and T_g is required.

Amide, methyl ester, phenyl ester, and phenyl amide pendant groups on PEIs enabled a systematic study on the chemical structures' and linkage types' impact on thermal properties. All pendant groups decreased the $T_{d,5\%}$ between 10-50 °C. All pendant groups increased the T_g . The methyl ester increased the T_g by 5-10 °C, while the amide and bulkier phenyl pendant groups increased the T_g by 5-30 °C. Neither the amide or methyl ester possessed stability in the melt, thus prohibiting melt rheological and viscoelastic characterization. These compositions require chemical imidization and solution casting to further understand their structure-property relationships. The phenyl ester/amide pendant groups should be stable in the melt, as aramids and polyarylates are commonly used and processed at high temperatures. Further analysis including melt rheology and viscoelastic property testing is required to understand the influence of these pendant groups and linkages off the backbone on processability.

8.6 Acknowledgements

The authors would like to thank Lindsey Anderson in Prof. Robert B. Moore's group for help with FTIR analysis, Dr. Charles Carfagna for help with TGA analysis, and Amber Miller for help with SEC. The authors would like to thank Dr. Maruti Hegde and Dr. Justin Sirrine for insightful discussions.

8.7 References

1. ULTEM(TM) RESIN 1000. SABIC Innovative Plastics: <https://www.sabic.com/en/products/specialties/ultem-resins/ultem-resin>, 2018.
2. Chuang, K. C. G., J. E.; Draper, R. D.; Shin, E.-S. E.; Patterson, C.; Santelle, T. D. In *Additive Manufacturing and Characterization of ULTEM Polymers and Composites*, The Composites and Advanced Materials Expo., Dallas, TX, Dallas, TX, 2015.
3. Floryan, D. E.; Serfaty, I. W., Polyetherimide - More Information on a New High-Performance Resin. *Mod Plast* **1982**, 59 (6), 146-&.
4. Johnson, R. O.; Burlhis, H. S., Polyetherimide - a New High-Performance Thermoplastic Resin. *J Polym Sci Pol Sym* **1983**, (70), 129-143.
5. Thiruvasagam, P.; Venkatesan, D., Synthesis and Characterization of Processable Aromatic Polyimides. *High Perform. Polym.* **2010**, 22 (6), 682-693.
6. Hegde, M.; Meenakshisundaram, V.; Chartrain, N.; Sekhar, S.; Tafti, D.; Williams, C. B.; Long, T. E., 3D Printing All-Aromatic Polyimides using Mask-Projection Stereolithography: Processing the Nonprocessable. *Adv. Mater.* **2017**, 29 (31).
7. Herzberger, J.; Meenakshisundaram, V.; Williams, C. B.; Long, T. E., 3D Printing All-Aromatic Polyimides Using Stereolithographic 3D Printing of Polyamic Acid Salts. *Acs Macro Lett* **2018**, 7 (4), 493-497.
8. Rau, D. A.; Herzberger, J.; Long, T. E.; Williams, C. B., Ultraviolet-Assisted Direct Ink Write to Additively Manufacture All-Aromatic Polyimides. *ACS Appl Mater Interfaces* **2018**.
9. Yang, K.; Grant, J. C.; Lamey, P.; Joshi-Imre, A.; Lund, B. R.; Smaldone, R. A.; Voit, W., Diels-Alder Reversible Thermoset 3D Printing: Isotropic Thermoset Polymers via Fused Filament Fabrication. *Adv. Funct. Mater.* **2017**, 27 (24).
10. Ding, M., Isomeric polyimides. *Prog. Polym. Sci.* **2007**, 32 (6), 623-668.
11. Dingemans, T. J.; Mendes, E.; Hinkley, J. J.; Weiser, E. S.; StClair, T. L., Poly(ether imide)s from Diamines with Para-, Meta-, and Ortho-Arylene Substitutions: Synthesis, Characterization, and Liquid Crystalline Properties. *Macromolecules* **2008**, 41 (7), 2474-2483.
12. Dennis, J. M.; Mondschein, R. J.; Hegde, M.; Odle, R.; Long, T. E., Synthesis and Characterization of Long-chain Branched Poly(ether imide)s. *In Press* **2018**.
13. Markoski, L. J.; Thompson, J. L.; Moore, J. S., Synthesis and characterization of linear-dendritic aromatic etherimide copolymers: Tuning molecular architecture to optimize properties and processability. *Macromolecules* **2000**, 33 (15), 5315-5317.
14. Moore, J. S.; Thompson, D. S.; Markoski, L. J. Branched and hyperbranched polyetherimides. 2001.
15. Susa, A.; Bose, R. K.; Grande, A. M.; van der Zwaag, S.; Garcia, S. J., Effect of the Dianhydride/Branched Diamine Ratio on the Architecture and Room Temperature Healing Behavior of Polyetherimides. *ACS Appl Mater Interfaces* **2016**, 8 (49), 34068-34079.
16. Yamanaka, K.; Jikei, M.; Kakimoto, M., Preparation and properties of hyperbranched aromatic polyimides via polyamic acid methyl ester precursors. *Macromolecules* **2000**, 33 (19), 6937-6944.

17. Yamanaka, K.; Jikei, M.; Kakimoto, M., Syntheses and Properties Polyimides with of Hyperbranched Aromatic Various End-groups. *J. Photopolym. Sci. Technol.* **2001**, *14* (1), 11-16.
18. Yi, L.; Huang, W.; Yan, D., Polyimides with side groups: Synthesis and effects of side groups on their properties. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55* (4), 533-559.
19. Koros, W. J. K., A. M. Thermally Crosslinked Polymeric Compositions and methods of making the same. 8664335 B2, 2014.
20. Kratochvil, A. M.; Koros, W. J., Decarboxylation-Induced Cross-Linking of a Polyimide for Enhanced CO₂ Plasticization Resistance. *Macromolecules* **2008**, *41* (21), 7920-7927.
21. Broadbelt, L. J.; Chu, A.; Klein, M. T., Thermal-Stability and Degradation of Aromatic Polyamides .2. Structure-Reactivity Relationships in the Pyrolysis and Hydrolysis of Benzamides. *Polym. Degrad. Stab.* **1994**, *45* (1), 57-70.
22. Broadbelt, L. J.; Dziennik, S.; Klein, M. T., Thermal-Stability and Degradation of Aromatic Polyamides .1. Pyrolysis and Hydrolysis Pathways, Kinetics and Mechanisms of N-Phenylbenzamide. *Polym. Degrad. Stab.* **1994**, *44* (2), 137-146.
23. Chartoff, R. P.; Maxwell, B., Viscoelastic Properties of Branched Polyethylene Melts. *Journal of Polymer Science Part a-2-Polymer Physics* **1970**, *8* (3), 455-&.
24. Hegde, M.; Lafont, U.; Norder, B.; Samulski, E. T.; Rubinstein, M.; Dingemans, T. J., SWCNT induced crystallization in amorphous and semi-crystalline poly(etherimide)s: Morphology and thermo-mechanical properties. *Polymer* **2014**, *55* (16), 3746-3757.
25. Carothers, W. H., Polymerization. *Chem. Rev.* **1931**, *8* (3), 353-426.

Chapter 9: Polymer structure-property requirements for stereolithographic 3D printing of soft tissue engineering scaffolds

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9.1 Abstract

This review highlights the synthesis, properties, and advanced applications of synthetic and natural polymers 3D printed using stereolithography for soft tissue engineering applications. Soft tissue scaffolds are of great interest due to the number of musculoskeletal, cardiovascular, and connective tissue injuries and replacements humans face each year. Accurately replacing or repairing these tissues is challenging due to the variation in size, shape, and strength of different types of soft tissue. With advancing processing techniques such as stereolithography, control of scaffold resolution down to the μm scale is achievable along with the ability to customize each fabricated scaffold to match the targeted replacement tissue. Matching the advanced manufacturing technique to polymer properties as well as maintaining the proper chemical, biological, and mechanical properties for tissue replacement is extremely challenging. This review discusses the design of polymers with tailored structure, architecture, and functionality for

stereolithography, while maintaining chemical, biological, and mechanical properties to mimic a broad range of soft tissue types.

9.2 Introduction

Tissue engineering is a multidisciplinary field that encompasses and integrates chemistry, biology, and engineering. The goal of tissue engineering is to create “functional substitutes for damaged tissue.”¹ With the increased demand for surgeries due to athletic activity, disease, and ageing, the need for regenerative medicine is ever increasing. Tens of billions of dollars per year are spent on approximately 35 million sustained musculoskeletal injuries.²⁻⁴ Macromolecules, both synthetic and natural, are of great interest as tissue engineering scaffolds due to their wide range of properties⁵ and tunability to match the needs of their specific replacement target.⁶

Controlling the porosity and architecture of engineered scaffolds is crucial in allowing suitable biological function in addition to mechanical integrity and mass transport (diffusion and permeability).⁷ Various methods to construct tissue engineering scaffolds include molding,⁸⁻⁹ solvent casting and particulate leaching,¹⁰ gas foaming,¹¹ and electrospinning.¹² Each of these fabrication methods has limitations when trying to mimic the biological function of natural tissue, due to the difficulty to finely control the scaffold architecture, dimensions, and porosity. Three-dimensional (3D) printing (additive manufacturing or rapid prototyping) is a fabrication technique that allows for precise control over the architecture and dimensions of constructed scaffolds.¹³⁻¹⁵ Ability to control feature size at the micro/nanoscale is achievable and is dependent on the 3D printing technique. Stereolithography (SLA) (vat photopolymerization (VPP)) is a common 3D

printing process that allows for greater control of the tissue scaffold's dimensions and features compared to other additive manufacturing techniques. Ability to precisely control architecture and features of the resulting scaffold offers great benefit to regenerative medicine, whether to construct repeatable identical scaffolds or to fabricate patient specific templates. SLA is used to construct a vast array of scaffolds using synthetic macromolecules, such as polyesters and polyethers, and natural macromolecules, such as polysaccharides and polypeptides.

Combining the polymer properties needed for SLA while ensuring the resulting scaffold maintains biological function and suitable mechanical strength is difficult. This challenge makes identifying polymers with optimal chemical, biological, and mechanical properties crucial. Commercial polymers offer characteristics that make them viable for select applications, but synthesizing novel materials greatly expands the ability to tune desired properties. New materials are needed that better replicate natural soft tissue properties.¹⁶⁻¹⁷ First, understanding polymer property requirements for SLA processing and how polymer structure and architecture influence each property is required. Properties such as viscosity, functionality, and cure times are crucial in determining if a polymer is an appropriate candidate for SLA processing. Secondly, understanding the properties of these printed materials, both mechanical and biological, provides feedback to tailor these materials to provide promising results in the future, as visualized in **Figure 9.1**. The scaffold ideally replicates the replaced tissue's mechanical properties, such as tensile strength and strain, flex strength and strain, elasticity, compression strength, and percent swelling.¹⁸ Lastly, desired biological properties include non-cytotoxicity, biodegradability, non-toxic degradation products, and the ability to adhere, proliferate, and

differentiate cells.¹⁹ As seen in **Figure 9.2**, a suitable scaffold is produced when the chemical, biological, and mechanical properties are balanced and best replicate the target replacement.

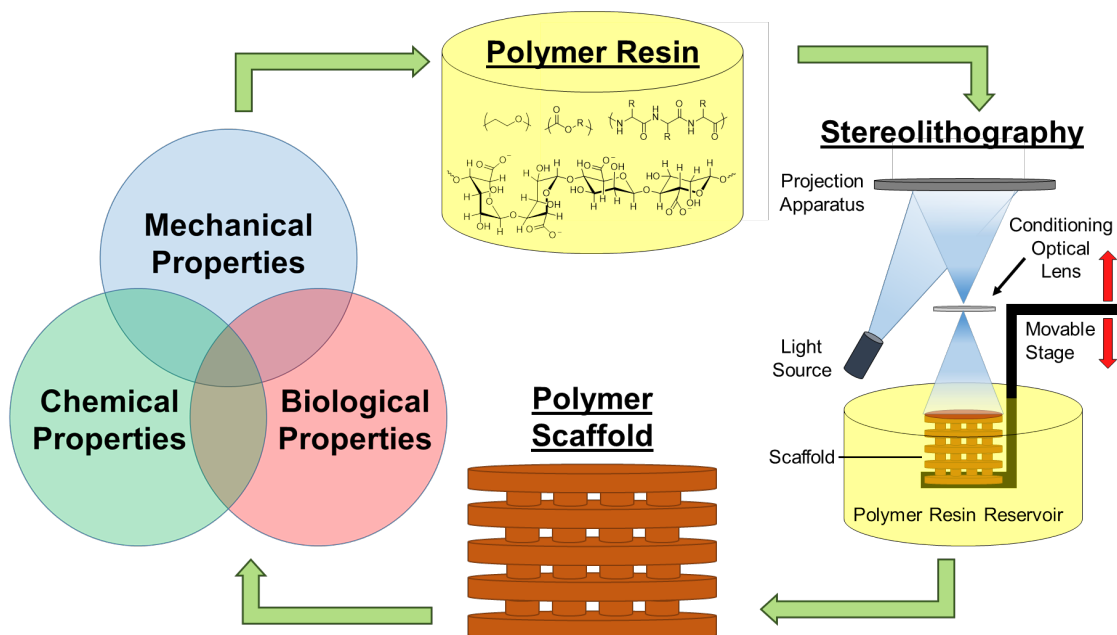


Figure 9.1: SLA fabricated polymer scaffold cyclic approach to discovery

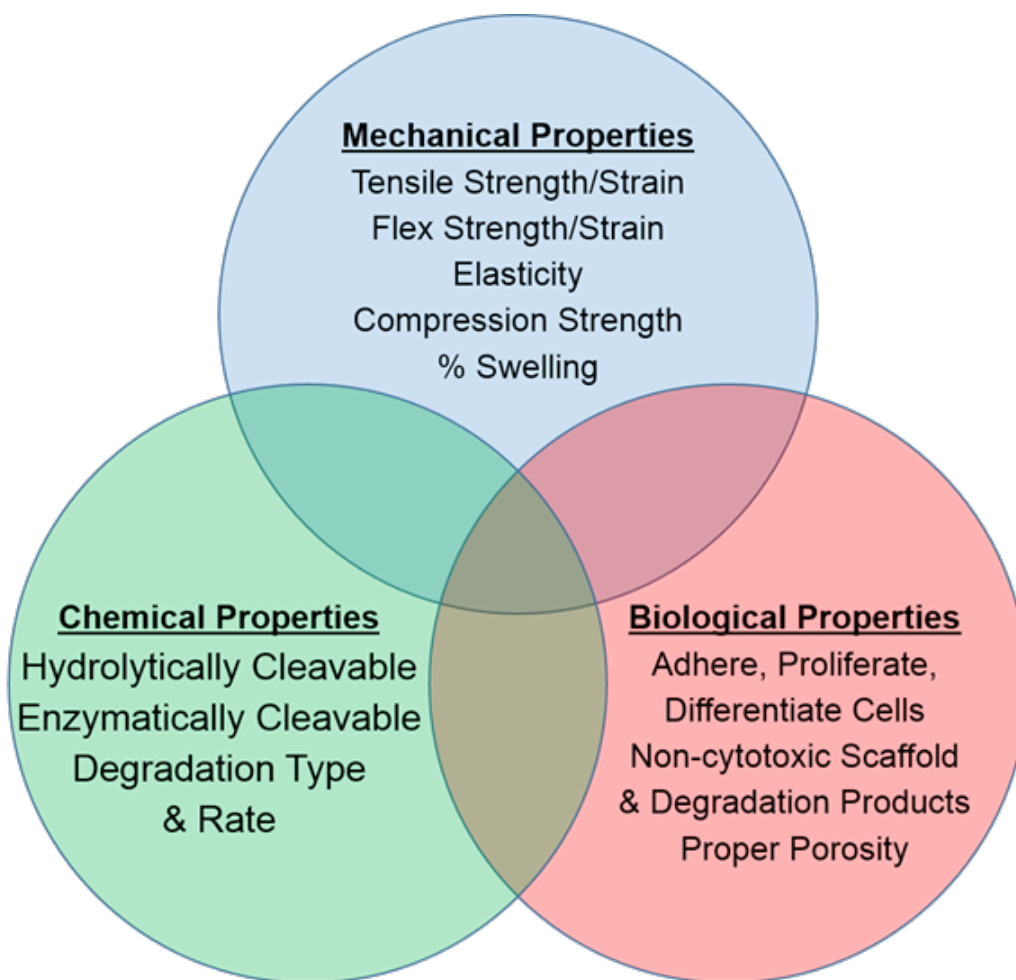


Figure 9.2: Mechanical, Chemical, and Biological Properties required for Biodegradable Tissue Engineering Scaffolds

Balancing the required properties is challenging when targeting soft tissue scaffolds. Mechanical and biological properties greatly differ between types of tissue such as tendon/ligament, skin, cardiovascular, cartilage, and individual organs. Factors such as patient's age, sex, race, etc. also affect the size, strength, and durability of similar tissue type from one person to another. The ease and ability to tune synthetic polymers to match the desired properties is crucial because of the variability between different individuals' tissue and the variability between tissue types. Different types of synthetic and natural polymers also exhibit inherently different properties. In choosing the appropriate class of

polymer for a specific application of SLA, the specific tissue-of-interest and end-goal must be key considerations. This review discusses the polymeric properties necessary to utilize SLA for soft tissue scaffolds, approaches to synthesize polymers with varying architecture targeting these properties, and the structure-property relationships of various polymers recently 3D printed as tissue scaffolds.

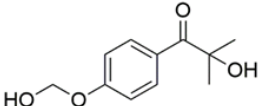
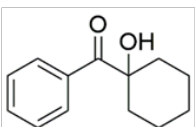
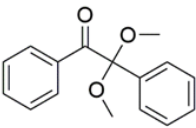
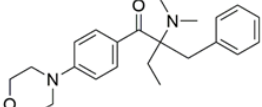
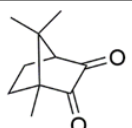
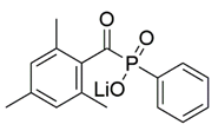
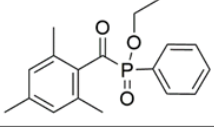
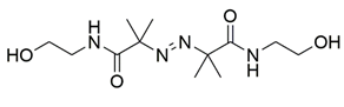
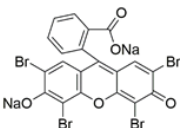
9.3 Key Scaffold Properties for Soft Tissue Engineering

9.3.1 Cytotoxicity

In order to potentially replace or repair living healthy tissues, synthetic or natural scaffolds must provide biomimetic binding sites required for cellular adhesion and proliferation. When designing tissue engineering scaffolds, cell placement and distribution in the scaffold is of key importance to allow for proper function and differentiation.²⁰ This function is related both to cell-extracellular matrix (ECM) interaction, as well as the impact of nutrient diffusion in the absence of an active vascular system. Scaffolds must not contain any cytotoxic elements that lead to cell necrosis or apoptosis. Common sources of cytotoxicity include the macromolecules constructing the scaffold, the initiator used in photopolymerization, organic solvent residue from polymer synthesis, and the products of polymer degradation. Photoinitiators garner the most concern, but toxicity depends on the cell type.²¹ The toxicity profiles of three common photoinitiators' (Irgacure 2959,^{15, 20-54} Irgacure 184,^{21, 25, 55} and Irgacure 651^{21, 25, 35, 50}) were determined using six cell populations: human fetal osteoblasts (hFOB), bovine chondrocytes (BC), corneal epithelial cells (SIRC), human mesenchymal stem cells (hMSC), goat mesenchymal stem cells (gMSC), and human embryonic germ cells (LVEC). Irgacure 2959 had the least toxicity of the three initiators tested, but had varying degrees of cytotoxicity depending on the cell lines.²¹ BC,

hMSCs, and gMSCs were less affected than LVEC, hFOB, and SIRC. Irgacure 2959 was found to be the most tolerant, which correlated well to the rate of proliferation studies, confirming it as the best candidate for use as a photoinitiator. Though a cell death mechanism was not determined, a correlation between proliferation and cell death was hypothesized.²¹ Increased amounts of free radicals damaging cells is thought to lead to higher cytotoxicity.⁵⁶ Alternatively, camphorquinone^{17, 21, 25, 50, 57-64} exposed to light induced apoptosis in submandibular acinar cells.⁵⁸ Another photoinitiator studied that showed promising cytotoxicity is lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP).^{23, 25, 40, 45, 50, 65-67} LAP offers advantages over Irgacure 2959 due to its increased water solubility, faster polymerization rates at 365 nm light, and ability to initiate with visible light due absorbance >400 nm.²⁵ Another initiator with visible light absorbance and decreased cytotoxicity compared to UV initiators such as Irgacures is eosin Y disodium salt.^{17, 23, 25, 40, 50, 68-69} Other common photoinitiators include Irgacure 369,^{20, 39} Lucirin TPO-L,^{45, 48-50, 57, 60, 62, 70-76} and VA-086.^{22-23, 31, 40, 50, 77} Optimizing the photoinitiator used in SLA is key in advancing scaffolds to exhibit greater biocompatibility, detailed in **Table 9.1**.

Table 9.1: Common photoinitiators used in SLA with their corresponding wavelength peak and properties to consider

Photoinitiator	Wavelength Peak	Properties	Reference
Irgacure 2959 	257-276 nm	- One of most common initiators - Least toxic of Irgacures	[15, 20-54]
Irgacure 184 	246, 280, 333 nm	More cytotoxic than Irgacure 2959	[21, 25, 55]
Irgacure 651 DMPA 	250, 340 nm	More cytotoxic than Irgacure 2959	[21, 25, 35, 50]
Irgacure 369 	233, 324 nm	More cytotoxic than Irgacure 2959	[20, 39]
Camphorquinone 	285, 400-500 nm	Can absorb blue light	[17, 21, 25, 50, 57-64]
LAP 	375 nm	- Relatively high water solubility - Initiate in visible light region	[23, 25, 40, 45, 50, 65-67]
Lucirin TPO-L 	380 nm	- Low yellowing - Water miscible	[45, 48-50, 57, 60, 62, 70-76]
VA-086 	385 nm	Narrow activation range	[22, 23, 31, 40, 50, 77]
eosin Y Disodium salt 	514 nm	- Usable with green light - Less toxic than Irgacure 2959	[17, 23, 25, 40, 50, 68, 69]

Previous literature explores the effects of scaffold porosity and architecture on cell viability and the cells ability to adhere, proliferate and differentiate.^{7, 62, 78} Nutrient

diffusion through a scaffold is important for proper cell growth. A lack of nutrient diffusion, or inability of the cells to migrate, hinders cell proliferation, thereby, reducing a scaffold's potential to accelerate tissue repair and regrowth efficiently. Gyroid shaped pore networks exhibit uniform interconnectivity and evenly distributed pore sizes, showing promise for construct design.^{39, 49, 79} Recently, growing interest in designing polymeric surfaces for regenerative medicine has prompted controlling and studying scaffold surface morphology. Surface engineering plays a significant role in a material's ability to support adhesion, proliferation and differentiation of cells, all of which influence tissue function.⁸⁰ All of these factors must be taken into consideration when designing new macromolecules and scaffolds, factoring in the cell-extracellular matrix (ECM) interaction, as well as nutrient diffusion implications.⁸¹

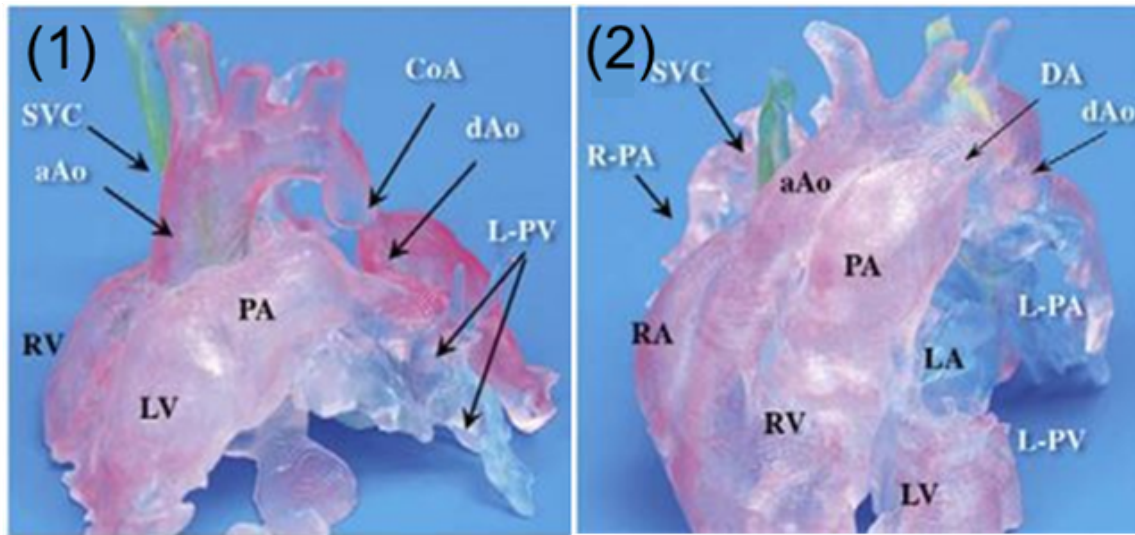


Figure 9.3: SLA printed biomodel of a 2-month old heart with isolated coarctation of aorta. Surgeons practiced surgery on and stitching of printed heart. Elastomeric material represented simulation conditions to natural tissue. Adapted from Shiraishi and Yagihara *et al.*⁸²

9.3.2 Scaffold Degradation

Important chemical properties for designing a new tissue engineering scaffold include degradation mechanism and degradation rate. Tissue engineering scaffolds are generally separated into two classifications, permanent and biodegradable. The two types of scaffolds hold different purposes and require different chemical and biological properties. Permanent scaffolds must not degrade and need to maintain and replicate the physical properties associated with the soft tissue it is replacing. Implantable permanent scaffolds are sought for use in extreme circumstances where tissue is damaged beyond bodily repair. Permanent scaffolds are more ideal for *in vitro/ex vivo* applications such as organ mimics for simulative operation,⁸² as seen in **Figure 9.3**, or microfluidic devices that mimic the functionality of an organ,^{67, 83-84} as seen in **Figure 9.4**. Recently, liver inspired designs for detoxification applications were fabricated using SLA.⁸⁵ Poly(ethylene glycol) diacrylate (PEGDA) was used as the base polymer while polydiacetylene (PDA) nanoparticles were dispersed in the matrix. The PDA nanoparticles allowed for toxin uptake while the liver lobule microstructure ensured even particle dispersion. Various shapes were also tested to investigate architecture on uptake of toxin, while the 3D printed constructs exhibited increased uptake as seen in **Figure 9.5**.

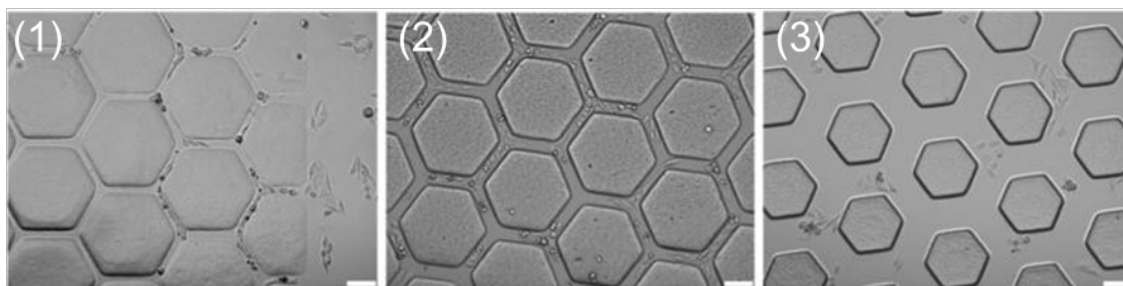


Figure 9.4: Poly(ethylene glycol) microstructures with varying channel sizes to study cancer cell flow. (1) has 25 μm wide channels, (2) has 45 μm wide channels and (3) has 120 μm wide channels Adapted from Huang and Chen *et al.*⁶⁷

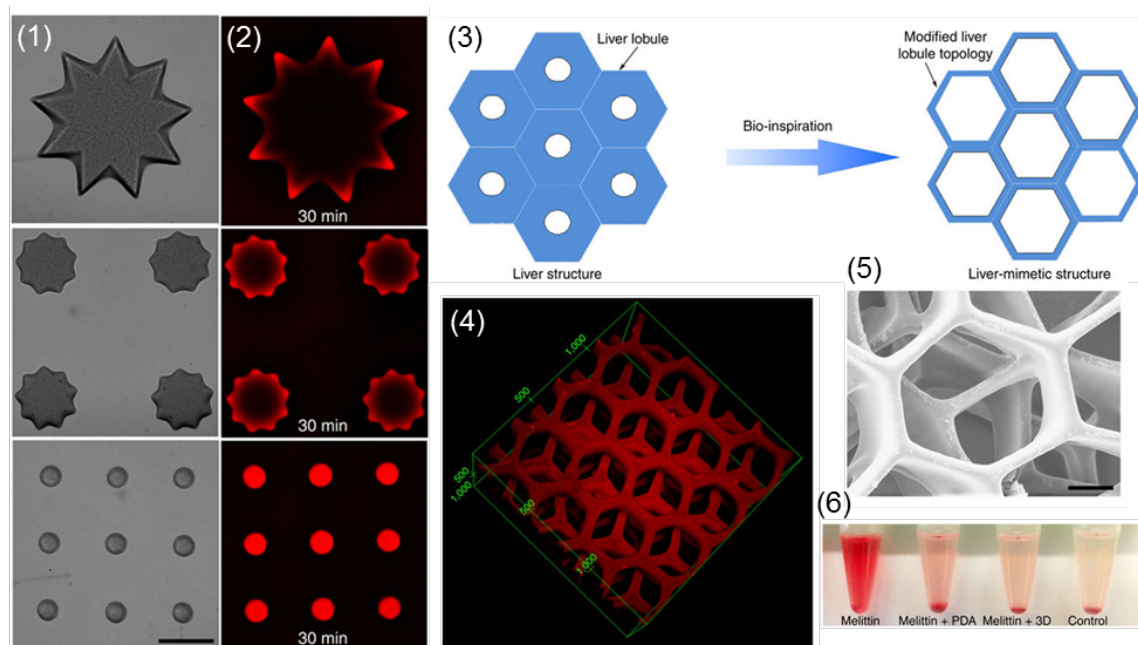


Figure 9.5: Column (1) shows resolution control of 3D printed hydrogel nanocomposites; scale bar 200 μm . Column (2) uses fluorescent imaging to determine uptake of toxins and efficiency of printed architecture. (3) illustrates the liver lobule inspiration for the 3D printed scaffold seen in (4) and (5). (6) confirms the increased uptake of toxin relative to controls. Adapted from Gou and Chen *et al.*⁸⁵

Controlling the degradation rate and type of degradation is very important for designing a scaffold for a particular application. Bulk erosion and surface erosion are the two most common forms of scaffold degradation.⁸⁶⁻⁸⁷ During surface erosion, the scaffold degrades from the outside in, slowly shrinking the scaffold, while during bulk erosion, the scaffold degrades more uniformly throughout as seen in **Figure 9.6**. Surface erosion is favored for applications that require maintained strength and physical properties throughout the tissue regeneration process.⁸⁸ Bulk erosion is potentially favorable for a scaffold with fast cell growth, needing the scaffold to degrade faster while being replaced by cell-secreted ECM.⁸⁹ A linear degradation profile results from surface erosion, allowing for easier modeling of property evolution as a function of time.⁹⁰ Previous literature has investigated optimizing cleavable linkages in polymers.⁹¹ The two most common

biodegradation mechanisms used for regenerative medicine are hydrolytically cleavable linkages and enzymatically cleavable linkages. The type of functionality and location of the linkage in the polymer influences the mechanism of erosion. For example, aliphatic polyesters tend to degrade more commonly from bulk erosion while polycarbonates tend to undergo surface erosion.⁹²

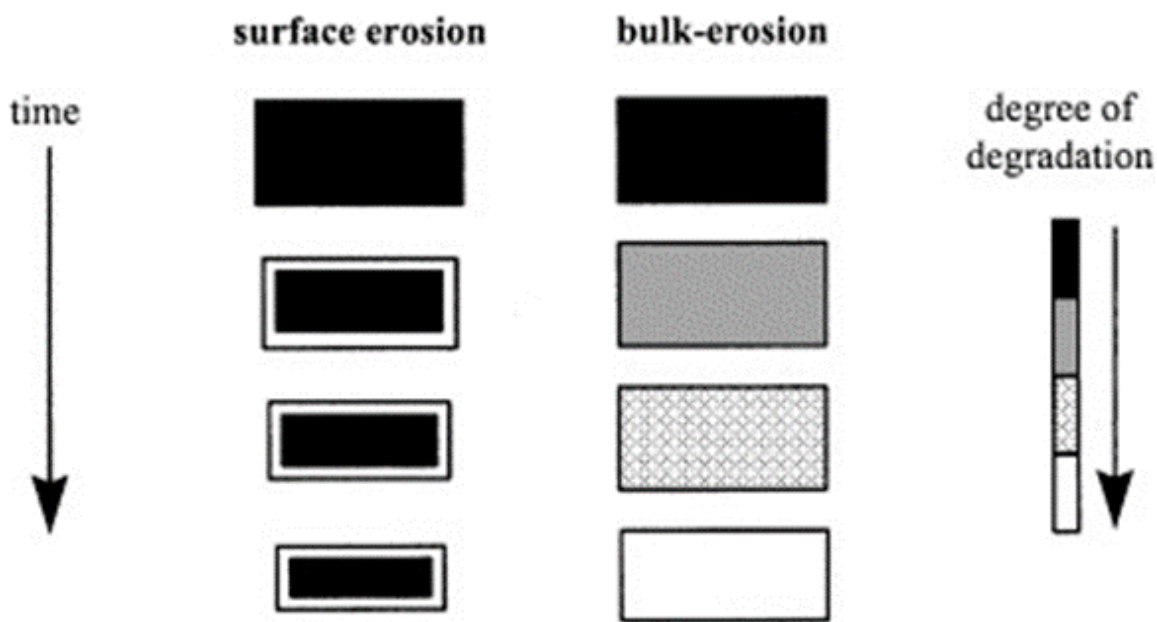
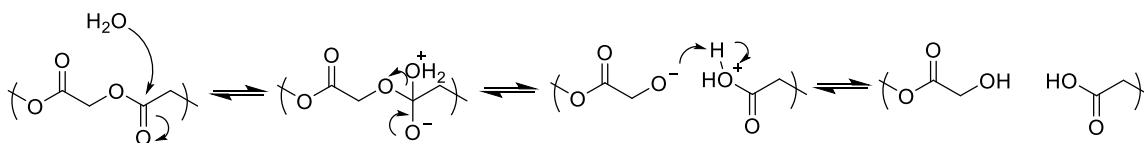


Figure 9.6: Surface versus bulk erosion as a function of time. Reproduced from von Burkersroda and Gopferich *et al.*⁸⁶

9.3.3 Hydrolytically cleavable linkages

Water comprises around 70% of the human body, motivating the wide use of hydrolytically cleavable linkages in tissue engineering scaffolds. When designing polymeric materials for biodegradable tissue engineering scaffolds, it is important to consider the chemistry needed to make the scaffold hydrolytically sensitive. The most common hydrolytically sensitive functionality in synthetic polymers is an ester bond. Esters are common organic functionalities that undergo hydrolysis to yield a carboxylic acid and an alcohol, as seen in **Scheme 9.1**. If the ester is in a polymer backbone, chain

scission occurs and the resulting small molecules are excreted out of the body. Esters are also commonly formed upon end functionalization of polymers for SLA. Reacting an acryloyl chloride or methacryloyl chloride with an alcohol produces an acrylate or methacrylate respectively, which contains an ester functionality. Changing the end group functionality influences the hydrolysis of a crosslinked acrylic scaffold. Methacrylates tend to degrade slower and to a lesser extent than acrylates.⁹³ The extra hydrophobic methyl group on the backbone makes the methacrylate polymer less hydrophilic and also introduces steric constraints when trying to hydrolyze the ester.



Scheme 9.1: Hydrolysis mechanism of an ester functionality in poly(glycolide)

Polymer composition, crosslink density, degree of crystallinity and scaffold additives all influence scaffold degradation rates. Poly(DL-lactide) (PLA), poly(glycolide) (PGA) and copolymers are common hard tissue engineering scaffolds since they result in tough, mechanically strong materials.⁶⁴ The hydrophobic/hydrophilic ratio determines the degradation rate, while the crystallinity controls the change in mechanical properties and loss profiles.⁹⁴ Polymers for soft tissue engineering applications need to be elastic and flexible, therefore eliminating semi-crystalline polymers from consideration. Blending these polyesters with other more flexible polymers results in altered degradation rates and materials with mechanical properties more suitable for soft tissue scaffolds. In one study, methacrylated oligolactides blended with triethyleneglycol dimethacrylate (TEGDMA) and hydroxyapatite (HAp) additive allowed for tailored degradation rates from altering the scaffold composition, the crosslink density, and the HAp additive amount.⁶⁴ Increasing the

crosslink density and HAp concentration slowed down the degradation rates, as seen in **Figure 9.7**. Hydrophilic polymer addition along with a polyester also alters degradation rates. PLA blended with PEG, increases scaffold hydrophilicity, significantly accelerating the degradation rate. The structural and mechanical properties are altered, and optimizing these compositions tailors products to have desired physical properties.⁹⁵ Other commonly used polyesters for soft tissue engineering scaffolds include poly(ϵ -caprolactone) (PCL)⁹⁶ derivatives and poly(glycerol sebacate).⁹

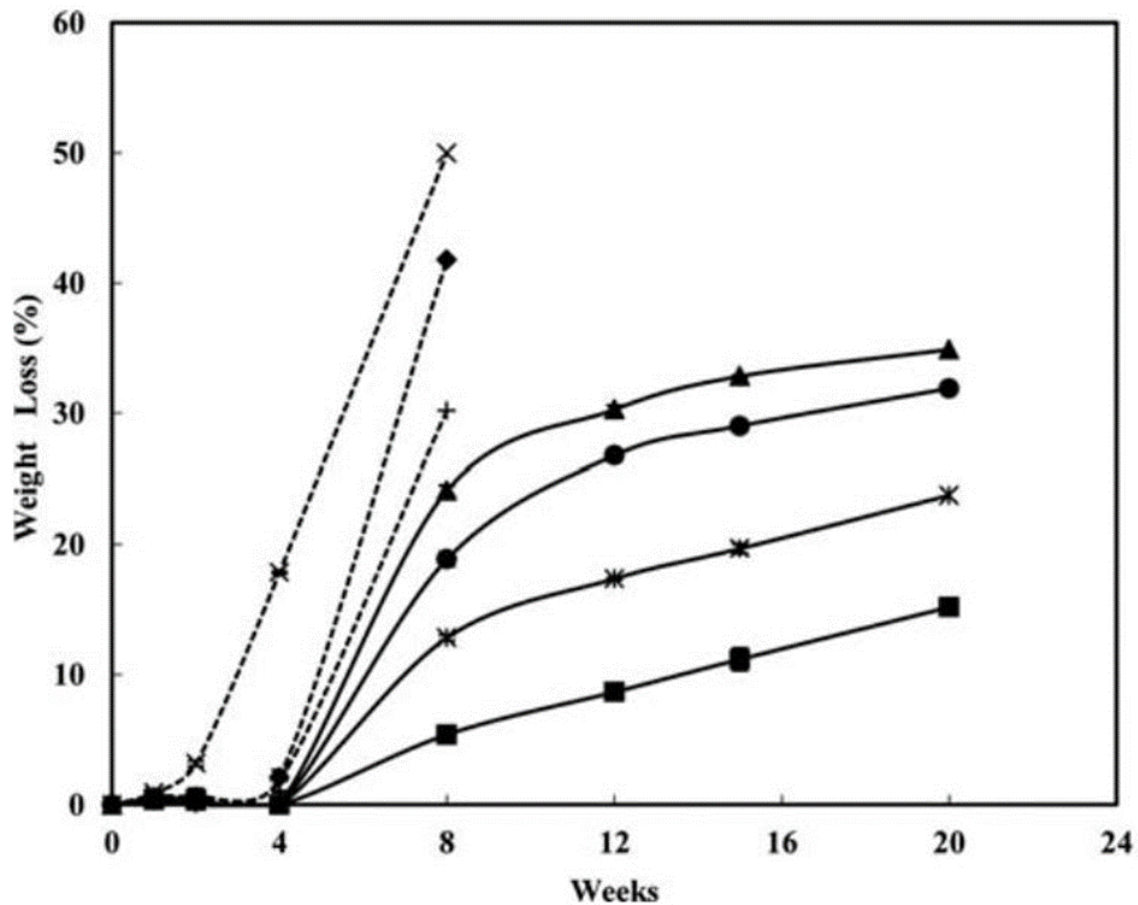


Figure 9.7: Degradation study of PLA/TEGDMA copolymers with hydroxyapatite as a filler at 37 °C in PBS. Dashed lines incorporate 70 % PLA while solid lines incorporate 50 % PLA. Hydroxyapatite incorporation increases going from triangle (0 %) to square (60 %) in 20 % intervals. Adapted from Tanodekaew and Uppanan *et al.*⁶⁴

One concern associated with polyester scaffolds is if the degradation rate is too fast, local pH reaches levels harmful to cells.⁹⁷ Degradation induces acid formation, leading to autocatalytic hydrolysis of polyesters.⁹⁸ Acids catalyze the hydrolysis of esters in the presence of water leading to faster degradation rates. Degradation also profoundly affects mechanical properties. PCL scaffolds showed a slight drop in ultimate tensile stress, from 3.48 ± 0.5 to 2.4 ± 0.32 MPa, after 3 weeks of degradation, while showing a larger drop in elastic modulus, from 7.8 ± 0.45 to 3.53 ± 0.5 MPa.⁹⁹ These changes impact cell viability through pH alteration.

9.3.4 Enzymatically Cleavable Linkages

Rapid random chain hydrolysis of polyesters leads to local tissue acidity due to low pH, thus negatively affecting cell growth and leading to compromised mechanical properties. Incorporating enzyme-cleavable linkages into the polymer network not only achieves controlled degradation of the scaffold but also serves as a bioactive moiety for cell adhesion and migration. Many materials utilized in tissue engineering and regenerative medicine applications hydrolytically degrade from the polymer backbone or pendant sidechains. Side group chemistry, crystallinity, hydrophilicity, etc., tailor the polymers ability to hydrolytically degrade.¹⁰⁰ By introducing enzymatically cleavable linkages in the polymeric backbone, the tissue regeneration and remodeling process mimics natural cell-driven ECM degradation, leading to cell migration and invasion, and thus a remodeled tissue.¹⁰¹⁻¹⁰² In native tissues, ECM proteolytic degradation causes cell migration in response to cell-secreted enzymes. Membrane bound proteases such as matrix metalloproteases (MMPs) assist the natural process of ECM remodeling and is ideally recreated in biomaterials through incorporation of natural proteins such as collagen or

fibrin that contain these protease-cleavable sequences.¹⁰²⁻¹⁰³ Numerous synthetic systems report the incorporation of enzyme-cleavable motifs to engineer proteolytic degradation mechanisms that are responsive to cell secreted enzymes.^{6, 102-104} Incorporating Arg-Gly-Asp (RGD) peptide sequences into various hydrogel scaffolds enables cellular protease degradation. Although RGD use is extensively reported, previous studies on peptide sequences such as IKLLI, IKVAV, LRE, PDSGR and YIGSR from laminin, DGEA from collagen I and GEFYFDLRLKGDK from collagen IV confirm that many enzyme cleavable peptide sequences are viable tools in tissue scaffold design.¹⁰⁵⁻¹⁰⁶ Although examples of photocrosslinked hydrogels with enzymatically cleavable linkages exist, few studies report 3D printing a synthetic polymer hydrogel system with proteolytically degradable linkages in the polymer network.

Acrylate end-capped PEG with grafted oligopeptides form hydrogels after photopolymerization, incorporating enzymatically cleavable sequences for targeted enzymes. Synthesized telechelic BAB block copolymers consisting of a central PEG block (A block) and either a APGL peptide (cleavage sites for MMP-1 degradation) or a VRN amino acid sequence (cleavage sites for plasmin) as the B block were end-capped with acrylates and photopolymerized to form gels. Specific proteases involved in cell migration degraded these gels through the enzymatically cleavable APGL peptide or VRN amino acid sequence. Degradation times in absence of proteases substantially increased compared to protease assisted degradation (500 minutes for protease assisted as opposed to days in absence of proteases). The ability to control material properties and degradation rate through protease cleavage demonstrates the advanced functionality of the system, which is of prime importance for biomaterials in tissue engineering.¹⁰⁴ Similarly, other biomimetic

ECM hydrogel systems exhibit control over cell adhesion and proteolytic degradation through specific sequences. Sequences that are sensitive to elastase, collagenase, and plasmin activity were included in synthesized acrylated ABA block copolymers of PEG (A) and peptides (B). This study used a photocurable polymer system that provides control over the adhesive availability and proteolytically degradable sequences such that their degradation rates and effects on cell migration were analyzed.¹⁰⁷ Such hydrogels with the ability to hydrolytically cleave while maintaining the ability to photopolymerize under UV are attractive candidates for SLA applications. In another study, photopolymerizable PEG hydrogels containing enzymatically degradable peptide sequences were studied as ECM mimics for smooth muscle cell growth in tissue engineering applications.¹⁰⁸ Enzymatic degradation of these hydrogels was successfully demonstrated using collagenase and elastase. The effect of enzyme activity on hydrogel degradation rates was also demonstrated for this material, providing evidence that in addition to hydrolytic cleavage, degradation profile was influenced by the inclusion of cell adhesive motifs, proteolytic degradation sites, and growth factors to enable cell-material-cell interaction. Comparisons of cell growth and tissue formation between non-degradable PEG diacrylate hydrogels to proteolytically cleavable ones revealed tissue formation was enhanced in degradable PEG diacrylates that contained elastin-sensitive polyalanine sequence.¹⁰⁸ This proteolytic degradation mechanism is important since cellular activity leads to resorption and degradation of the synthetic material.

Ideally for a tissue engineering scaffold, the rate of degradation of a hydrogel scaffold (or the rate of material resorption) should match the rate of new tissue formation. Tailoring the degradation rate of these scaffolds is accomplished by changing the type of

enzyme specific cleavable linkage or by changing the concentration of the peptides. Since the regeneration time-frame varies for different types of tissue, the effect of changing the specific enzyme cleavable linkages and the concentration of these peptides is important in the design of new systems. Studying the impact of these parameters on the 3D printed structure and its degradation is crucial for enzymatically cleavable scaffolds prepared using SLA. Thiol-ene photopolymerized PEG hydrogels with specific peptide sequences created an enzyme-responsive drug delivery platform.¹⁰⁹⁻¹¹⁰ Previous reviews have detailed the existing design strategies for synthesizing enzyme responsive hydrogels.¹¹¹⁻¹¹² In the context of designing enzyme degradable polymers for SLA applications, the first reported studies were on photocrosslinkable PEG systems with MMP-degradable peptides. Optimizing 3D hydrogel constructs using SLA processing requires photoactive sites allowing crosslinked network formation discussed earlier.

Employing enzyme-cleavable sequences allow cells to adhere and migrate through the polymer scaffolds through degrading the oligopeptides, which serve as sites for enzyme cleavage. This process closely mimics natural tissue regeneration processes where cell-associated enzymatic activity remodels the ECM. Altering the oligopeptide domain, its length, and the spacer domain length separating it from the polymer or crosslink sites, allows for control of the degradation properties as well as the selectivity of cleavage. Hepatic tissue constructs, previously studied with three-dimensional photopatterned structures, utilized multilayered PEGDA hydrogels containing an RGD peptide sequence to bind $\alpha_5\beta_1$ integrins, which are expressed by cultured hepatocytes.¹¹³ Synthesizing oligopeptide sequences for incorporation into synthetic polymers or as photocrosslinkable biopolymers is complex and potentially difficult to achieve.

9.3.5 Mechanical Properties

In order to replicate *in vivo* tissue properties, particularly in regards to biomechanical function, tissue engineering scaffolds ideally should replicate the native tissue's mechanical properties. Gender, race, and age all heavily influence tensile, compression and flexural properties, leading to a wide range of values for similar tissue sites.¹¹⁴ Soft tissue mechanical properties well studied include cardiovascular tissue such as valves, aorta, and heart muscle,^{34, 114-115} dense connective tissue such as ligaments^{18, 114, 116} and tendons,^{18, 114, 116} loose connective tissue such as cartilage,^{18, 41, 114, 117} and epithelial tissue such as those lining organs, intestines, and skin.^{18, 114}

Bulk mechanical properties offer little value as a starting point when choosing a polymer to replicate a target tissue. While common synthetic and natural polymers offer a broad range of properties, these properties are of high molecular weight, entangled systems, which are unfit to undergo SLA, as previously described. Oligomeric properties drastically change with varying the molecular weight. This allows for ideal tuning of scaffold stiffness to match the target tissue. The layer-by-layer assembly and ability to control the microstructure of the scaffold also offers increased control to tune the resulting scaffold's mechanical properties through architectural design.^{57, 118-119} Other ways to control the mechanical properties of a construct include resin additives,⁷² supramolecular interactions, and crosslink density.¹²⁰⁻¹²² 3D printed synthetic and natural polymers with appropriate mechanical properties, as seen in **Table 9.2** and highlighted in upcoming sections, show promise for future application in tissue regeneration.

Table 9.2: Mechanical Properties of Various Tissue Compared to Synthetic Scaffolds with Similar Properties

Cardio-vascular Tissue	Property			Ref
	Tensile			
	Strength (MPa)	Strain at Break (%)	Modulus (MPa)	
Aorta/Vena cava	0.3 - 1.5	24 - 100	0.04 - 1.9	[114, 115]
Valves	0.2 - 2.5	15 - 30	1.0 - 1.3	[114-115, 34]
Vasculature	0.9 - 1.1	64 - 150	0.1 - 0.55	[114]
Heart Muscle	0.11	64	0.08	[114]
PEG-Based Scaffolds	--	0.5	0.01 - 0.1	[41, 44]
Gelatin-MA	--	80 - 100	0.6 - 1.0	[46]
Cyanoethyl-based, PEG Scaffolds	0.12 - 0.15	67 - 98	0.22 - 0.41	[34]

Connective Tissue	Property			Ref
	Tensile			
	Strength (MPa)	Strain at Break (%)	Modulus (MPa)	
Cartilage	2.9 - 40	15 - 120	4.5 - 24	[18, 114, 117]
Skin	1 - 20	30 - 70	0.3	[18, 114]
Tendon	40 - 100	9 - 15	250 - 345	[18, 114, 116]
Ligament	36 - 100	10 - 15	640	[18, 114, 116]
3-arm PCL	2.0 - 2.6	19 - 79	6.7-15.4	[39]
PTMO-diacylate	--	--	5.7-27.5	[175]
PDLLA-Fumaric Acid	7 - 20	3 - 7.3	200-800	[68]

9.4 SLA 3D Printing

Additive manufacturing enables the fabrication of new and unique structures, not typically achievable using standard processing techniques.¹²³ Material extrusion 3D printing technologies such as fused deposition modeling (FDM), nozzle-deposition direct printing,⁹⁵ melt-plotting,⁹⁶ or molding⁹ are used with metals or thermoplastics, such as semi-crystalline polyesters, due to high thermal transitions. Extrusion and molding additive manufacturing processes generally deposit molten sample upon demand in a tool-path fashion.¹²⁴ Granular printing techniques such as selective laser sintering (SLS) use polymeric powders to construct scaffolds. These techniques sinter specific layers individually to construct a 3D scaffold.¹²⁵⁻¹²⁶ Another common additive manufacturing technique used for scaffolding is photopolymerization, such as SLA. The ability to manufacture an entire layer at one time using a digital mask projection device (DMD) provides advantages in print speed compared to material extrusion and SLS. Typical layer cure times take 2-100 s, leading to print speeds in the range of 5-1000 mm/h (height).¹²⁷⁻¹²⁸ Total fabrication times are dependent on size of printed parts, desired overall feature resolution, height layer thickness, and photopolymer cure kinetics. The light from a mask projection SLA cures one-layer at a time, in contrast to a nozzle or a laser rastering to cure a layer such as in material extrusion or SLS/SLA respectively. SLA is also advantageous compared to material extrusion or SLS when targeting soft tissue scaffolds since SLA is more versatile in printable materials and allows for printing flexible, soft materials.¹⁷ Lastly, visible-light SLA enables scaffold fabrication in presence of cells, giving more evenly dispersed cell-scaffold constructs and eliminating post-fabrication seeding.^{40, 50, 66} SLA is used in additive manufacturing for tissue engineering and is the focus of this review.

SLA fabrication uses a light source to precisely control polymer scaffold microscale (DMD mask projection) and nanoscale (two-photon polymerization or advanced lithographic techniques) dimensions.^{53, 129} Layer-by-layer assembly of the construct is achieved using a stage that moves the distance of a desired thickness allowing for a new layer to photocure. Common layer heights in SLA range from 25-200 μm .¹²⁷ Computer aided design (CAD) software is commonly used to pattern the light controlling architectures and dimensions printed. CAD files of a designed object or computer-processed computed tomography (CT) scans of a 3 dimensional object are sliced into separate layers. These layers are used to direct the light source to cure the polymer. This technique allows for personalized medicine since imaging a patient's tissue enables production of 3D replicas that are nearly identical to the tissue replaced. The light source and imaging optics control the scaffolds (overall size and individual features) ultimate dimension, resolution, and fidelity. Minimum feature resolution ranges from 5-300 μm .^{26, 127} Light sources typically used for SLA include broad spectrum ultraviolet (UV) lamp, monochromatic laser, and visible light.^{50, 66, 129} The source dictates the emitted wavelength of light, reviewed extensively in previous literature.¹³⁰⁻¹³¹ SLA light sources (UV light and laser) will affect cells and introduce mutations, damaging cells. Visible light SLA techniques eliminate harmful effects of UV light and allow fabrication of scaffolds with cells dispersed throughout the polymer resin.^{40, 50} SLA setups are generally designed using a bottom-up or a top-down approach, referring to the direction of light irradiation on the vat, as seen in **Figure 9.8**. Specific photopolymer characteristics are required for SLA processing and are further discussed in the next section.

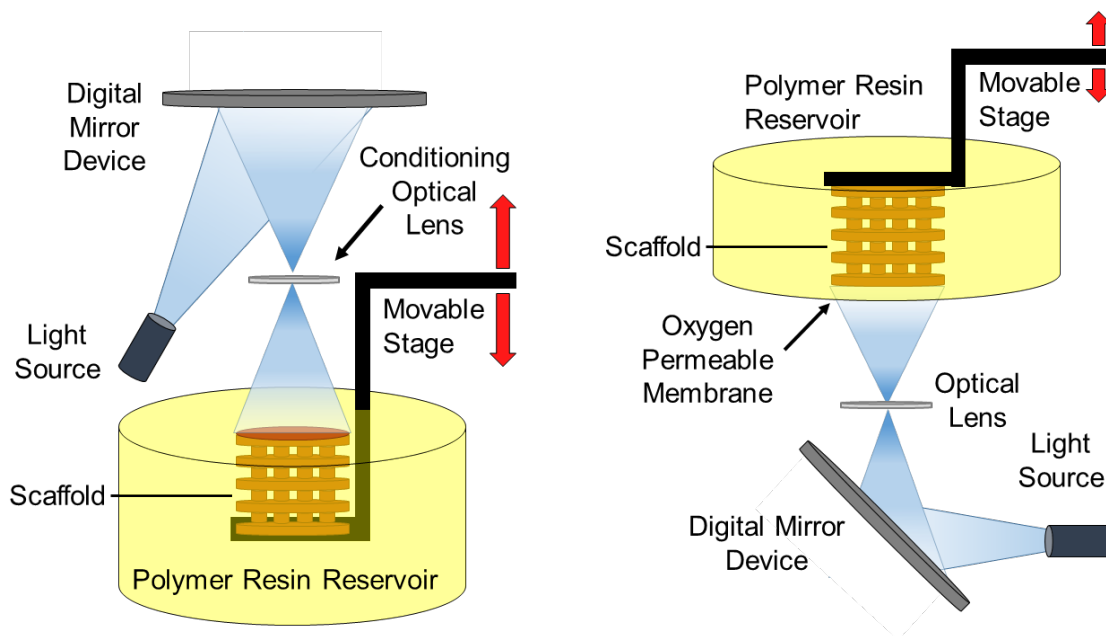


Figure 9.8: Schematic for a top-down laser SLA setup (left) versus a bottom-up light projected digital mirror device SLA setup (right). Light source direction to the polymer resin determines top-down versus bottom-up terminology. An oxygen permeable membrane, employed in some of the newer bottom-up printers, prevents resin attachment to the window.¹²⁸

9.5 Polymeric Properties Needed for SLA

SLA requires certain polymer characteristics, as described in **Table 9.3**. Polymers should have a melting temperature (T_m) below room temperature or the processing temperature and a glass transition temperature (T_g) low enough to maintain the polymer liquid-like at processing temperatures, allowing chain mobility. Low viscosity is also important at processing temperature. Viscosity, or resistance to flow, is a function of molecular weight and large chain entanglement.¹³²⁻¹³⁴ Viscosities suitable for SLA resins are around 1 Pa·s,⁴⁹ but range from 0.25 Pa·s for low molecular weight and/or diluted samples, to 10 Pa·s for higher molecular weight samples.^{76, 135} Liquid comonomers and non-reactive diluents (e.g. solvent) added to the photopolymer act as plasticizers, decreasing viscosity of printable resins.⁷¹ Lower viscosity allows the reactive

functionalities to interact and increase cure rates, decreasing overall construction times. Low viscosity is also important in allowing the construct to undergo the recoating process and for the resin to self-level.¹³⁶ Higher viscosity resins take longer to recoat and self-level leading to increased construction times.¹³⁷ Some SLA techniques recently developed allow for continuous printing, eliminating the need for recoating.¹²⁸ Polymers with low viscosity are also beneficial when cleaning excess resin from the construct after printing. Post-printing UV-curing ensures complete reaction of functional end groups, but uncured resin left in the construct affects specific dimensions and features post-curing. Therefore, resin is generally removed before post-curing steps. Solvent is commonly used to extract unreacted resin from pores or the construct interior. Polymer architecture also modulates viscosity. Short polymer chains, such as oligomers, involve fewer inter-chain entanglements, reducing viscosity. Non-linear polymers including hyperbranched¹³⁸ and multi-arm star⁴⁹ polymers also afford low viscosity due to less entanglement. Star and hyperbranched polymer architectures offer an increased number of reactive sites for crosslinking, affecting cure and gel rates.

Table 9.3: Properties desired for SLA and methods used to achieve them

Polymeric Properties Desired for Vat Photopolymerization	Methods Used to Achieve Properties
<u>Low Viscosity</u> 0.25-10 Pa·s [49, 76, 135]	• Polymer Architecture • Oligomers • Stars • Hyperbranched/Dendrimers • Liquid comonomers • Non-reactive diluents (plasticizers/solvents)
<u>Fast Cure Times</u> 2-100 s [127, 128]	• Many photopolymerizable functionality • More reactive end groups • Higher intensity of light
<u>Crosslinkable Materials</u> Functionality >2 [168]	• Multifunctional monomers/polymers
<u>Photopolymerizable Functionality</u>	• Acrylate/methacrylates • Epoxides • Electron deficient alkene for 2+2 cycloaddition

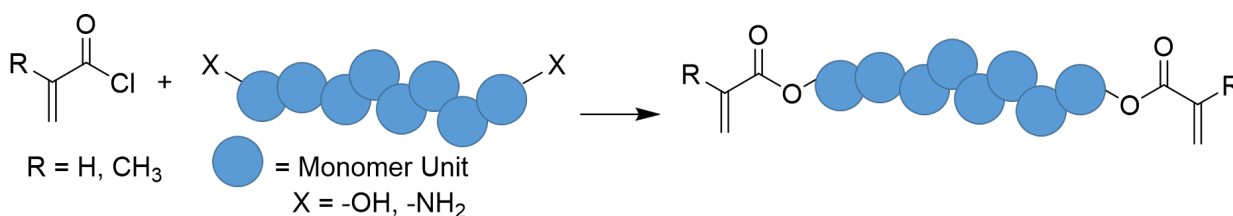
Fast cure kinetics and gel times are favorable and are tailorable using different photoreactive functionalities. Short individual layer cure times facilitate rapid fabrication, which is desired for mass production. Multifunctional polymer chains are necessary to form solid 3D constructs through crosslinking. Insufficient crosslinking leads to poor mechanical properties and consequently the material may fail to maintain the desired shape. Reactive diluents (liquid comonomers) act as plasticizers, which allow for greater chain and end-group mobility as well as easier processing conditions.¹³⁷ Organic solvents are not favorable due to toxicity. These solvents also negatively affect dimensional control as a result of scaffold shrinkage, due to inconsistent swelling or drying of solvent from constructed parts.¹⁶ All polymers and monomers cured require photoactive functionality. Photopolymerizable functionalities such as acrylates or epoxides are most common. Other functionalities used for photocrosslinking include cinnamates,¹³⁹⁻¹⁴⁰ coumarins,¹⁴¹⁻¹⁴⁴ thiol-

ene reactions, and fumarates^{137, 145-146} that undergo 2+2 cycloaddition upon exposure to UV. Altering the reactive end functionality influences the reaction kinetics. For example, the tertiary radical formed from a methacrylate monomer is more stable compared to an acrylate affording faster cure kinetics in near identical conditions. Photocycloaddition crosslink rates are generally slower compared to radical methods but offer various advantages, such as low molecular weight degradation products and reversible crosslinking. Photocrosslinking using 2+2 cycloaddition chemistry also eliminates use of radical initiators. These are generally toxic, and miscibility issues are a concern with photopolymer resins, leading to photoprocessing complications. Oligomers, star polymers, and hyperbranched systems are generally end-group or pendant functionalized with these photoactive sites for use as SLA resins.

9.5.1 Functionalized Oligomers

Functionalized oligomers are the most common polymer architecture used for SLA. Low to intermediate molecular weight oligomers possess different properties compared to their high molecular weight analogues. They offer lower viscosity and increased solubility affording easier processing compared to larger macromolecules. Telechelic oligomers are typically designed so the end-groups are reactive sites that attach photoactive functionality. Acryloyl chloride or methacryloyl chloride are commonly used with an alcohol in an esterification reaction or with an amine in an amidation reaction to produce oligomers with crosslinkable end groups, as seen in **Scheme 9.2**. Polyether diols such as poly(ethylene glycol) (PEG) are commonly functionalized oligomers due to the commercial availability of varying molecular weight samples, ease of functionalization, and biocompatible properties.^{44, 50, 67, 147-148} Other commonly functionalized synthetic oligomers include

polyesters.⁶⁴ For polyesters, a terminal alcohol is generally functionalized using methacrylic anhydride, as this does not generate a strong acid compared to acid chlorides. This step limits acid catalyzed ester degradation through hydrolysis.⁶⁴ Another option for photocurable functionalization is reacting a terminal alcohol or amine with 2-isocyanatoethyl methacrylate.¹⁴⁹ While an acid chloride or anhydride functionalization affords byproducts requiring purification, 2-isocyanatoethyl methacrylate generates a urethane linkage with no resulting byproduct. Urethanes connecting the oligomer to the photocurable functionality add hydrogen bonding donors and acceptors that will influence properties. Natural oligomeric polymers commonly functionalized for use in SLA include polysaccharides^{52, 69, 150} and polypeptides.^{43, 46, 51, 151} Similarly photocurable monomers are used when functionalizing natural macromolecules, however various challenges exist. Most natural macromolecules have limited solubility in common solvents making them difficult to functionalize relative to synthetic macromolecules.¹⁵²⁻¹⁵³ Polysaccharides also have multiple functionalization sites along the structural backbone, leading to uncertainty in molecular weight between crosslinks.



Scheme 9.2: End-group functionalization of an alcohol or amine to a photopolymerizable diacrylate or dimethacrylate

Advantages	• Low viscosity • Faster cure times • Easy to process	• Medium viscosity • Acceptable cure times • Processable • Similar properties to linear polymer	• Nearly identical properties to linear polymer
Molecular Weight	Low	Optimal	High
Disadvantages	• Properties unlike high molecular weight linear polymer		• High viscosity • Slow cure times • Hard to process

Figure 9.9: General properties to consider when optimizing the molecular weight of a polymer. Every polymer composition will have a different optimal molecular weight for SLA 3D printing

One method to synthesize oligomers is step-growth polymerization. Modifying the Carother's equation, either an excess of one bifunctional monomer or a monofunctional end-capping monomer is used to target a specific number-average molecular weight.¹⁵⁴ Since most step-growth polymers are not photopolymerizable without end group functionalization, an excess of a difunctional monomer with a reactive group, such as an alcohol is preferred. Synthesizing oligomers instead of using commercial materials diversifies the potential macromolecules used in SLA for tissue engineering scaffolds. Selecting optimal molecular weight is important when balancing processability and cure times versus final properties, as seen in **Figure 9.9**. Oligomers with too low a molecular weight are easier to process into a low viscosity resin, but resulting constructs may not have physical properties comparable to the native tissues that they mimic. On the other hand, oligomers with higher molecular weight afford scaffolds with properties comparable to high molecular weight bulk polymer, but high viscosity and slow cure rates makes processing difficult. Lastly, molecular weight distributions (MWD) of synthesized polymers affects properties, mainly due to crosslink density changes. Altering the MWD

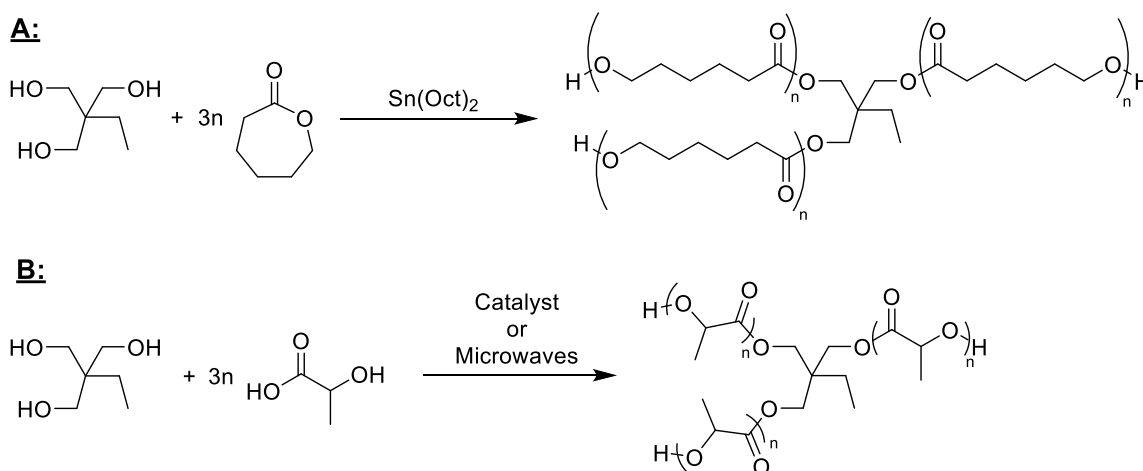
or crosslink density allows for tuning of properties such as the storage modulus or stiffness.¹⁵⁵

9.5.2 *Star/Branched Polymers*

Star/branched polymers are another architecture option for achieving desired SLA printing properties.^{48-49, 76} Star architectures contain multiple polymeric arms extending from a core. Non-linear chains are more difficult to pack together and include fewer entanglements, leading to lower viscosity and better solubility compared to similar molecular weight linear analogues. 4- and 6-arm star polyisoprenes, with similar molecular weight as linear versions, have 20-30 % lower viscosity.¹⁵⁶ 3-arm star polyisoprenes show a 20% decrease in viscosity compared to 4-arm stars.¹⁵⁷ Alternatively, if molecular weight of the arms becomes too high, the viscosity becomes independent of the number of arms.¹⁵⁷ Ensuring star polymers with 3 to 5 arms and the arm molecular weight low, star polymers exhibit enhanced rheological properties for SLA compared to their linear counterparts.¹⁵⁸⁻¹⁵⁹ With increasing amounts of end-groups per molecule, star architectures also offer more rapid cure kinetics. Biodegradable star poly(ester anhydrides) show ~35% faster cure times compared to their linear analogues.⁵⁹ Alternatively, 5 to 10% of poly(ϵ -caprolactone) star polymers incorporated into linear systems did not affect gel times substantially, but doubled end-group conversion at the gel time.¹⁶⁰ Increasing conversion at the gel time helps reduce post processing cure needs. Lastly, drug loading and nutrient diffusion has also shown to be core, molecular weight, and hydrophobic/philic dependent.¹⁶¹

While star/branched polymers offer certain enhanced properties, they pose challenges in synthesis. Typical synthesis involves ring opening polymerization or mixing a multifunctional core with monomers that extend from the core, as seen in **Scheme 9.3**.

Incorporating too much multifunctional monomer with difunctional monomers results in crosslinking. Reacting a multifunctional core with a difunctional monomer, which has one functionality to react with the core and one functionality to extend from the core, results in a star/branched architecture. Using this approach, the reactive functionality of the core and the end functionality of the growing arms remains the same throughout the reaction. Short oligomers arise from this method when chains do not react with the multifunctional core. Star polymers also need photoactive end-groups and similar end-functionalization methods are applied to star architectures as oligomers.^{49, 76, 159, 162-163} SLA on star/branched polymers is of interest due to the alteration in mechanical and elastic properties as well as the influence on processing.⁷⁶

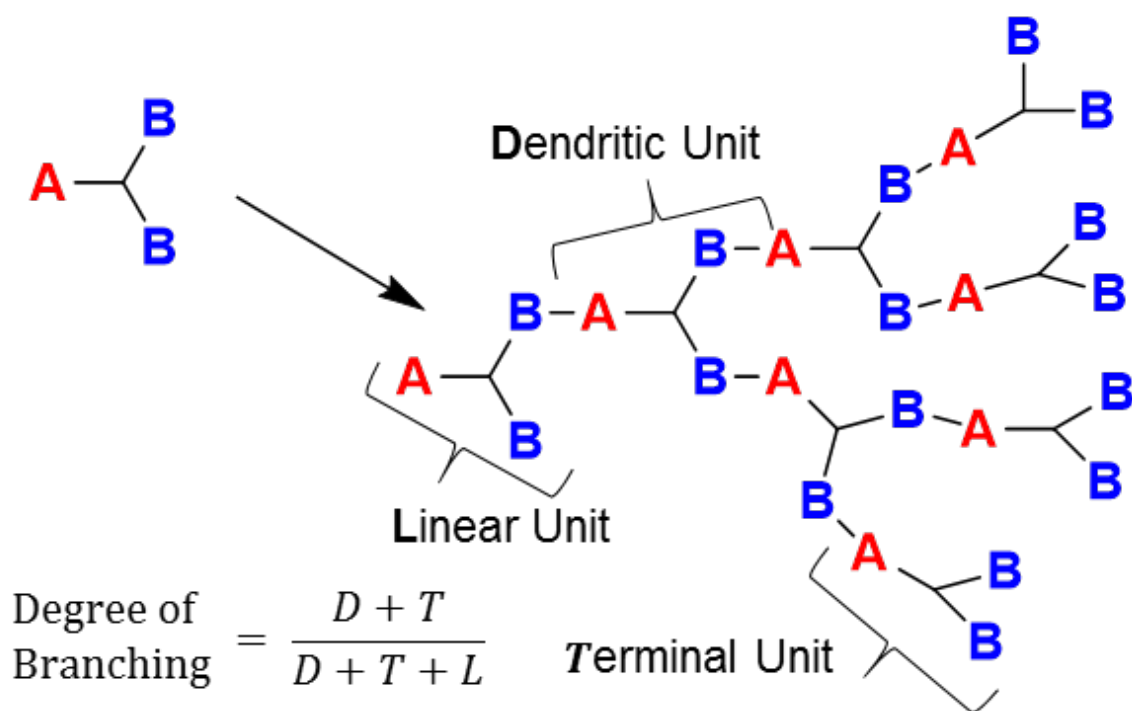


Scheme 9.3: Common star architecture synthetic schemes for ring opening polymerization of poly(ϵ -caprolactone) PCL, **A**, and condensation step-growth polymerization of polylactic acid (PLA), **B**.

9.5.3 Hyperbranched Polymers

Another polymer architecture affording properties suitable for SLA is hyperbranching. Hyperbranched materials are defined as AB_x systems, where x is greater than 1. Since there is one A functionality per monomer, no crosslinking occurs as the growing polymer

only reacts with other branching polymers or another monomer, as seen in **Scheme 9.4**. Hyperbranched systems result in 10 to 250% decrease in viscosity compared to linear analogues.¹⁶⁴⁻¹⁶⁵ Degree of branching impacts polymer physical properties.¹⁶⁶ Polymers with low degrees of branching exhibit properties close to linear analogues, while increasing the degree of branching decreases entanglements, lowering viscosity.¹⁶⁷ Degree of branching is defined as the ratio of dendritic units and terminal units divided by the total number of units, as seen in **Scheme 9.4**.¹⁶⁸ Determining degree of branching is difficult as distinguishing the different units is challenging.



Scheme 9.4: Hyperbranched polymer synthesis using an AB₂ monomer. Degree of branching formula is given along with unit classifications

Hyperbranched polymer solubility is also dependent on the degree of branching. The high degree of end group functionality and branching makes hyperbranched polymers more soluble compared to linear analogues. Changing end group structure greatly

influences solvent solubility.¹⁶⁹ Polymers with polar end-group functionality, such as alcohols or amines, are more soluble in polar solvents compared to acrylate end-capped polymers, which are more soluble in non-polar solvents. Similar end-functionalization methods are used for hyperbranched systems compared to oligomer and star architectures.^{54, 138, 170} Unlike star polymers, hyperbranched systems exhibit slower gel times.¹⁷¹ This decrease in gel time is attributed to end-group diffusion. The increase in solubility also influences diffusion properties. Diffusion properties are important in biological applications to ensure proper nutrients reach cells. Hyperbranched systems take up more small molecules, such as drugs or nutrients, than linear analogues.¹⁷² The potential for hyperbranched polymers to be loaded with increased drug amounts, and to demonstrate increased nutrient diffusion rates suggest interesting applications for these polymers in SLA tissue engineering applications.

Identifying the optimal polymer architecture requires balancing the targeted tissue application's biological and mechanical requirements with polymer/processing properties as seen in **Table 9.4**. Tuning gel times results from varying oligomer architecture, e.g. an increased number of photoactive functionality per molecule decreases gel times, while end-group diffusion limitations increase gel times for highly-hyperbranched molecules. Hyperbranched architectures offer a large decrease in viscosity compared to linear analogues, while star polymers viscosity is dependent on core functionality and arm molecular weight. Lastly, hyperbranched systems possess the highest drug loading capability while also retaining higher small molecule diffusion constant relative to linear and star polymers. Tuning the diffusion rates in star systems is accomplished by altering the number and molecular weight of the arms, while tuning hyperbranched systems

involves controlling the degree of branching.¹⁷³ Star polymer offer higher drug loading compared to linear analogues.

Table 9.4: General SLA processing property comparisons for various polymer architectures compared to high molecular weight linear polymer of the same composition

Polymer Architecture	Gel Times	Viscosity	Drug Loading & Diffusion
Linear Oligomers	Intermediate [168]	Intermediate [168]	Lowest
Star Polymers	Fastest[59, 160]	Core and MW dependent [156-159]	Core and MW dependent [161]
Hyperbranched	Slowest [171]	Lowest [164, 165]	Highest [172]

9.6 Recent Soft Tissue Scaffolds Prepared Using SLA

A major focus for biodegradable soft tissue engineering scaffolds currently involves synthetic polymers. Synthetic polymers offer the widest range of properties chemically, physically, and biologically. Synthetic polymers are desirable to use for tissue engineering scaffolds due to the ability to tune properties using various polymer compositions, fabrication methods, and additives. Some of the most common synthetic scaffolds include polyethers and polyesters, while some of the most common natural scaffolds include polysaccharides and polypeptides.

9.6.1 Synthetic Polymers

9.6.1.1 Polyethers

Polyethers are a class of polymers commonly investigated for biomedical applications. PEG is one of the most commonly used polymers for regenerative medicine due to its

biocompatibility, commercial availability, hydrophilicity, flexibility, and solubility. The equilibrium water content, overall hydrophilicity, elastic modulus, and mesh size of PEG photopolymerized hydrogels is increased or decreased when altering the molecular weight of the crosslinked polymer used.¹⁴⁷ Photopolymerized methacrylated PEG shows comparable mechanical properties to that of soft tissue, and these properties are commonly tuned for particular applications.¹⁴⁸ Since PEG scaffolds are not naturally cell-adhesive, combinations with other biomaterials such as polyesters, polysaccharides, or polypeptides is common. Collagen fibrillized within diacrylated PEG accompanied with alginate was used in SLA to produce highly accurate aortic valve geometries.⁴⁴ These scaffolds exhibited a large elastic modulus range (5.3 ± 0.9 to 74.6 ± 1.5 kPa), fast printing times (14 to 45 min), accurate shape dimensions and high viability of encapsulated porcine aortic valve interstitial cells over a 3 week span.⁴⁴ PEG gives the structure suitable elastic modulus for soft tissue while the fibrillized collagen promotes cell adhesion and proliferation. PEG's hydrophilic nature leads to various swelling capacities based on core functionality and molecular weight. Changing the swelling ratio or total volume of water in the hydrogel greatly impacts the mechanical properties of a scaffold. Elastic modulus values ranging from 4.73 ± 0.46 to 503 ± 57 kPa were shown for various molecular weight PEG hydrogels, as seen in **Figure 9.10**.¹⁷⁴ The increase in modulus is due to the increase in chemical crosslinks, resulting in a lower maximum swelling ratio. Another polyether with the desired flexible structure of a soft tissue scaffold is poly(tetrahydrofuran) (PTMO). PTMO printed to dimensions close to that of blood vessels or capillaries shows no cytotoxicity, and also demonstrates shape-memory, as seen in **Figure 9.11**.¹⁷⁵ Capillary like constructs of the material possessed physical properties similar to natural capillaries,

with Young's modulus ranging from 5.7 to 27.5 MPa, bending strength ranging from 1.1 to 3.5 MPa, and water swelling ranging from 1.3 to 1.9 %.¹⁷⁵ These constructs are promising candidates for capillary replacement scaffolds due to minimal degradation of the scaffold, a high degree of biocompatibility, and biomimetic mechanical properties.

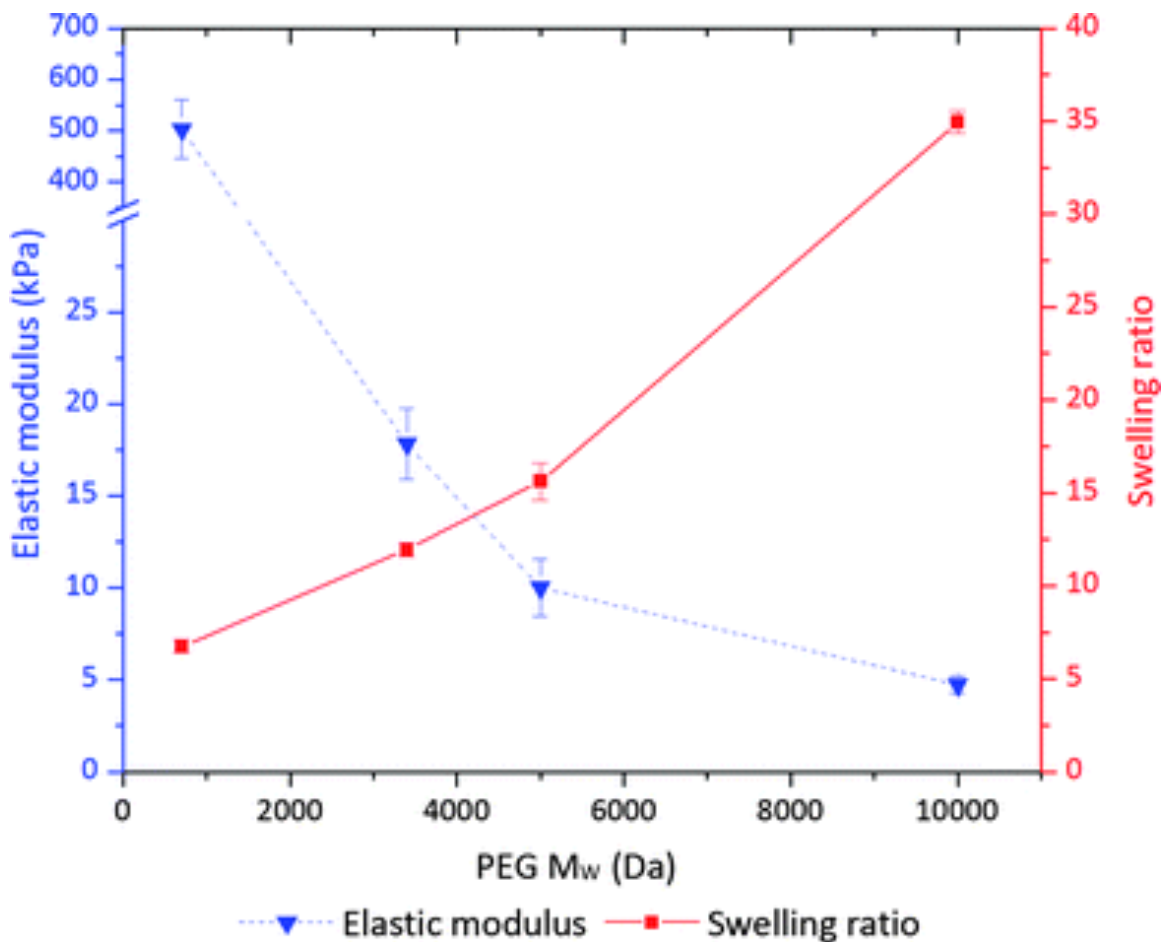


Figure 9.10: PEG hydrogels exhibiting a loss in elastic modulus (blue; left y-axis) and an increase in swelling ratio (red; right y-axis) as molecular weight between crosslinks increases. Adapted from Chan and Bashir *et al.*¹⁷⁴

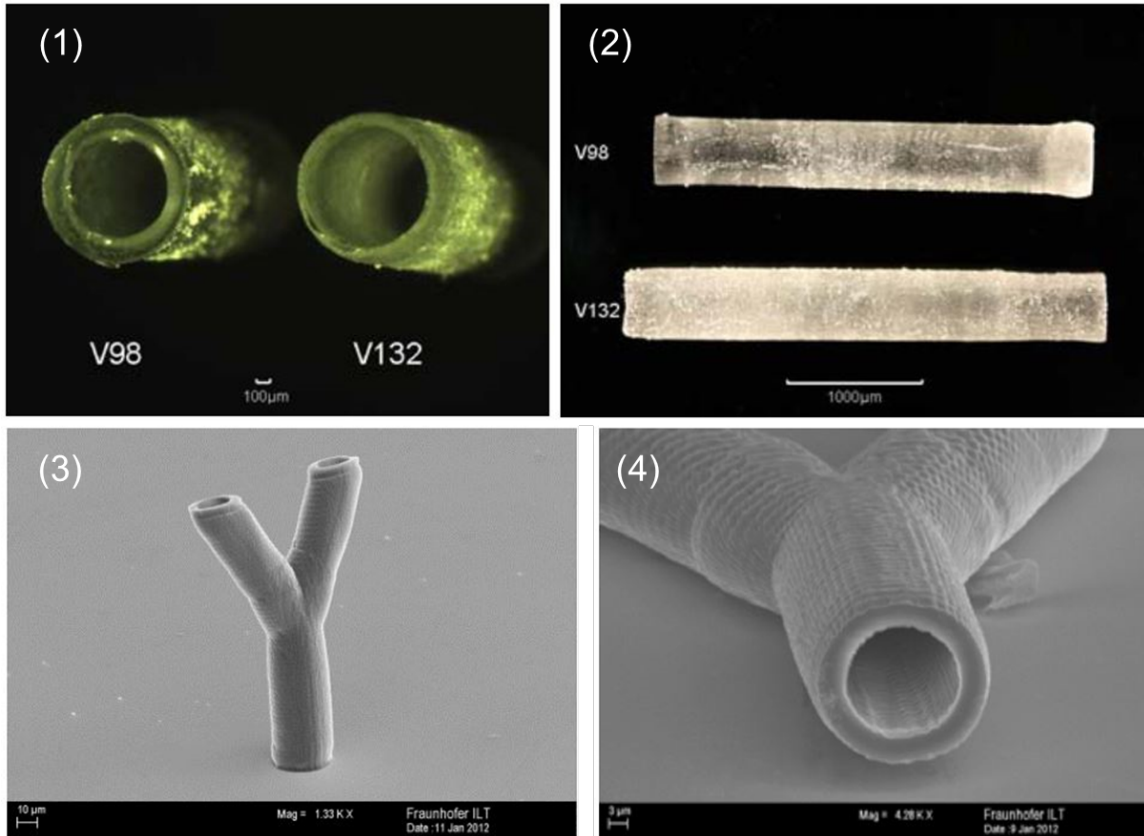


Figure 9.11: Poly(tetrahydrofuran) (PTMO) printed using SLA to afford capillary inspired tubes with inner diameters smaller than 2 mm. (1) and (2) show 3D tubes printed with microscale pore sizes. (3) and (4) display a branched tubular system with an inner diameter of 18 μm and a wall thickness of 3 μm . Adapted from Meyer and Kruger *et al.*¹⁷⁵

9.6.1.2 Polyester

PLA oligomers photopolymerized along with TEGDMA and HAp additive using SLA resulted in scaffolds with controllable degradation rates and a flexural modulus ranging from 75 ± 10 to 3980 ± 177 MPa.⁶⁴ These scaffolds showed limited cell viability, due to an acidic environment resulting from polyester hydrolysis. One common method to increase cell viability is to incorporate PEG into the scaffold or polymer structure. Poly(DL-lactide)-poly(ethylene glycol)-poly(DL-lactide) oligomers (PDLLA-PEG-

PDLLA) end functionalized with methacrylic anhydride constructed into gyroid pore networks using SLA, as seen in **Figure 9.12**, exhibited swollen compressive modulus of 14-420 kPa, similar to cartilage soft tissue,¹⁷⁶ while displaying appropriate cell viability.⁷⁴ μ CT analyzed the printed hydrogels and confirmed high resolution structures with pore sizes between 387 and 558 μ m, achieving a porosity of 52%, with 55% being the targeted design. hMSCs exhibited adhesion and proliferation in the hydrogels over a 5-day period. These scaffolds rapidly degraded in mineralized water but degraded much slower in demineralized water, indicating a fast degrading scaffold application.

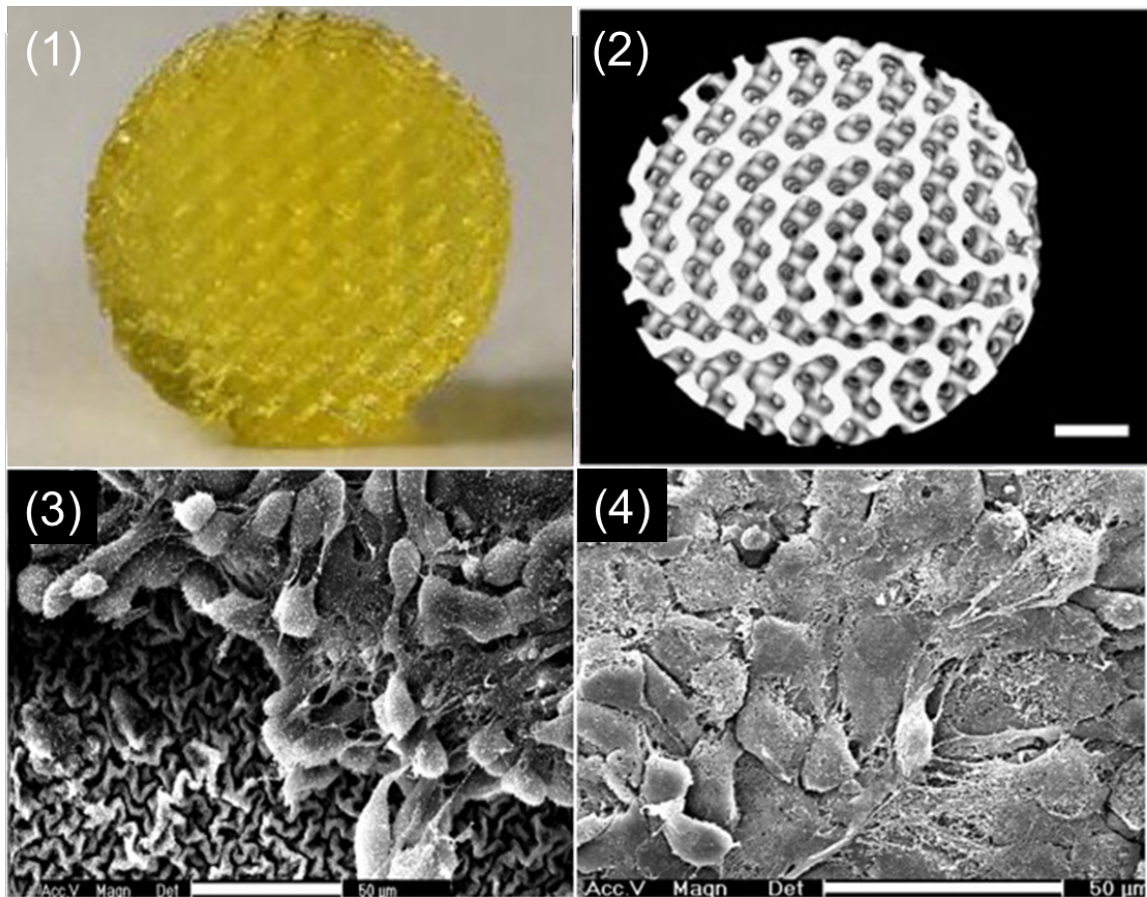


Figure 9.12: PDLLA-PEG-PDLLA scaffolds printed using SLA. (1) shows a porous hydrogel scaffold after extraction. (2) is μ CT analysis of (1), scale bar is 1 mm. (3) shows cell adhesion after 24 h using SEM and (4) exhibits cell proliferation after 5 d using SEM. Adapted from Seck and Grijpma *et al.*⁷⁴

Three arm star poly(ϵ -caprolactone) (PCL) polymers fabricated with SLA produced tissue engineering scaffolds, as seen in **Figure 9.13**. These constructs show elastic mechanical properties, with Young's modulus in the range of 6.7 ± 0.4 to 15.4 ± 0.7 MPa.³⁹ The scaffolds also exhibit biocompatibility over a week with fibroblast cells displaying cell adhesion and proliferation.³⁹ Degradation studies of these scaffolds are needed to verify the ability of these materials to degrade in an appropriate time. Combining the strength and tunability of degradation rates makes polyesters a promising tissue engineering scaffolds polymer.

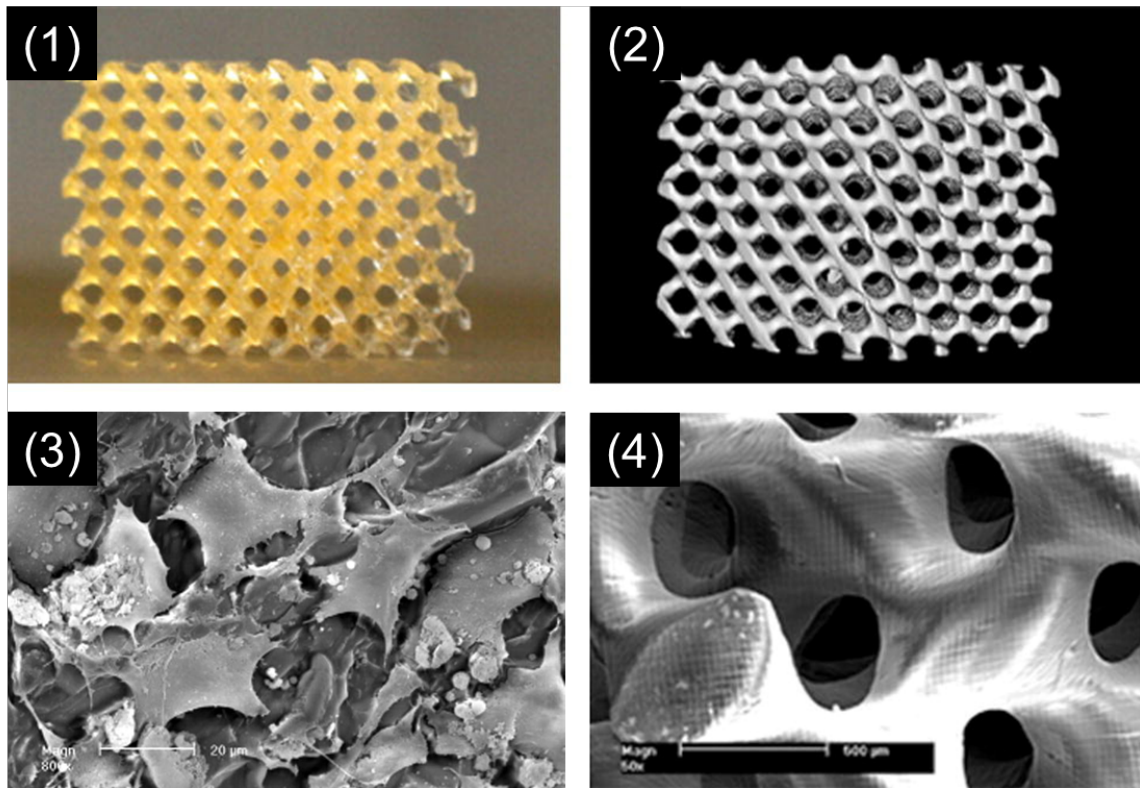


Figure 9.13: Three arm star PCL scaffolds printed using SLA. (1) shows a picture of the fabricated scaffold. (2) is μ CT analysis of (1). (3) scaffold exhibits fibroblast cell adhesion and proliferation after 7 d using SEM. (4) shows pore feature and interconnectivity of scaffold from SEM. Adapted from Elomaa and Grijpma *et al.*³⁹

9.6.1.3 Other synthetic polymers

While polyethers and polyesters encompass a majority of the synthetic macromolecules currently studied for SLA fabricated soft tissue scaffolds, other classes of macromolecules are also of interest. Polyurethanes offer an ability to hydrogen bond inter/intramolecularly, leading to physically crosslinked networks. These macromolecules are commonly used as adhesives and elastomers due to the hydrogen bonding ability along with tailored flexibility from macromolecular design. Poly(dimethyl siloxane)/polyurethane blends afforded non-cytotoxic materials while exhibiting mechanical and elastic properties similar to various soft tissues.¹⁷⁷ Tailoring these macromolecules for SLA fabrication could lead to interesting new scaffolds. Due to the hydrophobic nature of the PDMS along with the hydrolytically and enzymatically stable urethane linkage, poly(dimethyl siloxane)/polyurethane blends seem more suitable for permanent or longer lasting implanted applications.

Other classes of polymers not as commonly studied for use as biomaterials in SLA include polycarbonates⁷⁰ and poly(β -thioesters).¹⁷⁸ Methacrylated three-arm poly(trimethylene carbonate) macromers were fabricated into gyroid pore architectures using SLA.⁷⁶ Seeding with bovine chondrocytes resulted in cell adhesion and proliferation, leading to an increase in compression modulus of about 50 % up to around 100 kPa, close to the modulus needed for soft connective tissue. Polycarbonates commonly undergo surface erosion, facilitated by enzymatic degradation.^{92, 179-180}

9.6.2 Natural Polymers

Unlike synthetic macromolecules, natural polymers' properties are difficult to control and manipulate. However, they offer the advantage of providing cells with binding

sites and chemistry that better mimic the *in vivo* environment. When synthesizing macromolecules, altering backbone structure is accomplished through changing the monomer selection. Changes in properties such as tensile modulus, compression strength, and degree of swelling, result from tuning the polymer structure and morphology through monomer selection and processing techniques. Natural polymer classes have similar backbone structures with minor changes or alterations, and are extremely difficult and expensive to synthesize in a lab. Therefore, property modification is most commonly accomplished through adding/altering pendant functionality on the polymer backbone. This is difficult due to limited solubility of some natural polymers and also the presence of multiple reactive sites or pendant functionality on each backbone repeating unit, as seen in **Figure 9.14**.

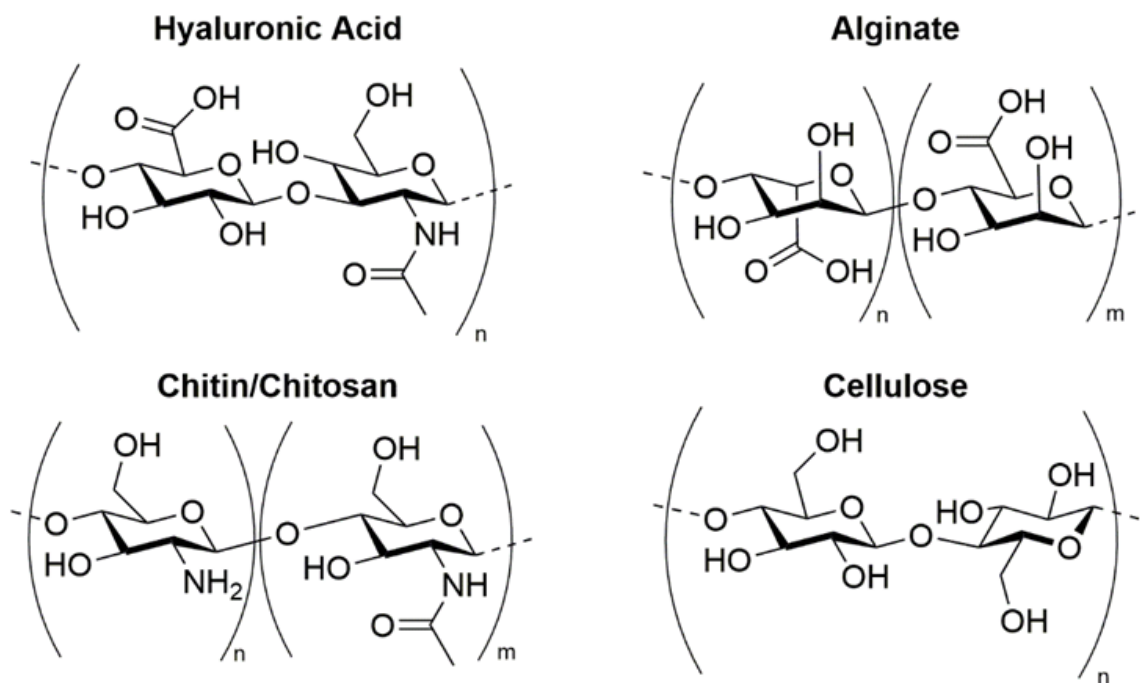


Figure 9.14: General chemical structure of polysaccharides hyaluronic acid, alginate, chitin/chitosan, and cellulose. Chitin contains more than 50% acetylated repeat units ($m > 50\%$) while chitosan contains less than 50% acetylated repeat units ($m < 50\%$).

Scaffolds of naturally derived material such as collagen, hyaluronic acid, alginate, etc. have been used in tissue engineering applications owing to their similarities to the ECM. These materials are either components of or have properties similar to natural ECM and possess desirable characteristics such as biocompatibility, biodegradability and inherent cell recognition sites. Polysaccharides and polypeptides are the main types of natural polymers that have been employed for tissue engineering applications. These polymers innately possess biofunctional groups that aid in the attachment, proliferation and growth of cells and are enzymatically biodegradable. These are generally modified by introducing methacrylate groups in the backbone of polymer matrix that affords photopolymerization to yield hydrogels.

9.6.2.1 Polysaccharides

9.6.2.1.1 Hyaluronic Acid

Hyaluronic acid (HA) also known as hyaluronan is a major glycosaminoglycan linked by $\beta(1,4)$ and $\beta(1,3)$ glucosidic bonds. Owing to its important physiological role in tissue repair, its biocompatibility, viscoelastic properties and the ease of functionalization, hydrogel scaffolds of unmodified and derivatized HA have been employed for a variety of biomedical applications.¹⁸¹

Fabrication and characterization of 3D scaffolds of HA for neural tissue repair and vascularization has been previously reported.^{32, 65} Synthesis of glycidyl methacrylate (GM) modified HA, which was later cross-linked in the presence of a photoinitiator, produced 3D freeform structures using a digital micro-mirror-array device. 3D microfabricated scaffolds of HA with micron-scale features of different geometries and pore sizes were synthesized to mimic native nerve tissue, as seen in **Figure 9.15**. The study reported a

control over the dimensions and geometry of the scaffold architecture by controlling the exposure to UV light. Biologically active HA scaffolds of circular and hexagonal geometries with 100-200 μm pore sizes were also reported to enable cell adhesion. Synthesis of customized scaffolds with microarchitecture such as cylindrical conduits enabled fabrication of channels and branches that resembles native branched nerves.³² However, the study did not report mechanical properties and modulus of these hydrogels. Another study utilized a visible-light-based projection stereolithography (VL-PSL) system to encapsulate human adipose-derived stem cells in a methacrylated biodegradable polymer of [poly-D,L-lactic acid/polyethylene glycol/poly-D,L-lactic acid (PDLLA-PEG)]/HA. The study reported synthesis of live cells constructs with customized architecture (spherical, cuboidal, and cylindrical) with mechanical properties that supported chondrogenesis of stem cells for cartilage regeneration. Methacrylated PDLLA-PEG and HA were prepared and their ratios were tuned to yield scaffolds with mechanical properties similar to that of cartilage. Post fabrication, cells exhibited and maintained high viability over a 28-day span, and maintained relatively high mechanical strength (compressive modulus of 780 kPa on day 0 vs. 240 kPa after 28 days). Cells seeded in scaffolds during fabrication and grown in chondrogenic medium showed increased chondrogenic gene expression and cartilage ECM deposition.¹⁸² Neocartilage was observed in methacrylated hyaluronic acid (MeHA) gels seeded with swine auricular chondrocytes.¹⁸³ Follow up of this system revealed optimal neocartilage formation with 50 kDa MeHA hydrogels *in vivo*.¹⁸⁴ A recently published study on photocrosslinkable HA reported a UV-light reactive cross-linkable HA matrix loaded with kartogenin (KGN) nanoparticles to induce chondrogenesis and hyaline cartilage formation *in vivo*.¹⁸⁵

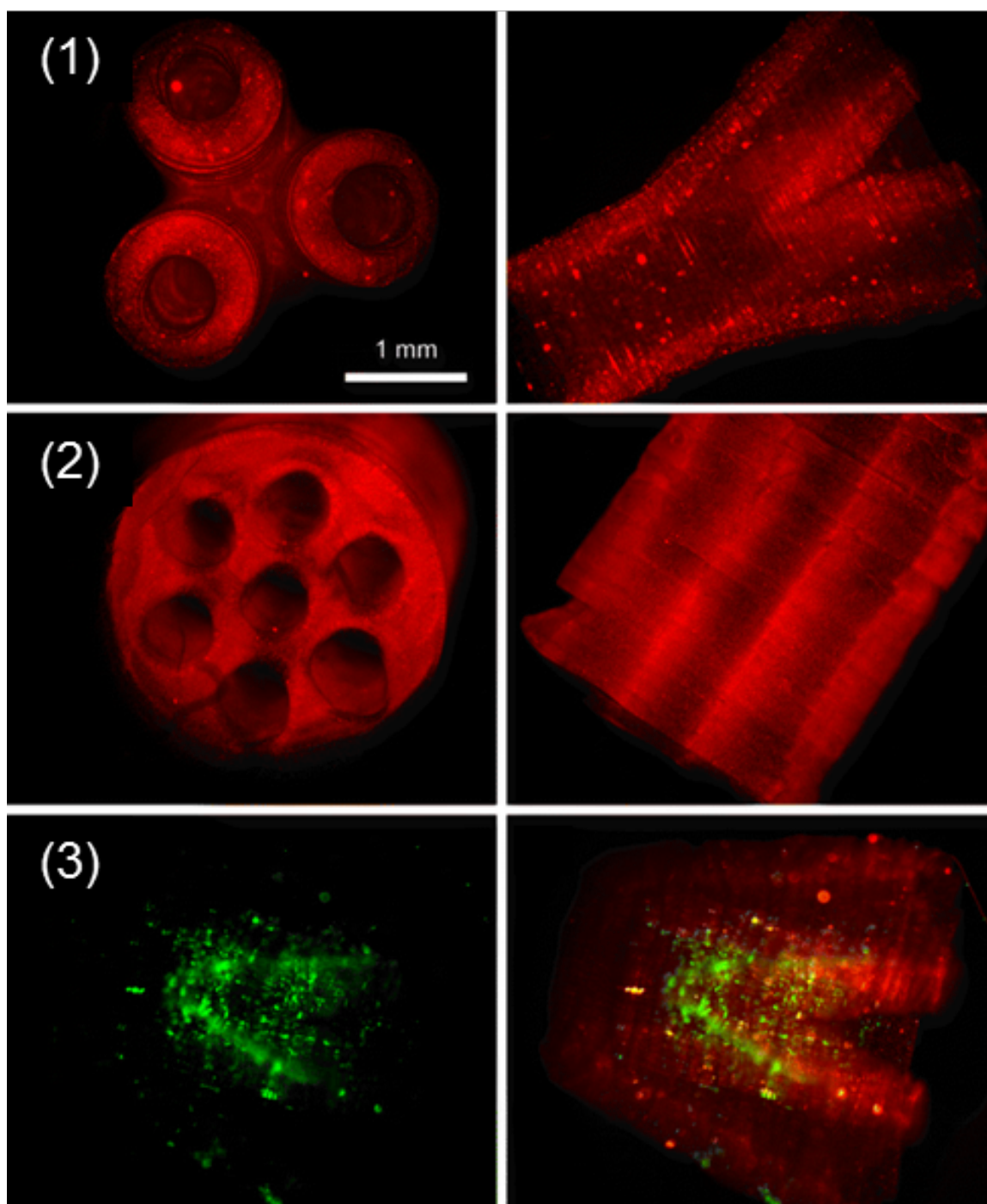


Figure 9.15: Fluorescence microscopy images of hyaluronic acid based SLA scaffolds. Row (1) shows the branched tubular portion of the vasculature like scaffold. Row (2) depicts the top and lateral scaffold sides. Row (3) confirms cell adhesion and viability in the tubular scaffold regions. Adapted from Suri and Schmidt *et al.*³²

Scaffolds of MeHA have also been studied for heart valve tissue engineering.¹⁸⁶ Methacrylated HA was investigated as a scaffold for valvular interstitial cell (VIC) growth and proliferation. The study reported that VICs spread and proliferated on HA-based scaffolds compared to collagen and laminin-coated surfaces. However, the study did not investigate mechanical properties of synthesized scaffolds or 3D printing using SLA. A follow-up on the methacrylated HA system from the previous study that supported growth and proliferation of VIC for heart valve engineering was reported. Physical properties of MeHA were tuned by varying the degree of methacrylation and/or by copolymerizing with PEGDA. Incorporation of PEG resulted in increased mechanical stiffness [12 kPa (0% PEG) vs. 54.7 kPa (10%PEG) compressive modulus]. The molecular weight of HA degradation products affected VIC proliferation, with lower molecular weight inducing higher proliferation. Low molecular weight of HA led to an increase in elastin production, an essential component of heart ECM. Other materials reported no detectable elastin content *in vitro*. Photopolymerized HA can be 3D printed with encapsulated VICs to yield a defined microarchitecture and stiffness for use in tissue-engineered heart valves.¹⁸⁷ Several other studies have reported modification of HA with methacrylic anhydride or glycidyl methacrylate to yield MeHA, which can be further photopolymerized to yield hydrogels.^{69, 188-191} Both the influence of degree of methacrylation on bulk mechanical properties of the hydrogels and the effect of degree of methacrylation, photoinitiator concentration and UV time exposure on hydrogel formation have been studied. Increase in crosslink density led to a decrease in degradation rates but had insignificant effect on human aortic endothelial cell viability. A tunable photocrosslinked MeHA system capable of encapsulating hMSCs has also been developed. By modulating elastic moduli over

several orders of magnitude, hMSC morphology and differentiation can be tuned towards a soft (cartilage) vs. stiff (bone) tissue. Thus, based on the application desired, these photocrosslinkable gels can be 3D printed to a desired architecture, porosity and stiffness that mimics the native tissue of interest.

9.6.2.1.2 Alginate

Alginate, a natural polysaccharide has two repeating monomer units, β -D-mannuronate and α -L-guluronate, that are joined by a $\beta(1-4)$ linkage. The ease of forming alginate gels, by exposing it to divalent ions such as calcium to form crosslinks, has made it a popular material for cell encapsulation, tissue engineering and drug delivery applications.¹⁹²

Although, the most commonly used method to crosslink alginate is by using divalent or trivalent ions to form ionic binding between G-blocks of alginate backbone giving rise to a three dimensional structure, few studies on photocrosslinked alginate networks have been reported. A hydrogel system consisting of oxidized methacrylic alginate (OMA) (linked with RGD) and poly(ethylene glycol) methyl ether methacrylate (PEGMEM) using SLA for myoblast cells (MC), adipose derived stem cells and rat hippocampal neurons (HN) was synthesized and characterized.³⁰ Elastic modulus of fabricated hydrogels was found to be around 12 kPa which is ideal for culturing skeletal muscle tissue. A detailed cell viability analysis of MC and HN alone in 3D encapsulated gels was performed followed by a co-culture of these cells. SLA afforded control over the spatial distribution and adhesion of multiple cell types. MCs alone proliferated in the hydrogels in presence of RGD and formed tube like structures while HNs extended throughout the gels over a 14-day period. Co-culture 3D systems showed enhanced

functionality and can be used to study differentiation of stem cells towards neurogenic or myogenic lineage (depending on modulus, environment, surrounding cell type, etc.). Another study reported synthesis of photocrosslinkable three-dimensional alginate-chondrocyte hydrogel scaffolds for cartilage regeneration.³¹ Alginate solution was modified with methacrylic anhydride and the effect of photoinitiator, UV exposure time and solvent on chondrocyte cell viability was studied. Gels of 10-20 kPa modulus range were obtained and cell viability of >90% was observed for a range of photoinitiators tested. 3D-photocrosslinked RGD-modified alginate hydrogels to support adipose progenitor cells (APC) to recreate ECM mechanics and tissue properties similar to normal and pathological adipose tissue has also been reported.⁷⁷ Photocrosslinkable alginate was functionalized with methacrylic anhydride followed by modification with RGD peptides. Crosslinking density was tuned to yield gels of 3.3, 7.9 and 12.4 kPa elastic moduli representing physiological (~2 kPa), intermediate, and pathological (~12 kPa) stiffness ranges. The study revealed increased ECM stiffness (higher degree of crosslinking owing to photocrosslinking by increased methacrylation) increased proliferative and angiogenic potential of cells while inhibiting adipose differentiation. Adipose regeneration is an important process for breast reconstruction for patients undergoing tumor resection. Composite photocrosslinked alginate hydrogels with compliant and stiff compartments can be synthesized to promote adipogenesis and angiogenesis to engineer adipose tissue regeneration.⁷⁷

9.6.2.1.3 Chitosan:

Chitosan is a positively charged polymer obtained from deacetylated chitin. It contains D-glucosamine with randomly dispersed N-acetyl-D-glycosamine groups linked

at the $\beta(1-4)$ site. Properties of chitosan are similar to HA due to their common monomer units. Therefore, chitosan closely simulates glycosaminoglycans within the ECM of tissues. Owing to its ease in processing, biocompatibility and degradability, chitosan has been used in hydrogels and scaffolds synthesis for tissue engineering.¹⁹³⁻¹⁹⁴ It also has antibacterial properties and can be used as a release system for bioactive factors.¹⁹⁵ Recently, SLA was used to fabricate a hybrid biocompatible resin of chitosan and PEGDA. Ear-shaped hybrid bioscaffolds were printed using different polymer ratios. The 3D printed scaffolds showed interconnected pore structure with a pore size of 50 μm and an elastic modulus of ~ 400 kPa, as seen in **Figure 9.16** and **Figure 9.17**. Long term viability of hMSCs was observed on these scaffolds. This hybrid scaffold system with pore interconnectivity and mechanical strength can be utilized for cartilage tissue engineering.¹⁹⁶ Chitosan along with heparin and hyaluronan was functionalized with a styryl or a methacryloyl group that formed hydrogels upon visible light irradiation. Tubular structures of methacrylated polysaccharide and methacrylated gelatin were formed by photocrosslinking that can be used for tissue engineering applications.¹⁹⁷ Photocrosslinkable chitosan has also been used to create patterned surfaces (lanes, squares, circles, triangles) with near μm resolution using a single mask and different UV exposure times. Cardiac fibroblasts, cardiomyocytes and osteoblasts seeded on these were viable up to 18 days.¹⁹⁸

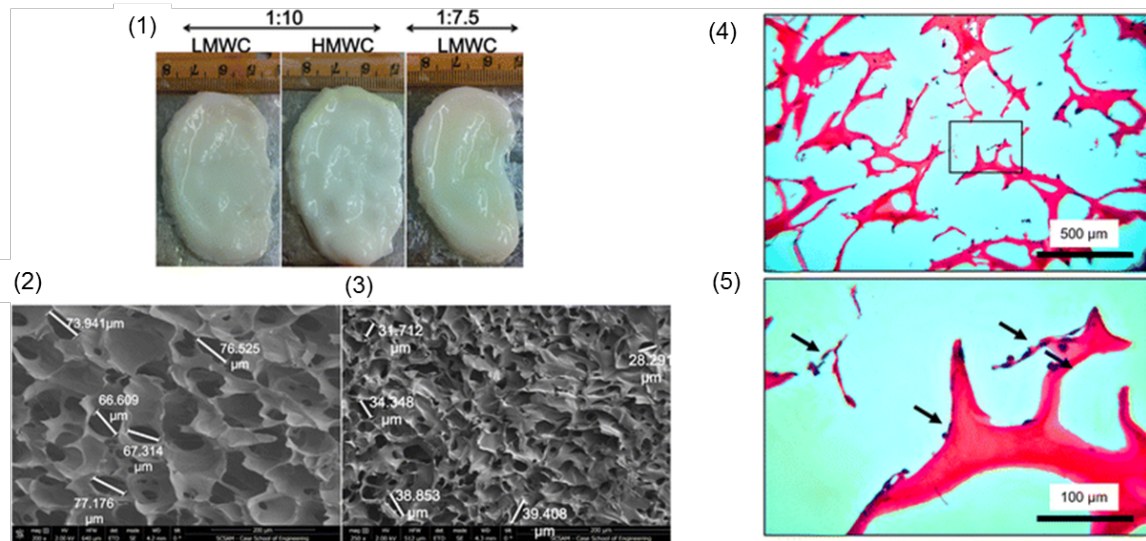


Figure 9.16: (1) demonstrates printed parts with various molecular weight chitosan and ratios to PEGDA. (2) and (3) demonstrate porosity of various compositions. (4) and (5) display cellular adhesion to scaffolds. Adapted from Morris and Akkus *et al.*¹⁹⁶

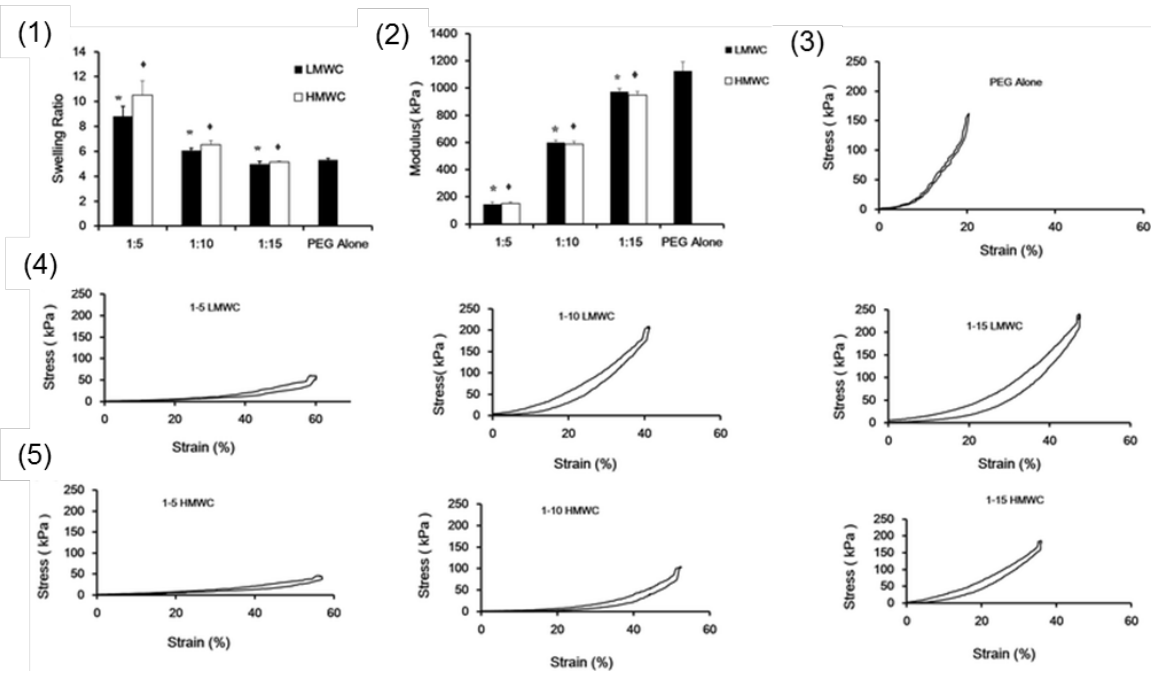


Figure 9.17: (1) demonstrates degree of swelling between low and high molecular weight chitosan. (2) shows compression modulus values for low and high molecular weight chitosan. (3) is a representative stress strain curve of PEGDA. (4) highlights stress strain curves of low molecular weight chitosan samples. (5) portrays stress strain curves of high molecular weight chitosan. Adapted from Morris and Akkus *et al.*¹⁹⁶

9.6.2.2 Polypeptides

Collagen is one of the most commonly used polymers in tissue engineering applications. It is a major component of musculoskeletal tissue and has several biological functions including providing tissue strength. It is composed of three polypeptide chains intertwined to form a triple helix, with a repeating sequence of glycine-X-Y, X and Y are generally proline and/or hydroxyproline. Gelatin is derived by denaturing the triple helix structure of collagen. Like collagen, it is used in a variety of cell based applications.²⁷

9.6.2.2.1 Gelatin

Methacrylated gelatin (MeGEL) was synthesized by reacting the primary amine groups in the backbone with methacrylic anhydride which was photocrosslinked with UV to form gels.⁴³ The effect of degree of methacrylation and gel concentration on mechanical properties was also studied. The compressive modulus of gels varied from 3-30 kPa depending on the degree of methacrylation, as seen in **Figure 9.18**. MeGEL allowed for cell (NIH3T3 fibroblasts and human umbilical vein endothelial cells) migration, organization and interaction in both 2D and 3D environment.⁴³ Another study reported methacrylamide modified gelatin which was photopolymerized to form gels and support hASC proliferation and differentiation into adipocytes.¹⁹⁹ In these experiments, gelatin was functionalized with methacrylic anhydride to introduce photocrosslinkable groups. They studied the effect of degree of substitution, UV exposure time, and initiator concentration on the modulus of the gels. The lysine and hydroxylysine residues on collagen backbone were modified to incorporate acrylate moiety onto them. Photocrosslinking of acrylated collagen under visible light in presence of rat aortic smooth muscle cells was performed. A significant increase in shear modulus of the gels was observed after crosslinking (30 vs.

160 kPa). Although the shear modulus was found to be lower than the strength required for *in vivo* application such as vascular grafts, cell viability and function was maintained after the crosslinking process.²⁰⁰ In addition to methacrylic anhydride, collagen has been modified using EDC/NHS conjugation to incorporate cinnamate groups onto collagen which can be further photocrosslinked. This study reported a Young's modulus of 1.31-3.78 MPa of photocrosslinked collagen gels comparable to those obtained by glutaraldehyde crosslinking.²⁰¹

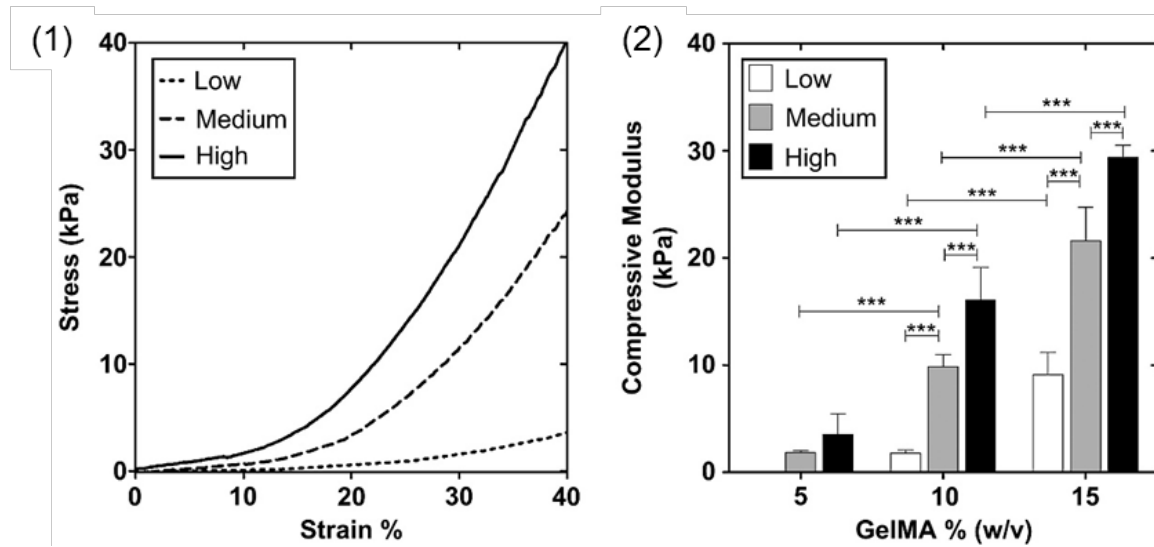


Figure 9.18: Mechanical properties of MeGEL hydrogels. (1) shows compressive modulus for varying % crosslinked hydrogels as a function of strain %. (2) depicts the compressive modulus values of the % crosslinked hydrogels at different (w/v) %. Adapted from Nichol and Khademhosseini *et al.*⁴³

Few examples exist of SLA fabricated scaffolds using polypeptides that test the mechanical properties necessary to mimic native tissue. One study fabricated scaffolds out of poly(ethylene glycol-*co*-depsipeptide) (PEG-*co*-PDP) using visible light SLA.⁶⁶ PEG-*co*-PDP was crosslinked with RGD functionalized PEG acrylate to enhance cellular adhesion and proliferation. Mechanical stiffness was determined to be from 3 ± 1 to 38 ± 13 kPa, dependent on the layer cure times. Degradation studies over 7 days in PBS resulted

in 13-21% mass loss and a loss of stiffness by ~10%. This SLA resin was used to fabricate tubular structures as scaffolds for vasculature, as seen in **Figure 9.19**. Another study fabricated porous scaffolds using MeGEL for meniscus scaffolding.²⁹ After cell adhesion, human avascular meniscus cells aligned along the scaffold strands. Scaffolds exhibited Young's modulus of 14.3 ± 4.0 kPa, appropriate for soft tissue, cartilage like applications. The scaffolds retained its modulus over 2 weeks with no cells and saw a decrease of ~10% after 2 weeks with cells. These initial attempts to determine mechanical and biological properties of gelatin based scaffolds help design the next set of advanced scaffolds for tissue engineering.

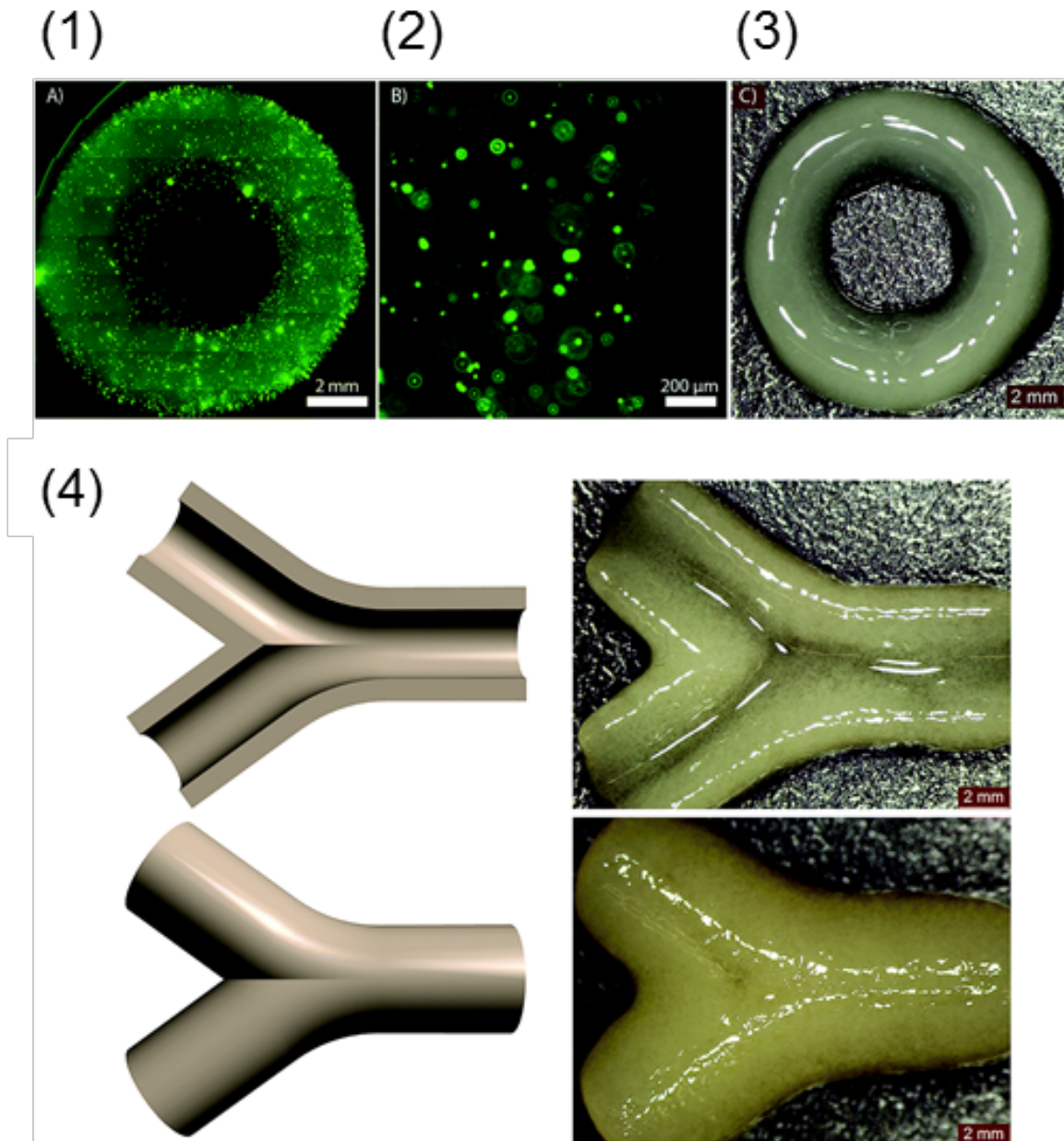


Figure 9.19: Poly(ethylene glycol-*co*-depsipeptide) fabricated scaffolds. (1) and (2) show fluorescent images of scaffolds. (3) is the cell-laden scaffold, while (4) depicts the CAD model and constructed vasculature. Adapted from Elomaa and Yang *et al.*⁶⁶

Natural polymers, by virtue of their origin, contain biofunctional moieties that are cytocompatible and biodegradable. The strategies described above to functionalize polysaccharides and polypeptides into photocrosslinkable polymers opens new avenues

and encourages further studies that are needed to use these functional biomaterials in SLA applications. There is scope, especially in case of polypeptides, to develop novel chemistries that enable introduction of photopolymerizable groups onto the backbone, while further utilizing the advantages of SLA system to obtain intricate geometries that mimic the tissue of interest.

9.7 Perspective

One way of accelerating the rate of 3D printing using SLA is to heat the polymer, making the resin less viscous, therefore increasing diffusion of the reactive groups and lower recoating times. The ability to heat the polymer bath also increases the number of printable materials using SLA due to increased temperatures lowering viscosity and allowing polymers with higher than room temperature thermal transitions to be processable. Concern arises in the final construct maintaining the desired dimensions, size, and shape of the scaffold. Heating typically causes expansion of the material and when the construct cools, shrinkage could lead to inaccurate dimensions and pore sizes of the scaffold. Understanding how heating the resin to increase printability and print times affects the final scaffold's dimensions and mechanical properties will help expand the library SLA printable materials to polymers with room temperature properties not suitable from this processing technique. Another area of concern from objects printed using SLA is anisotropic properties arising from the direction of printing a scaffold. More work on how the printing orientation compared to the scaffold's orientation affects mechanical properties is needed to ensure constructs maintain sufficient properties for use.

Combining the knowledge of chemistry, materials science, and biology is key to developing a practical biodegradable soft tissue engineering scaffold. Using SLA, the

architecture and porosity needed for tissue engineering scaffolds is easily tuned in fabricated scaffolds. Synthetic or natural polymers alone do not exhibit all of the properties necessary for an optimal scaffold. Testing new polymers and combining the properties of polymeric systems already studied helps develop new and improved biodegradable tissue engineering scaffolds. The first step is suitable polymers for SLA. Oligomers, star polymers, and hyperbranched systems all help attain the properties necessary for SLA. These polymers must also retain the ability to degrade and must maintain the mechanical properties necessary to replace the target tissue once processed. Understanding the chemical, mechanical and biological properties of synthetic and natural polymers, new scaffolds combining various materials with enhanced properties stemming from the individual polymeric parts can be constructed to afford new and improved biodegradable tissue engineering scaffolds.

Synthetic polymers offer ease of tuning properties through monomer selection, molecular weight targeting, and functionalization. This allows for a broader range of targeted applications relative to natural polymers. One drawback is that not all synthetic polymers have the desired biodegradability and ability to adhere, differentiate, and proliferate cells. Most natural polymers inherent ability to interact with cells make them ideal candidates for tissue scaffolds but limited work has been done on natural polymers with SLA due to cost and difficulty achieving desired tissue-mimicking properties. Therefore, combining synthetic, tunable polymer mechanical properties with natural polymer's biological properties gives the best chance of combining the desired mechanical properties with biological properties to create a functional tissue engineering scaffold.

9.8 References

1. Langer, R.; Vacanti, J. P., Tissue Engineering. *Science* **1993**, 260 (5110), 920-926.
2. Nichol, J. L.; Morozowich, N. L.; Allcock, H. R., Biodegradable alanine and phenylalanine alkyl ester polyphosphazenes as potential ligament and tendon tissue scaffolds. *Polymer Chemistry* **2013**, 4 (3), 600-606.
3. Caliarì, S. R.; Ramirez, M. A.; Harley, B. A. C., The development of collagen-GAG scaffold-membrane composites for tendon tissue engineering. *Biomaterials* **2011**, 32 (34), 8990-8998.
4. Butler, D. L.; Juncosa-Melvin, N.; Boivin, G. P.; Galloway, M. T.; Shearn, J. T.; Gooch, C.; Awad, H., Functional tissue engineering for tendon repair: A multidisciplinary strategy using mesenchymal stem cells, bioscaffolds, and mechanical stimulation. *J Orthopaed Res* **2008**, 26 (1), 1-9.
5. Ozdil, D.; Aydin, H. M., Polymers for medical and tissue engineering applications. *Journal of Chemical Technology & Biotechnology* **2014**, 89, 1793-1810.
6. Place, E. S.; George, J. H.; Williams, C. K.; Stevens, M. M., Synthetic polymer scaffolds for tissue engineering. *Chemical Society Reviews* **2009**, 38 (4), 1139-1151.
7. Annabi, N.; Nichol, J. W.; Zhong, X.; Ji, C. D.; Koshy, S.; Khademhosseini, A.; Dehghani, F., Controlling the Porosity and Microarchitecture of Hydrogels for Tissue Engineering. *Tissue Eng Part B-Re* **2010**, 16 (4), 371-383.
8. Hollister, S. J.; Maddox, R. D.; Taboas, J. M., Optimal design and fabrication of scaffolds to mimic tissue properties and satisfy biological constraints. *Biomaterials* **2002**, 23 (20), 4095-4103.
9. Kemppainen, J. M.; Hollister, S. J., Tailoring the mechanical properties of 3D-designed poly(glycerol sebacate) scaffolds for cartilage applications. *J Biomed Mater Res A* **2010**, 94A (1), 9-18.
10. Zhang, P. B.; Hong, Z. K.; Yu, T.; Chen, X. S.; Jing, X. B., In vivo mineralization and osteogenesis of nanocomposite scaffold of poly (lactide-co-glycolide) and hydroxyapatite surface-grafted with poly(L-lactide). *Biomaterials* **2009**, 30 (1), 58-70.
11. Ji, C. D.; Annabi, N.; Khademhosseini, A.; Dehghani, F., Fabrication of porous chitosan scaffolds for soft tissue engineering using dense gas CO₂. *Acta Biomater* **2011**, 7 (4), 1653-1664.
12. Pham, Q. P.; Sharma, U.; Mikos, A. G., Electrospinning of polymeric nanofibers for tissue engineering applications: A review. *Tissue Eng* **2006**, 12 (5), 1197-1211.
13. Bajaj, P.; Schweller, R. M.; Khademhosseini, A.; West, J. L.; Bashir, R., 3D biofabrication strategies for tissue engineering and regenerative medicine. *Annual review of biomedical engineering* **2014**, 16, 247-76.
14. Gross, B. C.; Erkal, J. L.; Lockwood, S. Y.; Chen, C. P.; Spence, D. M., Evaluation of 3D Printing and Its Potential Impact on Biotechnology and the Chemical Sciences. *Anal. Chem.* **2014**, 86 (7), 3240-3253.
15. Hockaday, L. A.; Duan, B.; Kang, K. H.; Butcher, J. T., 3D-Printed Hydrogel Technologies for Tissue-Engineering Heart Valves. *3D Printing and Additive Manufacturing* **2014**, 1, 122-136.
16. Huttmacher, D. W.; Sittinger, M.; Risbud, M. V., Scaffold-based tissue engineering: rationale for computer-aided design and solid free-form fabrication systems. *Trends Biotechnol* **2004**, 22 (7), 354-362.

17. Peltola, S. M.; Melchels, F. P. W.; Grijpma, D. W.; Kellomaki, M., A review of rapid prototyping techniques for tissue engineering purposes. *Ann Med* **2008**, *40* (4), 268-280.
18. LeMaitre, J., *Handbook of Materials Behavior Models, Three-Volume Set: Nonlinear Models and Properties*. Academic Press: 2001.
19. O'Brien, F. J., Biomaterials & scaffolds for tissue engineering. *Mater Today* **2011**, *14* (3), 88-95.
20. Wust, S.; Muller, R.; Hofmann, S., Controlled Positioning of Cells in Biomaterials-Approaches Towards 3D Tissue Printing. *Journal of functional biomaterials* **2011**, *2* (3), 119-154.
21. Williams, C. G.; Malik, A. N.; Kim, T. K.; Manson, P. N.; Elisseeff, J. H., Variable cytocompatibility of six cell lines with photoinitiators used for polymerizing hydrogels and cell encapsulation. *Biomaterials* **2005**, *26* (11), 1211-1218.
22. Occhetta, P.; Visone, R.; Russo, L.; Cipolla, L.; Moretti, M.; Rasponi, M., VA-086 methacrylate gelatine photopolymerizable hydrogels: A parametric study for highly biocompatible 3D cell embedding. *J Biomed Mater Res A* **2015**, *103* (6), 2109-2117.
23. Wang, Z. J.; Abdulla, R.; Parker, B.; Samanipour, R.; Ghosh, S.; Kim, K., A simple and high-resolution stereolithography-based 3D bioprinting system using visible light crosslinkable bioinks. *Biofabrication* **2015**, *7* (4).
24. Pedde, R. D.; Mirani, B.; Navaei, A.; Styran, T.; Wong, S.; Mehrali, M.; Thakur, A.; Mohtaram, N. K.; Bayati, A.; Dolatshahi-Pirouz, A.; Nikkhah, M.; Willerth, S. M.; Akbari, M., Emerging Biofabrication Strategies for Engineering Complex Tissue Constructs. *Adv. Mater.* **2017**, *29* (19).
25. Fairbanks, B. D.; Schwartz, M. P.; Bowman, C. N.; Anseth, K. S., Photoinitiated polymerization of PEG-diacrylate with lithium phenyl-2,4,6-trimethylbenzoylphosphinate: polymerization rate and cytocompatibility. *Biomaterials* **2009**, *30* (35), 6702-6707.
26. Raman, R.; Bhaduri, B.; Mir, M.; Shkumatov, A.; Lee, M. K.; Popescu, G.; Kong, H.; Bashir, R., High-Resolution Projection Microstereolithography for Patterning of Neovasculature. *Adv Healthc Mater* **2016**, *5* (5), 610-619.
27. Yue, K.; Trujillo-de Santiago, G.; Alvarez, M. M.; Tamayol, A.; Annabi, N.; Khademhosseini, A., Synthesis, properties, and biomedical applications of gelatin methacryloyl (GelMA) hydrogels. *Biomaterials* **2015**, *73*, 254-271.
28. Soman, P.; Chung, P. H.; Zhang, A. P.; Chen, S. C., Digital Microfabrication of User-Defined 3D Microstructures in Cell-Laden Hydrogels. *Biotechnol Bioeng* **2013**, *110* (11), 3038-3047.
29. Grogan, S. P.; Chung, P. H.; Soman, P.; Chen, P.; Lotz, M. K.; Chen, S. C.; D'Lima, D. D., Digital micromirror device projection printing system for meniscus tissue engineering. *Acta Biomater* **2013**, *9* (7), 7218-7226.
30. Zorlutuna, P.; Jeong, J. H.; Kong, H.; Bashir, R., Stereolithography-Based Hydrogel Microenvironments to Examine Cellular Interactions. *Advanced Functional Materials* **2011**, *21* (19), 3642-3651.
31. Rouillard, A. D.; Berglund, C. M.; Lee, J. Y.; Polacheck, W. J.; Tsui, Y.; Bonassar, L. J.; Kirby, B. J., Methods for Photocrosslinking Alginate Hydrogel Scaffolds with High Cell Viability. *Tissue Eng Part C-Me* **2011**, *17* (2), 173-179.

32. Suri, S.; Han, L. H.; Zhang, W. D.; Singh, A.; Chen, S. C.; Schmidt, C. E., Solid freeform fabrication of designer scaffolds of hyaluronic acid for nerve tissue engineering. *Biomed Microdevices* **2011**, *13* (6), 983-993.
33. Melhem, M. R.; Park, J.; Knapp, L.; Reinkensmeyer, L.; Cvetkovic, C.; Flewellyn, J.; Lee, M. K.; Jensen, T. W.; Bashir, R.; Kong, H.; Schook, L. B., 3D printed stem cell-laden, microchanneled hydrogel patch for the enhanced release of cell-secreting factors and treatment of myocardial infarctions. *ACS Biomaterials Science & Engineering* **2016**.
34. Baudis, S.; Heller, C.; Liska, R.; Stampfl, J.; Bergmeister, H.; Weigel, G., (Meth)Acrylate-Based Photoelastomers as Tailored Biomaterials for Artificial Vascular Grafts. *J. Polym. Sci. Pol. Chem.* **2009**, *47* (10), 2664-2676.
35. Warner, J.; Soman, P.; Zhu, W.; Tom, M.; Chen, S., Design and 3D Printing of Hydrogel Scaffolds with Fractal Geometries. *ACS Biomaterials Science & Engineering* **2016**.
36. Zant, E.; Grijpma, D. W., Synthetic Biodegradable Hydrogels with Excellent Mechanical Properties and Good Cell Adhesion Characteristics Obtained by the Combinatorial Synthesis of Photo-Cross-Linked Networks. *Biomacromolecules* **2016**, *17*, 1582-1592.
37. Akopova, T. A.; Demina, T. S.; Bagratashvili, V. N.; Bardakova, K. N.; Novikov, M. M.; Selezneva, I. I.; Istomin, A. V.; Svidchenko, E. A.; Cherkaev, G. V.; Surin, N. M.; Timashev, P. S., Solid state synthesis of chitosan and its unsaturated derivatives for laser microfabrication of 3D scaffolds. *IOP Conference Series: Materials Science and Engineering* **2015**, *87*, 012079.
38. Neiman, J. A. S.; Raman, R.; Chan, V.; Rhoads, M. G.; Raredon, M. S. B.; Velazquez, J. J.; Dyer, R. L.; Bashir, R.; Hammond, P. T.; Griffith, L. G., Photopatterning of Hydrogel Scaffolds Coupled to Filter Materials Using Stereolithography for Perfused 3D Culture of Hepatocytes. *Biotechnol Bioeng* **2015**, *112* (4), 777-787.
39. Elomaa, L.; Teixeira, S.; Hakala, R.; Korhonen, H.; Grijpma, D. W.; Seppala, J. V., Preparation of poly(epsilon-caprolactone)-based tissue engineering scaffolds by stereolithography. *Acta Biomater* **2011**, *7* (11), 3850-3856.
40. Lin, H.; Cheng, A. W.; Alexander, P. G.; Beck, A. M.; Tuan, R. S., Cartilage tissue engineering application of injectable gelatin hydrogel with in situ visible-light-activated gelation capability in both air and aqueous solution. *Tissue engineering. Part A* **2014**, *20* (17-18), 2402-11.
41. Nguyen, Q. T.; Hwang, Y.; Chen, A. C.; Varghese, S.; Sah, R. L., Cartilage-like mechanical properties of poly (ethylene glycol)-diacrylate hydrogels. *Biomaterials* **2012**, *33* (28), 6682-6690.
42. Hutson, C. B.; Nichol, J. W.; Koshy, S.; Bae, H.; Aubin, H.; Khademhosseini, A., PEG-methacrylated gelatin composite hydrogels with tunable mechanical and cell responsive properties. *Tissue Engineering: Part A* **2010**, *239*.
43. Nichol, J. W.; Koshy, S. T.; Bae, H.; Hwang, C. M.; Yamanlar, S.; Khademhosseini, A., Cell-laden microengineered gelatin methacrylate hydrogels. *Biomaterials* **2010**, *31* (21), 5536-5544.
44. Hockaday, L. A.; Kang, K. H.; Colangelo, N. W.; Cheung, P. Y. C.; Duan, B.; Malone, E.; Wu, J.; Girardi, L. N.; Bonassar, L. J.; Lipson, H.; Chu, C. C.; Butcher, J. T.,

Rapid 3D printing of anatomically accurate and mechanically heterogeneous aortic valve hydrogel scaffolds. *Biofabrication* **2012**, 4 (3).

45. Pereira, R. F.; Bártolo, P. J., Photocrosslinkable Materials for the Fabrication of Tissue-Engineered Constructs by Stereolithography. In *Computational Methods in Applied Sciences*, Springer Netherlands: 2014; Vol. 31, pp 149-178.
46. Gauvin, R.; Chen, Y. C.; Lee, J. W.; Soman, P.; Zorlutuna, P.; Nichol, J. W.; Bae, H.; Chen, S. C.; Khademhosseini, A., Microfabrication of complex porous tissue engineering scaffolds using 3D projection stereolithography. *Biomaterials* **2012**, 33 (15), 3824-3834.
47. Horn-Ranney, E. L.; Curley, J. L.; Catig, G. C.; Huval, R. M.; Moore, M. J., Structural and molecular micropatterning of dual hydrogel constructs for neural growth models using photochemical strategies. *Biomed Microdevices* **2013**, 15 (1), 49-61.
48. Jansen, J.; Melchels, F. P. W.; Grijpma, D. W.; Feijen, J., Fumaric Acid Monoethyl Ester-Functionalized Poly(D,L-lactide)/N-vinyl-2-pyrrolidone Resins for the Preparation of Tissue Engineering Scaffolds by Stereolithography. *Biomacromolecules* **2009**, 10 (2), 214-220.
49. Melchels, F. P. W.; Feijen, J.; Grijpma, D. W., A poly(D,L-lactide) resin for the preparation of tissue engineering scaffolds by stereolithography. *Biomaterials* **2009**, 30 (23-24), 3801-3809.
50. Lin, H.; Zhang, D. N.; Alexander, P. G.; Yang, G.; Tan, J.; Cheng, A. W. M.; Tuan, R. S., Application of visible light-based projection stereolithography for live cell-scaffold fabrication with designed architecture. *Biomaterials* **2013**, 34 (2), 331-339.
51. Chan, V.; Jeong, J. H.; Bajaj, P.; Collens, M.; Saif, T.; Kong, H.; Bashir, R., Multi-material bio-fabrication of hydrogel cantilevers and actuators with stereolithography. *Lab Chip* **2012**, 12 (1), 88-98.
52. Chung, C.; Mesa, J.; Randolph, M. A.; Yaremchuk, M.; Burdick, J. A., Influence of gel properties on neocartilage formation by auricular chondrocytes photoencapsulated in hyaluronic acid networks. *J Biomed Mater Res A* **2006**, 77A (3), 518-525.
53. Melchels, F. P. W.; Feijen, J.; Grijpma, D. W., A review on stereolithography and its applications in biomedical engineering. *Biomaterials* **2010**, 31 (24), 6121-6130.
54. Oudshoorn, M. H. M.; Penterman, R.; Rissmann, R.; Bouwstra, J. A.; Broer, D. J.; Hennink, W. E., Preparation and characterization of structured hydrogel microparticles based on cross-linked hyperbranched polyglycerol. *Langmuir* **2007**, 23 (23), 11819-11825.
55. Patel, P. N.; Smith, C. K.; Patrick, C. W., Rheological and recovery properties of poly(ethylene glycol) diacrylate hydrogels and human adipose tissue. *J Biomed Mater Res A* **2005**, 73A (3), 313-319.
56. Liu, V. A.; Bhatia, S. N., Three-dimensional photopatterning of hydrogels containing living cells. *Biomed Microdevices* **2002**, 4 (4), 257-266.
57. Melchels, F. P. W.; Bertoldi, K.; Gabbriellini, R.; Velders, A. H.; Feijen, J.; Grijpma, D. W., Mathematically defined tissue engineering scaffold architectures prepared by stereolithography. *Biomaterials* **2010**, 31 (27), 6909-6916.
58. Roll, E. B.; Dahl, J. E.; Runnigen, G.; Morisbak, E., In vitro cell death induced by irradiation and chemicals relevant for dental applications; dose-response and potentiation effects. *Eur J Oral Sci* **2004**, 112 (3), 273-279.

59. Hakala, R. A.; Korhonen, H.; Meretoja, V. V.; Seppala, J. V., Photo-Cross-Linked Biodegradable Poly(Ester Anhydride) Networks Prepared from Alkenylsuccinic Anhydride Functionalized Poly(epsilon-caprolactone) Precursors. *Biomacromolecules* **2011**, *12* (7), 2806-2814.
60. Elomaa, L.; Kang, Y. Q.; Seppala, J. V.; Yang, Y. Z., Biodegradable Photocrosslinkable Poly(depsipeptide-co-epsilon-caprolactone) for Tissue Engineering: Synthesis, Characterization, and In Vitro Evaluation. *J. Polym. Sci. Pol. Chem.* **2014**, *52* (23), 3307-3315.
61. Gunatillake, P. A. A., R., Biodegradable Synthetic Polymers for Tissue Engineering. *Eur. Cells Mater.* **2003**, *5*, 1-16.
62. Melchels, F. P. W.; Barradas, A. M. C.; van Blitterswijk, C. A.; de Boer, J.; Feijen, J.; Grijpma, D. W., Effects of the architecture of tissue engineering scaffolds on cell seeding and culturing. *Acta Biomater* **2010**, *6* (11), 4208-4217.
63. Seppala, J.; Korhonen, H.; Hakala, R.; Malin, M., Photocrosslinkable Polyesters and Poly(ester anhydride)s for Biomedical Applications. *Macromol Biosci* **2011**, *11* (12), 1647-1652.
64. Tanodekaew, S.; Channasanon, S.; Uppanan, P., Preparation and degradation study of photocurable oligolactide-HA composite: A potential resin for stereolithography application. *J Biomed Mater Res B* **2014**, *102* (3), 604-611.
65. Zhu, W.; Qu, X.; Zhu, J.; Ma, X.; Patel, S.; Liu, J.; Wang, P.; Sun, C.; Lai, E.; Gou, M.; Xu, Y.; Zhang, K.; Chen, S., Direct 3D bioprinting of prevascularized tissue constructs with complex microarchitecture. *Biomaterials* **2017**, *124*, 106-115.
66. Elomaa, L.; Pan, C. C.; Shanjani, Y.; Malkovskiy, A.; Seppala, J. V.; Yang, Y. Z., Three-dimensional fabrication of cell-laden biodegradable poly(ethylene glycol-co-depsipeptide) hydrogels by visible light stereolithography. *J Mater Chem B* **2015**, *3* (42), 8348-8358.
67. Huang, T. Q.; Qu, X.; Liu, J.; Chen, S. C., 3D printing of biomimetic microstructures for cancer cell migration. *Biomed Microdevices* **2014**, *16* (1), 127-132.
68. Bahney, C. S.; Lujan, T. J.; Hsu, C. W.; Bottlang, M.; West, J. L.; Johnstone, B., Visible light photoinitiation of mesenchymal stem cell-laden bioresponsive hydrogels. *Eur. Cells Mater.* **2011**, *22*, 43-55.
69. Smeds, K. A.; Grinstaff, M. W., Photocrosslinkable polysaccharides for in situ hydrogel formation. *J. Biomed. Mater. Res.* **2001**, *55* (2), 254-255.
70. Schuller-Ravoo, S.; Zant, E.; Feijen, J.; Grijpma, D. W., Preparation of a designed poly(trimethylene carbonate) microvascular network by stereolithography. *Adv Healthc Mater* **2014**, *3* (12), 2004-11.
71. van Bochove, B.; Hannink, G.; Buma, P.; Grijpma, D. W., Preparation of Designed Poly(trimethylene carbonate) Meniscus Implants by Stereolithography: Challenges in Stereolithography. *Macromol Biosci* **2016**, *16* (12), 1853-1863.
72. Guillaume, O.; Geven, M. A.; Grijpma, D. W.; Tang, T. T.; Qin, L.; Lai, Y. X.; Yuan, H.; Richards, R. G.; Eglin, D., Poly(trimethylene carbonate) and nano-hydroxyapatite porous scaffolds manufactured by stereolithography. *Polym. Adv. Technol.* **2016**.
73. Oesterreicher, A.; Wiener, J.; Roth, M.; Moser, A.; Gmeiner, R.; Edler, M.; Pinter, G.; Griesser, T., Tough and degradable photopolymers derived from alkyne

- monomers for 3D printing of biomedical materials. *Polym. Chem.* **2016**, 7 (32), 5169-5180.
74. Seck, T. M.; Melchels, F. P. W.; Feijen, J.; Grijpma, D. W., Designed biodegradable hydrogel structures prepared by stereolithography using poly(ethylene glycol)/poly(D,L-lactide)-based resins. *J Control Release* **2010**, 148 (1), 34-41.
 75. Skoog, S. A.; Goering, P. L.; Narayan, R. J., Stereolithography in tissue engineering. *J Mater Sci-Mater M* **2014**, 25 (3), 845-856.
 76. Schuller-Ravoo, S.; Teixeira, S. M.; Feijen, J.; Grijpma, D. W.; Poot, A. A., Flexible and Elastic Scaffolds for Cartilage Tissue Engineering Prepared by Stereolithography Using Poly(trimethylene carbonate)-Based Resins. *Macromol Biosci* **2013**, 13 (12), 1711-1719.
 77. Chandler, E. M.; Berglund, C. M.; Lee, J. S.; Polacheck, W. J.; Gleghorn, J. P.; Kirby, B. J.; Fischbach, C., Stiffness of Photocrosslinked RGD-Alginate Gels Regulates Adipose Progenitor Cell Behavior. *Biotechnol Bioeng* **2011**, 108 (7), 1683-1692.
 78. Kim, K.; Dean, D.; Wallace, J.; Breithaupt, R.; Mikos, A. G.; Fisher, J. P., The influence of stereolithographic scaffold architecture and composition on osteogenic signal expression with rat bone marrow stromal cells. *Biomaterials* **2011**, 32 (15), 3750-3763.
 79. Gabbrielli, R.; Turner, I. G.; Bowen, C. R., Development of Modelling Methods for Materials to be Used as Bone Substitutes. *Key Eng. Mater.* **2008**, 361-363, 903-906.
 80. Rashidi, H.; Yang, J.; Shakesheff, K. M., Surface engineering of synthetic polymer materials for tissue engineering and regenerative medicine applications. *Biomater. Sci.* **2014**, 2, 1318-1331.
 81. Chan, B. P.; Leong, K. W., Scaffolding in tissue engineering: general approaches and tissue-specific considerations. *Eur Spine J* **2008**, 17, S467-S479.
 82. Shiraishi, I.; Yamagishi, M.; Hamaoka, K.; Fukuzawa, M.; Yagihara, T., Simulative operation on congenital heart disease using rubber-like urethane stereolithographic biomodels based on 3D datasets of multislice computed tomography. *Eur J Cardio-Thorac* **2010**, 37 (2), 302-306.
 83. Bhatia, S. N.; Ingber, D. E., Microfluidic organs-on-chips. *Nature biotechnology* **2014**, 32 (8), 760-772.
 84. Reza, A.; Stephanie, K.; Alexander, H.; Bekir, Y.; Fariba, G.; Sara, K.; Michael, M.; Ali, K.; Savas, T., 3D-printed microfluidic devices. *Biofabrication* **2016**, 8 (2), 022001.
 85. Gou, M.; Qu, X.; Zhu, W.; Xiang, M.; Yang, J.; Zhang, K.; Wei, Y.; Chen, S., Bio-inspired detoxification using 3D-printed hydrogel nanocomposites. *Nat Commun* **2014**, 5, 3774.
 86. von Burkersroda, F.; Schedl, L.; Gopferich, A., Why degradable polymers undergo surface erosion or bulk erosion. *Biomaterials* **2002**, 23 (21), 4221-4231.
 87. Morozowich, N. L.; Mondschein, R. J.; Allcock, H. R., Comparison of the Synthesis and Bioerodible Properties of N-Linked Versus O-Linked Amino Acid Substituted Polyphosphazenes. *J. Inorg. Organomet. Polym. Mater.* **2014**, 24 (1), 164-172.
 88. Subramanian, A.; Krishnan, U. M.; Sethuraman, S., Development of biomaterial scaffold for nerve tissue engineering: Biomaterial mediated neural regeneration. *J Biomed Sci* **2009**, 16.

89. Shoichet, M. S., Polymer Scaffolds for Biomaterials Applications. *Macromolecules* **2010**, *43* (2), 581-591.
90. Wang, Y.; Kim, Y. M.; Langer, R., *In vivo* degradation characteristics of poly(glycerol sebacate). *J Biomed Mater Res A* **2003**, *66A* (1), 192-197.
91. Wei, H.; Zhuo, R. X.; Zhang, X. Z., Design and development of polymeric micelles with cleavable links for intracellular drug delivery. *Prog Polym Sci* **2013**, *38* (3-4), 503-535.
92. Bat, E.; Harmsen, M. C.; Platinga, J. A.; van Luyn, M. J. A.; Feijen, J.; Grijpma, D. W., Flexible scaffolds based on poly(trimethylene carbonate) networks for cardiac tissue engineering. *J. Controlled Release* **2010**, *148*, e74-e76.
93. Baines, F. C.; Bevington, J. C., A Tracer Study of the Hydrolysis of Methyl Methacrylate and Methyl Acrylate Units in Homopolymers and Copolymers. *J. Polym. Sci. Pol. Chem.* **1968**, *6*, 2433-2440.
94. Reed, A. M.; Gilding, D. K., Biodegradable Polymers for Use in Surgery - Poly(Glycolic)-Poly(Lactic Acid) Homo and Co-Polymers .2. Invitro Degradation. *Polymer* **1981**, *22* (4), 494-498.
95. Serra, T.; Ortiz-Hernandez, M.; Engel, E.; Planell, J. A.; Navarro, M., Relevance of PEG in PLA-based blends for tissue engineering 3D-printed scaffolds. *Mat Sci Eng C-Mater* **2014**, *38*, 55-62.
96. Seyednejad, H.; Gawlitta, D.; Kuiper, R. V.; de Bruin, A.; van Nostrum, C. F.; Vermonden, T.; Dhert, W. J. A.; Hennink, W. E., *In vivo* biocompatibility and biodegradation of 3D-printed porous scaffolds based on a hydroxyl-functionalized poly(epsilon-caprolactone). *Biomaterials* **2012**, *33* (17), 4309-4318.
97. Agrawal, C. M.; Ray, R. B., Biodegradable polymeric scaffolds for musculoskeletal tissue engineering. *Journal of biomedical materials research* **2001**, *55* (2), 141-150.
98. Reis, R. L.; Roman, J. S., *Biodegradable Systems in Tissue Engineering and Regenerative Medicine*. CRC Press: 2004.
99. Sant, S.; Iyer, D.; Gaharwar, A. K.; Patel, A.; Khademhosseini, A., Effect of biodegradation and de novo matrix synthesis on the mechanical properties of valvular interstitial cell-seeded polyglycerol sebacate-polycaprolactone scaffolds. *Acta Biomater* **2013**, *9* (4), 5963-5973.
100. Hubbell, J. A., Bioactive biomaterials. *Current opinion in biotechnology* **1999**, *10* (2), 123-9.
101. Kloxin, A. M.; Kasko, A. M.; Salinas, C. N.; Anseth, K. S., Photodegradable hydrogels for dynamic tuning of physical and chemical properties. *Science (New York, N.Y.)* **2009**, *324* (5923), 59-63.
102. Pratt, A. B.; Weber, F. E.; Schmoekel, H. G.; Muller, R.; Hubbell, J. A., Synthetic extracellular matrices for in situ tissue engineering. *Biotechnology and bioengineering* **2004**, *86* (1), 27-36.
103. Sokic, S.; Papavasiliou, G., FGF-1 and proteolytically mediated cleavage site presentation influence three-dimensional fibroblast invasion in biomimetic PEGDA hydrogels. *Acta biomaterialia* **2012**, *8* (6), 2213-22.
104. West, J. L.; Hubbell, J. A., Polymeric Biomaterials with Degradation Sites for Proteases Involved in Cell Migration. *Macromolecules* **1999**, *32* (1), 241-244.

105. Salber, J.; Grater, S.; Harwardt, M.; Hofmann, M.; Klee, D.; Dujic, J.; Jinghuan, H.; Ding, J.; Kippenberger, S.; Bernd, A.; Groll, J.; Spatz, J. P.; Moller, M., Influence of different ECM mimetic peptide sequences embedded in a nonfouling environment on the specific adhesion of human-skin keratinocytes and fibroblasts on deformable substrates. *Small (Weinheim an der Bergstrasse, Germany)* **2007**, 3 (6), 1023-31.
106. Weber, L. M.; Hayda, K. N.; Haskins, K.; Anseth, K. S., The effects of cell-matrix interactions on encapsulated β -cell function within hydrogels functionalized with matrix-derived adhesive peptides. *Biomaterials* **2007**, 28 (19), 3004-3011.
107. Gobin, A. S.; West, J. L., Cell migration through defined, synthetic ECM analogs. *FASEB journal : official publication of the Federation of American Societies for Experimental Biology* **2002**, 16 (7), 751-3.
108. Mann, B. K.; Gobin, A. S.; Tsai, A. T.; Schmedlen, R. H.; West, J. L., Smooth muscle cell growth in photopolymerized hydrogels with cell adhesive and proteolytically degradable domains: synthetic ECM analogs for tissue engineering. *Biomaterials* **2001**, 22 (22), 3045-3051.
109. Aimetti, A. A.; Machen, A. J.; Anseth, K. S., Poly(ethylene glycol) hydrogels formed by thiol-ene photopolymerization for enzyme-responsive protein delivery. *Biomaterials* **2009**, 30 (30), 6048-6054.
110. Kyburz, K. A.; Anseth, K. S., Three-dimensional hMSC motility within peptide-functionalized PEG-based hydrogels of varying adhesivity and crosslinking density. *Acta biomaterialia* **2013**, 9 (5), 6381-6392.
111. Lowe, S. B.; Tan, V. T. G.; Soeriyadi, A. H.; Davis, T. P.; Gooding, J. J., Synthesis and High-Throughput Processing of Polymeric Hydrogels for 3D Cell Culture. *Bioconjugate Chemistry* **2014**, 25 (9), 1581-1601.
112. Zelzer, M.; Todd, S. J.; Hirst, A. R.; McDonald, T. O.; Ulijn, R. V., Enzyme responsive materials: design strategies and future developments. *Biomaterials Science* **2013**, 1 (1), 11-39.
113. Liu Tsang, V.; Chen, A. A.; Cho, L. M.; Jadin, K. D.; Sah, R. L.; DeLong, S.; West, J. L.; Bhatia, S. N., Fabrication of 3D hepatic tissues by additive photopatterning of cellular hydrogels. *FASEB journal : official publication of the Federation of American Societies for Experimental Biology* **2007**, 21 (3), 790-801.
114. Herman, I. P., Physics of the Human Body. In *Biological and Medical Physics, Biomedical Engineering*, Greenbaum, E., Ed. Springer: 2007; pp 193-261.
115. Albanna, M. Z.; Bou-Akl, T. H.; Walters, H. L.; Matthew, H. W. T., Improving the mechanical properties of chitosan-based heart valve scaffolds using chitosan fibers. *J Mech Behav Biomed* **2012**, 5 (1), 171-180.
116. Butler, D. L.; Kay, M. D.; Stouffer, D. C., Comparison of Material Properties in Fascicle-Bone Units from Human Patellar Tendon and Knee Ligaments. *J Biomech* **1986**, 19 (6), 425-432.
117. Race, A.; Amis, A. A., The Mechanical-Properties of the 2 Bundles of the Human Posterior Cruciate Ligament. *J Biomech* **1994**, 27 (1), 13-24.
118. Hollister, S. J., Scaffold Design and Manufacturing: From Concept to Clinic. *Adv. Mater.* **2009**, 21 (32-33), 3330-3342.
119. Lin, C. Y.; Kikuchi, N.; Hollister, S. J., A novel method for biomaterial scaffold internal architecture design to match bone elastic properties with desired porosity. *J Biomech* **2004**, 37 (5), 623-636.

120. Peterson, G. I.; Schwartz, J. J.; Zhang, D.; Weiss, B.; Ganter, M. A.; Storti, D. W.; Boydston, A. J., Production of Materials with Spatially-Controlled Crosslink Density via Vat Photopolymerization. *ACS Appl Mater Interfaces* **2016**.
121. Stampfl, J.; Baudis, S.; Heller, C.; Liska, R.; Neumeister, A.; Kling, R.; Ostendorf, A.; Spitzbart, M., Photopolymers with tunable mechanical properties processed by laser-based high-resolution stereolithography. *J Micromech Microeng* **2008**, *18* (12).
122. Farkas, B.; Romano, I.; Ceseracciu, L.; Diaspro, A.; Brandi, F.; Beke, S., Four-order stiffness variation of laser-fabricated photopolymer biodegradable scaffolds by laser parameter modulation. *Mat Sci Eng C-Mater* **2015**, *55*, 14-21.
123. Kruth, J. P.; Leu, M. C.; Nakagawa, T., Progress in Additive Manufacturing and Rapid Prototyping. *Annals of the CIRP* **1998**, *47*, 525-540.
124. Zein, I.; Hutmacher, D. W.; Tan, K. C.; Teoh, S. H., Fused deposition modeling of novel scaffold architectures for tissue engineering applications. *Biomaterials* **2002**, *23* (4), 1169-1185.
125. Eshraghi, S.; Das, S., Mechanical and microstructural properties of polycaprolactone scaffolds with one-dimensional, two-dimensional, and three-dimensional orthogonally oriented porous architectures produced by selective laser sintering. *Acta Biomater* **2010**, *6* (7), 2467-2476.
126. Williams, J. M.; Adewunmi, A.; Schek, R. M.; Flanagan, C. L.; Krebsbach, P. H.; Feinberg, S. E.; Hollister, S. J.; Das, S., Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering. *Biomaterials* **2005**, *26* (23), 4817-4827.
127. Sears, N. A.; Seshadri, D. R.; Dhavalikar, P. S.; Cosgriff-Hernandez, E., A Review of Three-Dimensional Printing in Tissue Engineering. *Tissue Engineering Part B-Reviews* **2016**, *22* (4), 298-310.
128. Tumbleston, J. R.; Shirvanyants, D.; Ermoshkin, N.; Januszewicz, R.; Johnson, A. R.; Kelly, D.; Chen, K.; Pinschmidt, R.; Rolland, J. P.; Ermoshkin, A.; Samulski, E. T.; DeSimone, J. M., Continuous liquid interface production of 3D objects. *Science* **2015**, *347* (6228), 1349-1352.
129. Hribar, K. C.; Soman, P.; Warner, J.; Chung, P.; Chen, S. C., Light-assisted direct-write of 3D functional biomaterials. *Lab Chip* **2014**, *14* (2), 268-275.
130. Lakowicz, J. R., Instrumentation for Fluorescence Spectroscopy. In *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer US: 2006.
131. Skoog, D. A.; Holler, F. J.; Crouch, S. R., Components of Optical Instruments. In *Principles of Instrumental Analysis*, 7 ed.; Cengage Learning: 2007.
132. Gupta, P.; Elkins, C.; Long, T. E.; Wilkes, G. L., Electrospinning of linear homopolymers of poly(methyl methacrylate): exploring relationships between fiber formation, viscosity, molecular weight and concentration in a good solvent. *Polymer* **2005**, *46* (13), 4799-4810.
133. McKee, M. G.; Wilkes, G. L.; Colby, R. H.; Long, T. E., Correlations of solution rheology with electrospun fiber formation of linear and branched polyesters. *Macromolecules* **2004**, *37* (5), 1760-1767.
134. Colby, R. H.; Fetters, L. J.; Graessley, W. W., Melt Viscosity Molecular-Weight Relationship for Linear-Polymers. *Macromolecules* **1987**, *20* (9), 2226-2237.

135. Hinczewski, C.; Corbel, S.; Chartier, T., Ceramic suspensions suitable for stereolithography. *J Eur Ceram Soc* **1998**, *18* (6), 583-590.
136. Brady, G. A.; Chu, T. M.; Halloran, J. W., Curing behavior of ceramic resin for stereolithography. In *7th Solid Freeform Fabrication Symposium*, University of Texas, Austin, 1996; pp 403-410.
137. Lee, K. W.; Wang, S. F.; Fox, B. C.; Ritman, E. L.; Yaszemski, M. J.; Lu, L. C., Poly(propylene fumarate) bone tissue engineering scaffold fabrication using stereolithography: Effects of resin formulations and laser parameters. *Biomacromolecules* **2007**, *8* (4), 1077-1084.
138. Zheng, Y. P.; Zhang, J. X.; Yang, X. D.; Lan, L., The synthesis of hyperbranched poly (amine-ester) and study on the properties of its UV-curing film. *J Adhes Sci Technol* **2013**, *27* (24), 2666-2675.
139. Morozowich, N. L.; Nichol, J. L.; Mondschein, R. J.; Allcock, H. R., Design and examination of an antioxidant-containing polyphosphazene scaffold for tissue engineering. *Polymer Chemistry* **2012**, *3* (3), 778-786.
140. Gupta, P.; Trenor, S. R.; Long, T. E.; Wilkes, G. L., In situ photo-cross-linking of cinnamate functionalized poly(methyl methacrylate-co-2-hydroxyethyl acrylate) fibers during electrospinning. *Macromolecules* **2004**, *37* (24), 9211-9218.
141. Huyck, R. H.; Trenor, S. R.; Love, B. J.; Long, T. E., Photodimerization of coumarin functionalized poly(alkyl acrylate) and poly(alkyl methacrylate) random copolymers: Influence of copolymer composition on photocrosslinking. *J Macromol Sci A* **2008**, *45* (1), 9-15.
142. Trenor, S. R.; Long, T. E.; Love, B. J., Development of a light-deactivatable PSA via photodimerization. *J Adhesion* **2005**, *81* (2), 213-229.
143. Trenor, S. R.; Shultz, A. R.; Love, B. J.; Long, T. E., Coumarins in polymers: From light harvesting to photo-cross-linkable tissue scaffolds. *Chem. Rev.* **2004**, *104* (6), 3059-3077.
144. Govindarajan, S. R.; Xu, Y.; Swanson, J. P.; Jain, T.; Lu, Y.; Choi, J.-W.; Joy, A., A Solvent and Initiator Free, Low-Modulus, Degradable Polyester Platform with Modular Functionality for Ambient-Temperature 3D Printing. *Macromolecules* **2016**.
145. Childers, E. P.; Wang, M. O.; Becker, M. L.; Fisher, J. P.; Dean, D., 3D printing of resorbable poly(propylene fumarate) tissue engineering scaffolds. *Mrs Bull* **2015**, *40* (2), 119-126.
146. Goncalves, F. A. M. M.; Costa, C. S. M. F.; Fabela, I. G. P.; Farinha, D.; Faneca, H.; Simoes, P. N.; Serra, A. C.; Bartolo, P. J.; Coelho, J. F. J., 3D printing of new biobased unsaturated polyesters by microstereo-thermallithography. *Biofabrication* **2014**, *6* (3).
147. Zhang, H. B.; Wang, L.; Song, L.; Niu, G. G.; Cao, H.; Wang, G. J.; Yang, H. A.; Zhu, S. Q., Controllable Properties and Microstructure of Hydrogels Based on Crosslinked Poly(ethylene glycol) Diacrylates with Different Molecular Weights. *J Appl Polym Sci* **2011**, *121* (1), 531-540.
148. Dhariwala, B.; Hunt, E.; Boland, T., Rapid prototyping of tissue-engineering constructs, using photopolymerizable hydrogels and stereolithography. *Tissue Eng* **2004**, *10* (9-10), 1316-1322.

149. Sirrine, J. M.; Pekkanen, A. M.; Nelson, A. M.; Chartrain, N. A.; Williams, C. B.; Long, T. E., 3D-Printable Biodegradable Polyester Tissue Scaffolds for Cell Adhesion. *Australian Journal of Chemistry* **2015**.
150. Jeon, O.; Bouhadir, K. H.; Mansour, J. M.; Alsberg, E., Photocrosslinked alginate hydrogels with tunable biodegradation rates and mechanical properties. *Biomaterials* **2009**, *30* (14), 2724-2734.
151. Kim, P.; Yuan, A.; Nam, K. H.; Jiao, A.; Kim, D. H., Fabrication of poly(ethylene glycol): gelatin methacrylate composite nanostructures with tunable stiffness and degradation for vascular tissue engineering. *Biofabrication* **2014**, *6* (2).
152. Dong, Y. F.; Mosquera-Giraldo, L. I.; Taylor, L. S.; Edgar, K. J., Amphiphilic Cellulose Ethers Designed for Amorphous Solid Dispersion via Olefin Cross-Metathesis. *Biomacromolecules* **2016**, *17* (2), 454-465.
153. Meng, X. T.; Matson, J. B.; Edgar, K. J., Olefin cross-metathesis, a mild, modular approach to functionalized cellulose esters. *Polymer Chemistry* **2014**, *5* (24), 7021-7033.
154. Allcock, H. R.; Lampe, F. W.; Mark, J. W., *Contemporary Polymer Chemistry*. 3rd ed.; Prentice Hall: 2003.
155. Sirrine, J. M.; Ashraf-Khorassani, M.; Moon, N. G.; Mondschein, R. J.; Long, T. E., Supercritical Fluid Chromatography with Evaporative Light Scattering Detection (SFC-ELSD) for Determination of Oligomer Molecular Weight Distributions. *Chromatographia* **2016**, *79* (15-16), 977-984.
156. Hadjichristidis, N.; Roovers, J. E. L., Synthesis and Solution Properties of Linear, 4-Branched, and 6-Branched Star Polyisoprenes. *J Polym Sci Pol Phys* **1974**, *12* (12), 2521-2533.
157. Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. J., Rheological Behavior of Star-Shaped Polymers. *Macromolecules* **1993**, *26* (4), 647-654.
158. Lapienis, G., Star-shaped polymers having PEO arms. *Progress in Polymer Science* **2009**, *34* (9), 852-892.
159. Storey, R. F.; Warren, S. C.; Allison, C. J.; Wiggins, J. S.; Puckett, A. D., Synthesis of Bioabsorbable Networks from Methacrylate-Endcapped Polyesters. *Polymer* **1993**, *34* (20), 4365-4372.
160. Morell, M.; Foix, D.; Lederer, A.; Ramis, X.; Voit, B.; Serra, A., Synthesis of a New Multiarm Star Polymer Based on Hyperbranched Poly(styrene) Core and Poly(epsilon-Caprolactone) Arms and Its Use as Reactive Modifier of Epoxy Thermosets. *J. Polym. Sci. Pol. Chem.* **2011**, *49* (21), 4639-4649.
161. Qiu, L. Y.; Bae, Y. H., Polymer architecture and drug delivery. *Pharm Res* **2006**, *23* (1), 1-30.
162. Karikari, A. S.; Williams, S. R.; Heisey, C. L.; Rawlett, A. M.; Long, T. E., Porous thin films based on photo-cross-linked star-shaped poly(D, L-lactide)s. *Langmuir* **2006**, *22* (23), 9687-9693.
163. Karikari, A. S.; Edwards, W. F.; Mecham, J. B.; Long, T. E., Influence of peripheral hydrogen bonding on the mechanical properties of photo-cross-linked star-shaped poly(D,L-lactide) networks. *Biomacromolecules* **2005**, *6* (5), 2866-2874.
164. Stiriba, S. E.; Kautz, H.; Frey, H., Hyperbranched molecular nanocapsules: Comparison of the hyperbranched architecture with the perfect linear analogue. *J. Am. Chem. Soc.* **2002**, *124* (33), 9698-9699.

165. Nunez, C. M.; Chiou, B. S.; Andraday, A. L.; Khan, S. A., Solution rheology of hyperbranched polyesters and their blends with linear polymers. *Macromolecules* **2000**, *33* (5), 1720-1726.
166. Jin, Y. H.; Cho, Y. H.; Schmidt, L. E.; Leterrier, Y.; Manson, J. A. E., A fast low-temperature micromolding process for hydrophilic microfluidic devices using UV-curable acrylated hyperbranched polymers. *J Micromech Microeng* **2007**, *17* (6), 1147-1153.
167. Magnusson, H.; Malmstrom, E.; Hult, A.; Johansson, M., The effect of degree of branching on the rheological and thermal properties of hyperbranched aliphatic polyethers. *Polymer* **2002**, *43* (2), 301-306.
168. Odian, G., *Principles of Polymerization*. 4th ed.; Wiley-Interscience: 2004.
169. Hawker, C. J.; Chu, F. K., Hyperbranched poly(ether ketones): Manipulation of structure and physical properties. *Macromolecules* **1996**, *29* (12), 4370-4380.
170. Schmidt, L. E.; Schmäh, D.; Leterrier, Y.; Manson, J. A. E., Time-intensity transformation and internal stress in UV-curable hyperbranched acrylates. *Rheol Acta* **2007**, *46* (5), 693-701.
171. Pedron, S.; Anseth, K.; Benton, J. A.; Bosch, P.; Peinado, C., Bioapplications of Networks Based on Photo-Cross-Linked Hyperbranched Polymers. *Macromol Sy* **2010**, *291-292*, 307-313.
172. Su, W.; Luo, X. H.; Wang, H. F.; Li, L.; Feng, J.; Zhang, X. Z.; Zhuo, R. X., Hyperbranched Polycarbonate-Based Multimolecular Micelle with Enhanced Stability and Loading Efficiency. *Macromol Rapid Comm* **2011**, *32* (4), 390-396.
173. Hedenqvist, M. S.; Yousefi, H.; Malmstrom, E.; Johansson, M.; Hult, A.; Gedde, U. W.; Trollsas, M.; Hedrick, J. L., Transport properties of hyperbranched and dendrimer-like star polymers. *Polymer* **2000**, *41* (5), 1827-1840.
174. Chan, V.; Zorlutuna, P.; Jeong, J. H.; Kong, H.; Bashir, R., Three-dimensional photopatterning of hydrogels using stereolithography for long-term cell encapsulation. *Lab Chip* **2010**, *10* (16), 2062-2070.
175. Meyer, W.; Engelhardt, S.; Novosel, E.; Elling, B.; Wegener, M.; Kruger, H., Soft Polymers for Building up Small and Smallest Blood Supplying Systems by Stereolithography. *Journal of functional biomaterials* **2012**, *3* (2), 257-68.
176. Schinagl, R. M.; Gurskis, D.; Chen, A. C.; Sah, R. L., Depth-dependent confined compression modulus of full-thickness bovine articular cartilage. *J Orthopaed Res* **1997**, *15* (4), 499-506.
177. Rajan, K. P.; Al-Ghamdi, A.; Parameswar, R.; Nando, G. B., Blends of thermoplastic polyurethane and polydimethylsiloxane rubber: assessment of biocompatibility and suture holding strength of membranes. *International journal of biomaterials* **2013**, *2013*, 240631.
178. Moon, N. G.; Mondschein, R. J.; Long, T. E., Poly(β -thioesters) containing monodisperse oxamide hard segments using a chemoselective thiol-Michael addition reaction. *Polymer Chemistry* **2017**, *8* (17), 2598-2608.
179. Song, Y.; Wennink, W. H.; Kamphuis, M. M. J.; Sterk, L. M. T.; Vermes, I.; Poot, A. A.; Feijen, J.; Grijpma, D. W., Dynamic Culturing of Smooth Muscle Cells in Tubular Poly(Trimethylene Carbonate) Scaffolds for Vascular Tissue Engineering. *Tissue engineering. Part A* **2011**, *17*, 381-387.

180. Chapanian, R.; Tse, M. Y.; Pang, S. C.; Amsden, B. G., The role of oxidation and enzymatic hydrolysis on the in vivo degradation of trimethylene carbonate based photocrosslinkable elastomers. *Biomaterials* **2009**, *30*, 295-306.
181. Schanté, C. E.; Zuber, G.; Herlin, C.; Vandamme, T. F., Chemical modifications of hyaluronic acid for the synthesis of derivatives for a broad range of biomedical applications. *Carbohydrate Polymers* **2011**, *85* (3), 469-489.
182. Sun, A. X.; Lin, H.; Beck, A. M.; Kilroy, E. J.; Tuan, R. S., Projection Stereolithographic Fabrication of Human Adipose Stem Cell-Incorporated Biodegradable Scaffolds for Cartilage Tissue Engineering. *Frontiers in bioengineering and biotechnology* **2015**, *3*, 115.
183. Burdick, J. A.; Chung, C.; Jia, X.; Randolph, M. A.; Langer, R., Controlled degradation and mechanical behavior of photopolymerized hyaluronic acid networks. *Biomacromolecules* **2005**, *6* (1), 386-91.
184. Chung, C.; Mesa, J.; Miller, G. J.; Randolph, M. A.; Gill, T. J.; Burdick, J. A., Effects of auricular chondrocyte expansion on neocartilage formation in photocrosslinked hyaluronic acid networks. *Tissue engineering* **2006**, *12* (9), 2665-73.
185. Shi, D.; Xu, X.; Ye, Y.; Song, K.; Cheng, Y.; Di, J.; Hu, Q.; Li, J.; Ju, H.; Jiang, Q.; Gu, Z., Photo-Cross-Linked Scaffold with Kartogenin-Encapsulated Nanoparticles for Cartilage Regeneration. *ACS Nano* **2016**, *10* (1), 1292-1299.
186. Masters, K. S.; Shah, D. N.; Walker, G.; Leinwand, L. A.; Anseth, K. S., Designing scaffolds for valvular interstitial cells: cell adhesion and function on naturally derived materials. *Journal of biomedical materials research. Part A* **2004**, *71* (1), 172-80.
187. Masters, K. S.; Shah, D. N.; Leinwand, L. A.; Anseth, K. S., Crosslinked hyaluronan scaffolds as a biologically active carrier for valvular interstitial cells. *Biomaterials* **2005**, *26* (15), 2517-2525.
188. Smeds, K. A.; Grinstaff, M. W., Photocrosslinkable polysaccharides for in situ hydrogel formation. *Journal of biomedical materials research* **2001**, *54* (1), 115-121.
189. Baier Leach, J.; Bivens, K. A.; Patrick, C. W., Jr.; Schmidt, C. E., Photocrosslinked hyaluronic acid hydrogels: natural, biodegradable tissue engineering scaffolds. *Biotechnology and bioengineering* **2003**, *82* (5), 578-89.
190. Marklein, R. A.; Burdick, J. A., Spatially controlled hydrogel mechanics to modulate stem cell interactions. *Soft Matter* **2010**, *6* (1), 136-143.
191. Bencherif, S. A.; Srinivasan, A.; Horkay, F.; Hollinger, J. O.; Matyjaszewski, K.; Washburn, N. R., Influence of the degree of methacrylation on hyaluronic acid hydrogels properties. *Biomaterials* **2008**, *29* (12), 1739-49.
192. Pawar, S. N.; Edgar, K. J., Alginate derivatization: A review of chemistry, properties and applications. *Biomaterials* **2012**, *33* (11), 3279-3305.
193. Di Martino, A.; Sittering, M.; Risbud, M. V., Chitosan: A versatile biopolymer for orthopaedic tissue-engineering. *Biomaterials* **2005**, *26* (30), 5983-5990.
194. Jayakumar, R.; Menon, D.; Manzoor, K.; Nair, S. V.; Tamura, H., Biomedical applications of chitin and chitosan based nanomaterials-A short review. *Carbohydr Polym* **2010**, *82* (2), 227-232.
195. Ono, K.; Saito, Y.; Yura, H.; Ishikawa, K.; Kurita, A.; Akaike, T.; Ishihara, M., Photocrosslinkable chitosan as a biological adhesive. *Journal of biomedical materials research* **2000**, *49* (2), 289-95.

196. Morris, V. B.; Nimbalkar, S.; Younesi, M.; McClellan, P.; Akkus, O., Mechanical Properties, Cytocompatibility and Manufacturability of Chitosan:PEGDA Hybrid-Gel Scaffolds by Stereolithography. *Ann Biomed Eng* **2016**.
197. Matsuda, T.; Magoshi, T., Preparation of Vinylated Polysaccharides and Photofabrication of Tubular Scaffolds as Potential Use in Tissue Engineering. *Biomacromolecules* **2002**, 3 (5), 942-950.
198. Karp, J. M.; Yeo, Y.; Geng, W.; Cannizarro, C.; Yan, K.; Kohane, D. S.; Vunjak-Novakovic, G.; Langer, R. S.; Radisic, M., A photolithographic method to create cellular micropatterns. *Biomaterials* **2006**, 27 (27), 4755-4764.
199. Ovsianikov, A.; Deiwick, A.; Van Vlierberghe, S.; Pflaum, M.; Wilhelmi, M.; Dubruel, P.; Chichkov, B., Laser Fabrication of 3D Gelatin Scaffolds for the Generation of Bioartificial Tissues. *Materials* **2011**, 4 (1), 288.
200. Brinkman, W. T.; Nagapudi, K.; Thomas, B. S.; Chaikof, E. L., Photo-Cross-Linking of Type I Collagen Gels in the Presence of Smooth Muscle Cells: Mechanical Properties, Cell Viability, and Function. *Biomacromolecules* **2003**, 4 (4), 890-895.
201. Dong, C. M.; Wu, X.; Caves, J.; Rele, S. S.; Thomas, B. S.; Chaikof, E. L., Photomediated crosslinking of C6-cinnamate derivatized type I collagen. *Biomaterials* **2005**, 26 (18), 4041-9.

Chapter 10: Characterization of Peptide Coatings Adhered to Synthetic Fibers: A Versatile Model for Peptide Nucleic Acids

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10.1 Abstract

Peptide nucleic acids (PNAs) are an emerging family of biomaterials designed to specifically target and treat diseased cells, most commonly in the antimicrobial-resistant bacteria MRSA. While PNAs offer great promise for the elimination of these bacteria, they are significantly more expensive than traditional peptides and often do not provide functionality for analysis. In this work, a model peptide (KFFCCQ) was developed to evaluate peptide coatings adhered to fibrous surfaces with multiple functional handles, i.e. the presence of a sulfur atom in cysteine and an aromatic ring in phenylalanine, to predict the durability of PNA coatings on 50/50 nylon/cotton blends (NyCo), which are commonly used in clothing such as combat and medical attire. Following elemental analysis through XPS and EDX-SEM, rinses were performed on the fabrics and the subsequent release of

peptide was evaluated with UV-Vis. As expected, elevated temperature and increased time resulted in higher KFFCCQ release levels from the NyCo fibers. Finally, EDX-SEM examined the presence of KFFCCQ following rinse cycles, revealing that a higher level of KFFCCQ released from nylon fibers compared to cotton fibers. This evaluation proves the utility of KFFCCQ as a preliminary model to evaluate adhesion and release of peptides from nylon and cotton fibrous surfaces.

10.2 Introduction

Textiles are a vital component to modern-day life and efficient modification of both synthetic and natural fibers is a crucial science and engineering concern. Most notably, dyes, antibacterials, and stain-resistant coatings must both adhere to woven fibers and survive external aqueous environments and mechanical agitation.¹⁻⁶ These coatings range in function from color fade resistance to therapeutic use.⁶⁻⁷ Recently, silver nanoparticles and tailored polymers as antibacterial coatings on fabrics justify the importance of developing and understanding biomaterial coatings and release profiles.^{3, 5, 8} The characterization of fiber coatings and their resistance to multiple aqueous washing cycles is crucial to evaluate any new potential textile.

Although traditional antibacterial coatings offer precedence, they are often deemed too broad a class of antimicrobials, leading to the subsequent loss of naturally occurring bacteria on skin.⁸ Peptide nucleic acids (PNAs) are an emerging biologic moiety that possess the potential to selectively eradicate numerous diseases.⁹⁻¹³ DNA base pairs covalently attached to a peptide backbone reminiscent of proteins compose PNAs, harnessing the ability to combine the therapeutic function of DNA/RNA and protein.⁹ Their action varies on the specific application, but their main attraction is their specificity to

target organisms. For example, Sato et al. described the use of PNAs as siRNA carriers to deliver these sensitive genes directly to the nucleus of cells.¹⁴ More commonly, drug-resistant bacteria, such as Methicillin-resistant *Staphylococcus aureus* (MRSA), requires PNAs for treatment.¹² These PNAs eliminate specific targets within MRSA, such as FtsZ, allowing other bacteria to survive.¹²

10.3 Results and Discussion

Due to the high cost and often difficult characterization of PNA samples, developing simpler and cheaper model peptides to study the adhesion to fibers is important. PNAs typically contain two separate functional sequences in the backbone. First is the cell-penetrating peptide (CPP) sequence, typically incorporating high amounts of cationic charge through lysine or arginine incorporation. Second is the active inhibiting sequence, specific to targeting pathways or signals from a particular target, such as MRSA. Therefore, our unique design of a model peptide contains both a lysine residue to mimic charge density, as well as cysteine and phenylalanine for easy analytical analysis. This yielded a peptide with similar charge density to PNAs, while maintaining the peptide backbone suitable for coating and adhesive analysis (KFFCCQ, EnoGene Biotech Co Ltd).¹⁵⁻¹⁶ UV-Vis spectroscopy detected phenylalanine residues while elemental analysis, such as X-ray Photoelectron Spectroscopy (XPS, PHI Quantera SXM) or scanning electron microscopy (SEM, FEI Quanta 600 FEG) equipped with electron dispersive X-ray spectroscopy (EDX, Bruker with Silicon Drifted Detector), identified sulfur atoms present in the cysteine residues.¹⁷

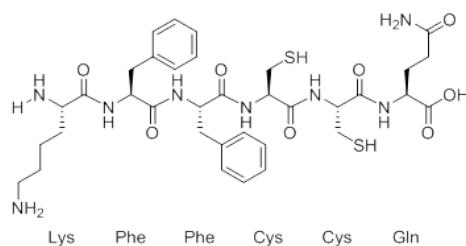


Figure 10.1: Model peptide consisting of Lysine-Phenylalanine-Phenylalanine-Cysteine-Cysteine-Glutamine (KFFCCQ) sequence.

XPS analysis of neat fabrics confirmed the lack of sulfur atoms present in commercially available 100 % cotton, 100 % nylon, or a 50/50 nylon/cotton (NyCo) blend, as shown in **Table 10.1**. All fibers showed a silicon signal, likely arising from a protective coating from a pre-treatment. NyCo samples reveal a magnesium peak, likely arising from dye or coating used on the fabric as demonstrated by a lack of magnesium upon bleach treatment.¹⁸ Elemental analysis proves crucial to confirm KFFCCQ presence after coating procedures. Following characterization of neat fibers and validation of the lack of interference in elemental signal from the fibers, the NyCo sample was identified for detailed study.

Sample	C1s	N1s	O1s	F1s	Na1s	Mg2s	Si2p	P2p	S2p	Cl2p	Ca2p
Cotton	74.95	0.33	24.65	0	0.14	0	0.51	0	0.19	0	0.23
Cotton (Autoclaved)	71.63	1.3	22.73	2.41	0.13	0	0.97	0.26	0	0	0.57
Nylon	74.11	9.44	14.73	0	0	0	1.38	0	0	0	0.34
Nylon (Autoclaved)	70.4	8.63	18.07	0.42	0	0	2.23	0	0	0	0.24
NyCo	83.43	1.72	13.31	0	0	0.44	0.54	0	0	0.15	0.4
NyCo (Autoclaved)	78.03	3.18	15.84	0	0	0.34	2.31	0	0	0	0.3
NyCo (Bleached)	74.96	5.87	11.71	0	0.88	0	0.41	0	0.14	6.04	0

Table 10.1: XPS analysis of Cotton (neat & autoclaved), Nylon (neat & autoclaved), and 50/50 Nylon/Cotton (NyCo) (neat, autoclaved, and bleached) revealing the presence of coatings and dyes. XPS confirms the utility in the model peptide through the lack of elemental interference from fibers.

Pad-dry and pad-dry-cure techniques proved viable methods to coat KFFCCQ to NyCo fibers.^{7, 19-20} To compare these techniques, NyCo was soaked in aqueous 0.1 wt % or 0.5 wt % KFFCCQ solution for 30 min, with gentle agitation every 10 min. Pad-dry proceeded to dry the samples at 95 °C for 1 h, while pad-dry-cure placed the samples at 95 °C for 90 s followed by 150 °C for 60 s. Both pad-dry and pad-dry-cure methods sufficiently adhered the KFFCCQ to the 50/50 NyCo blend, with no discernible difference noticed between techniques. **Table 10.2** demonstrates changes in global elemental compositions (through XPS analysis) of fibers after adhering the peptide coating with varying weight percent KFFCCQ. As expected, 0.5 wt % KFFCCQ elicited higher sulfur content than 0.1 wt %, indicating a higher incorporation. The lack of variation between pad-dry and pad-dry-cure techniques for KFFCCQ incorporation suggests utility in the reduced-time pad-dry-cure method notwithstanding potential changes in function.⁷

Sample	C1s	N1s	O1s	Si2p	S2p	Cl2p
0.1 wt % Pad Dry	76.68	2.91	18.26	2.16	0	0
0.1 wt % Pad Dry Cure	80.24	4.2	14.06	0.86	0.41	0.22
0.5 wt % Pad Dry	74.01	5.4	17.43	2.14	0.73	0.3
0.5 wt % Pad Dry Cure	79.85	4.36	13.35	1.52	0.71	0.2

Table 10.2: XPS analysis of NyCo samples treated with 0.1 and 0.5 weight percent model peptide solutions, undergoing both pad dry and pad dry cure methods.

A broad S2p binding energy peak at 164 eV confirmed the retention of cysteine residues adhered to fiber surfaces following 0.5 wt % pad-dry and pad-dry-cure procedures, as shown in **Figure 10.2**.²¹

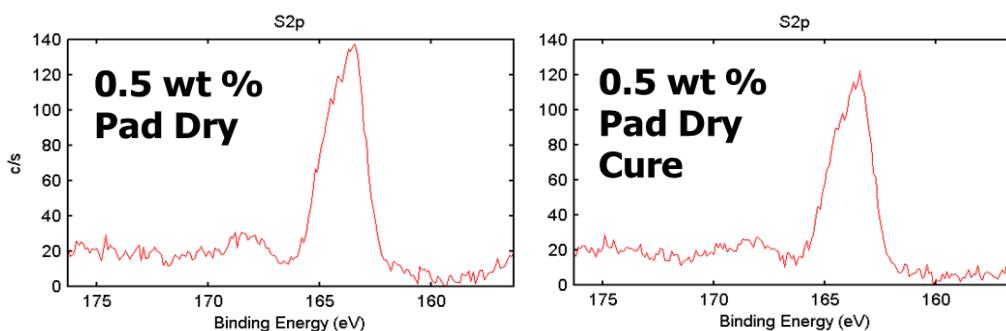


Figure 10.2: High resolution sulfur analysis performed on NyCo samples with 0.5 wt % pad-dry and pad-dry-cure treatment reveals retention of peptide structure upon coating.

SEM provided further confirmation of the utility of both pad-dry and pad-dry-cure techniques as compared to neat NyCo fibers. As seen in **Figure 10.3a**, cotton presented as rough, twisting fibers, while nylon presented smooth, cylindrical fibers. As seen in **Figure 10.3b-d**, the surface morphology of both fiber types after coating suggested successful adhesion of KFFCCQ throughout the NyCo sample. Regions of pad-dry samples exhibited bridging between fibers, while pad-dry-cure samples retain well-defined morphology.

These images indicate slight differences in both KFFCCQ content as well as coating morphology, suggestive of nuanced differences between the techniques not seen with XPS.

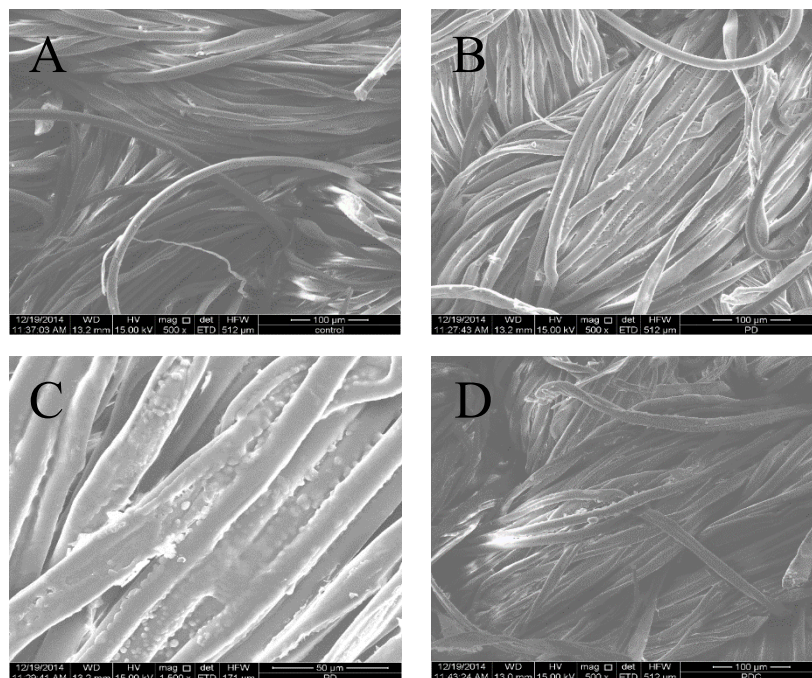


Figure 10.3: A. 500x SEM images of 50/50 Nylon/Cotton fibers treated with water. B. 500x SEM image of Pad-Dry 0.5 wt % model peptide treated NyCo fibers. A change in morphology is seen in the coating and bumpy, rough features. C. 1500x SEM image of Pad-Dry 0.5 wt % model peptide treated NyCo fibers. A change in morphology is seen in the coating and rough features. D. 500x SEM image of Pad-Dry-Cure 0.5 wt % model peptide treated NyCo fibers. A change in morphology is seen in the rough features on the fibers.

In conjunction with SEM imaging, EDX elemental analysis confirmed the presence of sulfur atoms on fiber surfaces after coating, as shown in **Figure 10.6**. **Figure 10.4** depicted neat NyCo fibers and revealed a lack of sulfur present in the sample, in concordance with XPS performed on neat fabric. EDX provided insight into elemental composition across the entire depth of the fabric sample, as a thin coating present only on the surface would not produce a detectable signal. XPS and EDX together provided

evidence that KFFCCQ is adhering to and coating both nylon and cotton fibers throughout the bulk of the sample.

The phenylalanine residues in KFFCCQ provide a metric to quantitatively determine release of KFFCCQ from NyCo fibers after aqueous rinsing. Absorbance of phenylalanine at 237 nm in water yielded a concentration-dependent absorption profile, which accurately probed samples of low concentration. The absorbance profile up to 2 mg/mL follows the linear fit

$$Absorbance = 0.2818c + 0.0317$$

where c indicates the concentration of KFFCCQ in mg/mL. KFFCCQ follows a linear fit at dilute concentrations, affording a method sensitive to low concentrations of peptide.

KFFCCQ-loaded NyCo was prepared by soaking in aqueous 0.5 wt % solution of KFFCCQ for 30 min with agitation every 10 min, followed by drying at 55 °C for 1 h. Dried, coated fabrics were rapidly stirred at 44 °C, 25 °C, or 16 °C in water for 0, 16, or 21 min. UV-Vis absorption (**Figure 10.5**) provided quantitative analysis of released KFFCCQ following lyophilization of collected water samples (n=3). KFFCCQ-loaded fabrics subjected to this rinse cycle exhibited a loss of peptide, with a rinse cycle performed at 44 °C for 16 min providing the most significant release of KFFCCQ from NyCo fibers, indicating a rapid release from fibers. Furthermore, NyCo subjected to a rinse cycle at 16 °C and 25 °C show marginal release from NyCo fibers, indicating warmer water disrupts KFFCCQ binding to a higher degree than colder water, as adhesion is most likely due to hydrogen bonding. Future studies revolve around the peptide-fiber binding mechanism.

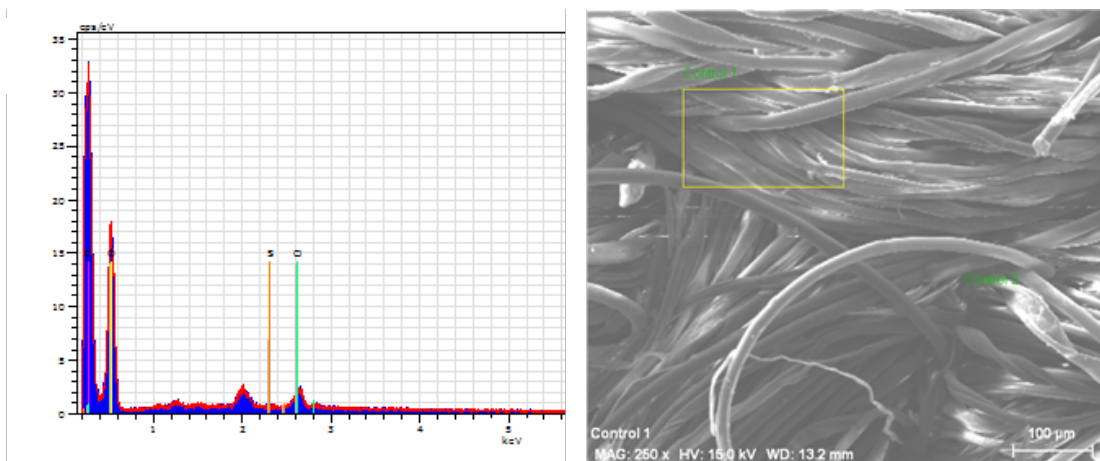


Figure 10.4: A. EDX analysis on SEM images of water treated NyCo fibers B. 0.5 weight % pad dry treated NyCo fibers C. 0.5 weight % pad dry cure treated NyCo fibers confirming the presence of KFFCCQ after coating steps.

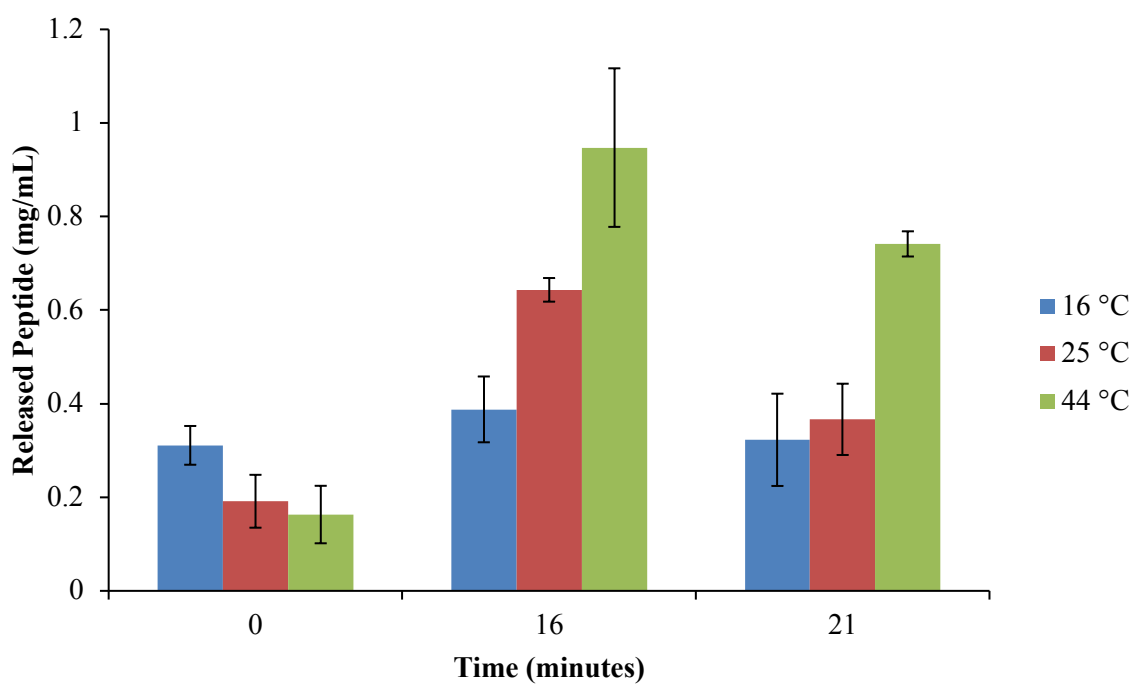


Figure 10.5: Total amount of peptide released from fiber surfaces as a function of temperature and time indicating an increase in the amount of release of KFFCCQ with increasing temperature and time.

Rinse cycles at 25 °C for 20 min provided a metric of resistance of KFFCCQ coating to repeated rinse cycles (1, 3, 5, 10, and 15 rinse steps followed by drying at 55 °C for 30 min). For visual analysis of KFFCCQ release, nylon fibers protruding from the fabric surface provide a consistent metric. **Figure 10.6** depicts a protruding fiber coated in KFFCCQ with corresponding EDX analysis indicating its presence. **Figure 10.7** shows images of KFFCCQ-coated NyCo after repeated rinse cycles, indicating a loss of KFFCCQ from nylon fibers over time. The sulfur peak seen with EDX diminishes as the number of rinse cycles increases, in concordance with the qualitative images. Interestingly, cotton fibers did not exhibit this trend, as shown in Figure 8. Cotton fibers retain KFFCCQ at a similar level regardless of number of rinse cycles, suggesting a stronger adhesion to cotton fibers as compared to nylon fibers.²² This increased adhesion suggests hydrogen bonding as the primary interaction between peptide and fiber, as the peptide would preferentially adhere to the nylon fibers if hydrophobic interactions dominated. This model could also be utilized to predict the release of peptide from fabric to skin, postulating that a coating adhered to nylon fibers would be exposed to the skin before those adherent to cotton fibers.

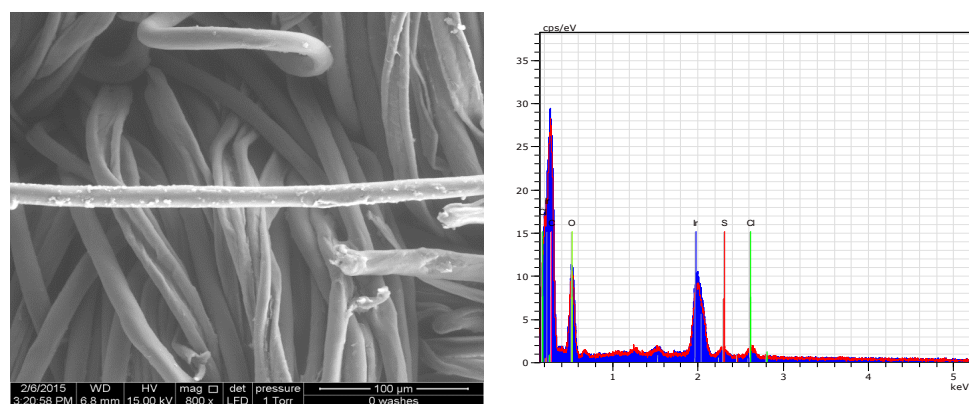


Figure 10.6: Control fabric and corresponding EDS for survivability studies which confirms the presence of KFFCCQ on fiber surfaces. The protruding nylon fiber provides a metric to compare between samples.

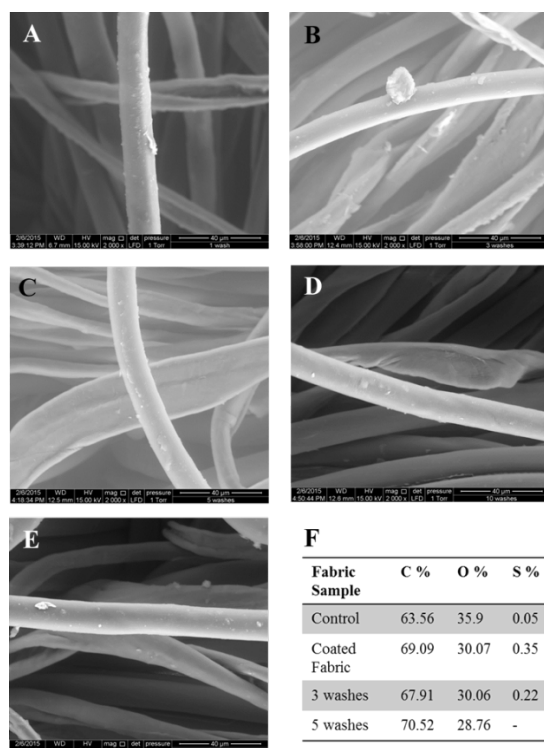


Figure 10.7: Model peptide coating on exposed nylon fibers as a function of number of rinse cycles, with 1 rinse (A) 3 rinses (B), 5 rinses (C), 10 rinses (D), and 15 rinses (E) examined. F. EDX confirms bulk loss of peptide as the number of rinse cycles increases.

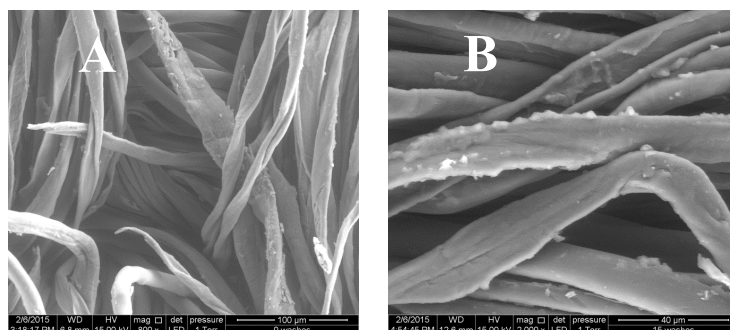


Figure 10.8: Cotton fibers after 0 rinses (left) and 15 rinses (right) indicating retention of the model peptide after multiple rinse cycles suggesting longevity of the coating.

10.4 Conclusions

The combination of elemental analysis through XPS and EDX, SEM imaging, and UV-Vis quantitative absorbance revealed both the KFFCCQ adhesion to NyCo fibers and its subsequent release following rinse cycles. While additional studies are needed for full evaluation of peptide release during more vigorous conditions, this study provided an initial metric for evaluation of peptide coatings and release from fibers. The utilization of this model peptide KFFCCQ provides an inexpensive alternative for testing PNA adhesion to fiber surfaces, while also allowing for coating durability and efficacy studies.

10.5 Acknowledgements

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10.6 References

1. Martin, T.; Kooi, S.; Chang, S.; Sedransk, K.; Gleason, K., Initiated chemical vapor deposition of antimicrobial polymer coatings. *Biomaterials* **2007**, 28 (6), 909-915.
2. Blyth, R. C.; Ucci, P. A., Stain resistant nylon fibers. US Patent 4,680,212: 1987.
3. Perelshtein, I.; Applerot, G.; Perkash, N.; Guibert, G.; Mikhailov, S.; Gedanken, A., Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity. *Nanotechnology* **2008**, 19 (24), 245705.
4. Heisey, C.; Wightman, J.; Pittman, E.; Kuhn, H., Surface and adhesion properties of polypyrrole-coated textiles. *Text Res J* **1993**, 63 (5), 247-256.
5. MacKeen, P. C.; Person, S.; Warner, S. C.; Snipes, W.; Stevens, S., Silver-coated nylon fiber as an antibacterial agent. *Antimicrob Agents Ch* **1987**, 31 (1), 93-99.
6. Xiao, X.; Liu, X.; Cao, G.; Zhang, C.; Xia, L.; Xu, W.; Xiao, S., Atomic layer deposition TiO₂/Al₂O₃ nanolayer of dyed polyamide/aramid blend fabric for high intensity UV light protection. *Polym Eng Sci* **2015**, 55 (6), 1296-1302.
7. Zhou, C.-E.; Kan, C.-w.; Yuen, C.-w. M.; Matinlinna, J. P.; Tsoi, J. K.-h.; Zhang, Q., Plasma treatment applied in the pad-dry-cure process for making rechargeable antimicrobial cotton fabric that inhibits *S. Aureus*. *Text Res J* **2015**, 1-14.
8. Xue, C.-H.; Chen, J.; Yin, W.; Jia, S.-T.; Ma, J.-Z., Superhydrophobic conductive textiles with antibacterial property by coating fibers with silver nanoparticles. *Appl Surf Sci* **2012**, 258 (7), 2468-2472.
9. Nielsen, P. E.; Egholm, M.; Buchardt, O., Peptide nucleic acid (PNA). A DNA mimic with a peptide backbone. *Bioconjugate Chem* **1994**, 5 (1), 3-7.
10. Gaylord, B. S.; Heeger, A. J.; Bazan, G. C., DNA detection using water-soluble conjugated polymers and peptide nucleic acid probes. *P Natl Acad Sci* **2002**, 99 (17), 10954-10957.
11. Wang, J.; Palecek, E.; Nielsen, P. E.; Rivas, G.; Cai, X.; Shiraishi, H.; Dontha, N.; Luo, D.; Farias, P. A., Peptide nucleic acid probes for sequence-specific DNA biosensors. *J Am Chem Soc* **1996**, 118 (33), 7667-7670.
12. Meng, J.; Da, F.; Ma, X.; Wang, N.; Wang, Y.; Zhang, H.; Li, M.; Zhou, Y.; Xue, X.; Hou, Z., Antisense growth inhibition of methicillin-resistant *Staphylococcus aureus* by locked nucleic acid conjugated with cell-penetrating peptide as a novel FtsZ inhibitor. *Antimicrob Agents Ch* **2015**, 59 (2), 914-922.
13. Machado, A.; Castro, J.; Cereija, T.; Almeida, C.; Cerca, N., Diagnosis of bacterial vaginosis by a new multiplex peptide nucleic acid fluorescence in situ hybridization method. *PeerJ* **2015**, 3, e780.
14. Sato, T.; Sato, Y.; Iwai, K.; Kuge, S.; Teramae, N.; Nishizawa, S., Fluorescence Imaging of siRNA Delivery by Peptide Nucleic Acid-based Probe. *Anal Sci* **2015**, 31 (4), 315-320.
15. Margus, H.; Arukuusk, P.; Langel, U. I.; Pooga, M., Characteristics of Cell-Penetrating Peptide/Nucleic Acid Nanoparticles. *Mol Pharm* **2016**, 13 (1), 172-179.
16. Nakase, I.; Takeuchi, T.; Futaki, S., Cell Penetrating Peptides for Chemical Biological Studies. In *Cell-Penetrating Peptides: Methods and Protocols*, 2015; pp 387-396.

17. Williams, S. R.; Lepene, B. S.; Thatcher, C. D.; Long, T. E., Synthesis and Characterization of Poly(ethylene glycol)–Glutathione Conjugate Self-Assembled Nanoparticles for Antioxidant Delivery. *Biomacromolecules* **2009**, *10* (1), 155-161.
18. Ida, S.; Endo, N., Method for coloring fibrous material composed of phenolic resins. US Patent 3,918,901: 1975.
19. Liu, Y.; Ma, K.; Li, R.; Ren, X.; Huang, T., Antibacterial cotton treated with N-halamine and quaternary ammonium salt. *Cellulose* **2013**, *20* (6), 3123-3130.
20. Perelshtein, I.; Perkash, N.; Gedanken, A., Ultrasonic Coating of Textiles by Antibacterial and Antibiofilm Nanoparticles. In *Handbook of Ultrasonics and Sonochemistry*, 2016; pp 1-27.
21. Girardeaux, C.; Zammattéo, N.; Art, M.; Gillon, B.; Pireaux, J.; Caudano, R., Amination of poly (ethylene-terephthalate) polymer surface for biochemical applications. *Plasma Polym* **1996**, *1* (4), 327-346.
22. Yu, Y.; Yuan, J.; Wang, Q.; Fan, X.; Wang, P.; Cui, L., A study of surface morphology and structure of cotton fibres with soluble immobilized-cellulase treatment. *Fiber Polym* **2014**, *15* (8), 1609-1615.

Chapter 11: Conclusion

Most academic research in polymer chemistry currently focuses on novel and exotic monomers and topologies with controlled radical polymerization. Research with these focuses typically enhances desirable properties or broadens potential application spaces for these types of polymers. The major drawback to these methods is the cost and feasibility of scalability and industrial adoption. Step-growth polymers encompass most of the polymers used in thermoplastic applications including consumer goods, packaging, construction, automotive, aerospace, and medical devices, due to the wider variety of chemical functionality and structures achievable.

Sometimes subtle changes make the largest impacts. When designing next-generation thermoplastics and high performance polymers, true innovation involves rationally improving key properties desired for specific applications, while maintaining feasibility both economically and synthetically. Commonly known as “drop-in” projects, the advancements generated minimally change the cost of the product and the infrastructure required to produce these polymers is already built. Common ways to subtly change the structure, but improve targeted properties, include changing backbone regiochemistry as well as incorporating new comonomers with pendant functionality.

First, altering the backbone regiochemistry of BB-based and dihydroxybenzene-based (co)polyesters offers a subtle way to disrupt order and chain packing, while targeting various property improvements. As seen in Chapter 2, Chapter 3, Chapter 4, and Chapter 5, changing from a more linear (*para*-substituted) regiochemistry to a more kinked (*meta*-

substituted) regiochemistry altered thermal, mechanical, thermomechanical, barrier, and viscoelastic properties.

In general, the more kinked (co)polyesters exhibited improved mechanical properties, better barrier performance, lower melt flow activation energies, and amorphous morphology for all compositions. The improvement in mechanical properties resulted from increased density in the amorphous state of the more kinked structures, due to an increase in *trans* conformations in the ethylene portions for the *meta*-substituted structures. The improvement in barrier performance is related to the increase in density as well as the hindered ring-rotation around the 1,3 *meta* linkage compared to the 1,4 *para* linkage. Interestingly, this same ring-rotation relaxation is postulated as one of the main contributors to the impact resistance properties of the polymer. One other common way to increase polymer impact performance is to achieve very high molecular weight. Thus, when designing, a trade-off typically occurs between barrier performance, impact resistance, and processability. Higher barrier performance by limiting the short range relaxations, thus reducing the diffusivity of gas through the polymers, also worsens the impact resistance. Improving the impact resistance through increasing molecular weight is both difficult from a synthetic view as well as makes processing a challenge due to the relationship between molecular weight and viscosity. Thus, innovation is required involving polymer structures or additives to balance both barrier performance and impact resistance.

Although the aforementioned polyester regioisomers resulted in similar trends for some properties, the molecular weight of entanglement (M_e) decreased when incorporating the kinked 3,4'BB but increased when incorporating the kinked hydroxyethylresorcinol

(HER). Further exploration is needed into coil sizes as well as radius of gyration (R_g) to relate the polymer composition to entanglement. Another discrepancy between incorporating more kinked monomers into the linear analogue relates to the fractional free volume at T_g (f_g). The 3,4'-BB-based copolyesters showed limited changes in f_g while HER-based copolymers showed a much larger change. Similar to M_e understanding, looking at the physical polymer properties relating to R_g and coil sizes is needed to help determine the origin of the changes.

When characterizing the (co)polyester regioisomers, SEC revealed large concentrations of low molecular weight species, attributed to cyclics, commonly produced during step-growth polymerization. Altering the backbone regiochemistry is known to influence the amount and preferential size of cyclic species, but few investigations relate the amount and size of cyclics formed based on starting monomer incorporation to key polymer properties such as mechanical performance and gas barrier. As seen in Chapter 6, more kinked HER-based compositions produced higher concentrations of cyclics as well as more preferential lower cyclic sizes, consistent previous literature comparing linear *versus* kinked polyester regioisomers. Further studies are required to relate the amount and size of cyclics to the polymer's bulk properties.

In order to identify the influence of cyclics on polymer properties, testing polymers with cyclics extracted and polymer with their equilibrium amount of cyclics is required. The challenge with extracting cyclics is that they are present at a thermodynamic equilibrium. Thus, any high temperature processing with polymers with cyclics extracted will reproduce the cyclics at the known equilibrium amount. In order to avoid this reproduction, solution processing is required. Semi-aromatic polyesters possess limited

solubility in common, nontoxic solvents, making solution extraction of cyclics and solution processing specimens possible. Another important factor when determining influence of cyclics is achieving high molecular weight sample. With high molecular weight sample, cyclic extraction through solution methods is easier and eliminates the presence of high concentrations of low molecular weight linear oligomers.

Processing challenges also exist with high performance polymers, such as polyetherimides (PEIs). As seen in Chapter 7, installing carboxylic acid pendant groups off of the PEI backbone provided a functional handle to react the polymer in the melt. High mol % of the carboxylic acid groups resulted in crosslinked PEIs. Low mol % of the carboxylic acid groups which were processed at elevated temperatures (340 °C) induced branching. The branching, and thus higher melt viscosity at low frequencies, imparted desirable flame resistance properties in PEI thin films. Commercial PEI thin films catch fire and remain burning which lead to flaming drips, whereas the branched samples caught on fire and quickly extinguished leaving charred material. No flaming drips resulted from the branched samples, thus improving the flame resistance. This enhanced flame resistance is desirable for automotive, aerospace, and microelectronic applications.

Installing amides, methyl esters, and phenyl ester/amides off of the same PEI backbone expanded the structure-property relationships of PEIs. These functional groups systematically changed the pendant chemistry. As seen in Chapter 8, all pendant groups reduced the thermal stability as evident by the lower onset of weight loss temperature ($T_{d,5\%}$). The amide and phenyl amide/ester pendant groups increased the T_g by 25-30 °C, while the methyl ester increased the T_g by 10-15 °C. Further studies into the flow behavior of the different pendant groups is required to understand the balance of increasing thermal

properties and melt flow processability. Pendant groups pushing chains apart, thus decreasing chain packing, should help flow properties but is detrimental to mechanical properties. Thus, understanding structure-property relationships relating to thermal properties, flow behavior, and mechanical properties of pendant functionalized PEIs helps design PEIs with enhanced/maintained properties with increased processability.

Chapter 12: Suggested Future Work

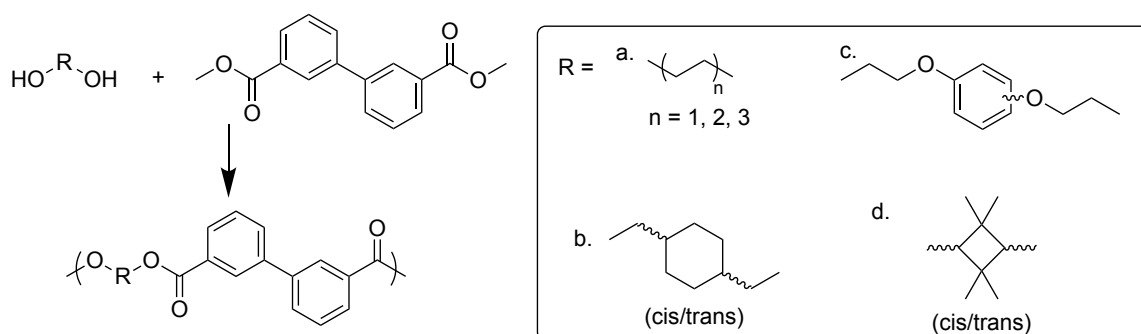
12.1 Synthesis and characterization of 3,3'-bibenzoate polyesters

Bibenzoate (BB)-based polyesters possess improved barrier, mechanical, and thermal properties compared to current commercial polyesters including poly(ethylene terephthalate) (PET), poly(ethylene isophthalate) (PEI), cyclobutanediol (CBDO)-based polyesters and cyclohexanediol (CHDM)-based polyesters (PETG, PCTG, PCT).¹⁻¹¹ 4,4'BB typically produced liquid crystalline or highly crystalline polyesters depending on the length and flexibility of the diol utilized. Disrupting the chain packing by incorporating the 3,4'BB regioisomer reduced the melting temperature and afforded melt processable BB-based polyesters.¹⁻²

The 3,4'BB-based polyester with EG and/or CHDM possessed 25% improved barrier performance compared to amorphous PET, tensile modulus/yield similar to bisphenol-A polycarbonate (BPA-PC) (poly(3,4'BB-EG)) and thermal properties similar commercial CBDO-based polyesters.¹⁻² The barrier performance was attributed to the increased density, similar to PET vs. PEI in the amorphous state. The increased density is attributed to the increase in *trans* conformation compared to *gauche* conformation imparted by the *meta* substitutions. Thus, a 3,3'BB-based polyester could possess an even denser amorphous state and as a result higher Young's modulus and yield strengths. The barrier performance is attributed to the lowering of diffusivity resulting from the more hindered rotation around the 1,3 (*meta*) substitution in the 3,4'BB compared to the 4,4'BB. Thus, incorporating the 3,3'BB should improve barrier properties more due to replacing both *para* linkages in the 4,4'BB and the one *para* linkage in the 3,4'BB, lowering the diffusivity further. Packaging polymers, typically PET, are semi-crystalline due to the

biaxial processing. Poly(3,4'BB-EG) is amorphous in standard 10 °C heat/cool/heat cycles in the DSC, suggesting limited ability to crystallize, necessary for comparison to biaxially oriented polyesters which possess the best barrier properties. The 3,3'BB monomer is slightly more symmetric compared to the 3,4'BB so annealing could produce semi-crystalline morphology. Combining the hindered ring rotations decreasing diffusivity with the semi-crystalline morphology would be promising in food packaging applications. Lastly, the T_g would most likely decrease compared to 3,4'BB/4,4'BB isomers due to more rotational degrees of freedom. Different monomers would be interesting to increase the T_g including CHDM and CBDO.

As seen in **Scheme 12.1.1**, synthesizing polyesters incorporating 3,3'BB enables the determination of structure-property relationships with multiple “kinks” in the backbone. Ethylene glycol (EG) diol is interesting for mechanical properties and barrier. Bis-hydroxyethylbenzene diols such as hydroxyethylresorcinol (HER) is interesting for good barrier performance. CHDM and CBDO are both interesting diols for their bulkier composition increasing the T_g . CBDO with 3,3'BB would be especially interesting due to CBDO-based polyesters' high T_g s but low impact/mechanical properties. If the 3,3'BB monomer promotes entanglement similarly to the 3,4'BB and imparts increased density resulting in improved mechanical properties could counteract the CBDO typically reducing these properties. Thus, a nice balance of T_g and mechanical properties could be realized for polyester homopolymers. The 3,3'BB could be synthesized similarly to the 3,4'BB monomer.¹²



Scheme 12.1.1. Synthesis of polyesters based on dimethyl 3,3'-bibenzoate (3,3'BB)

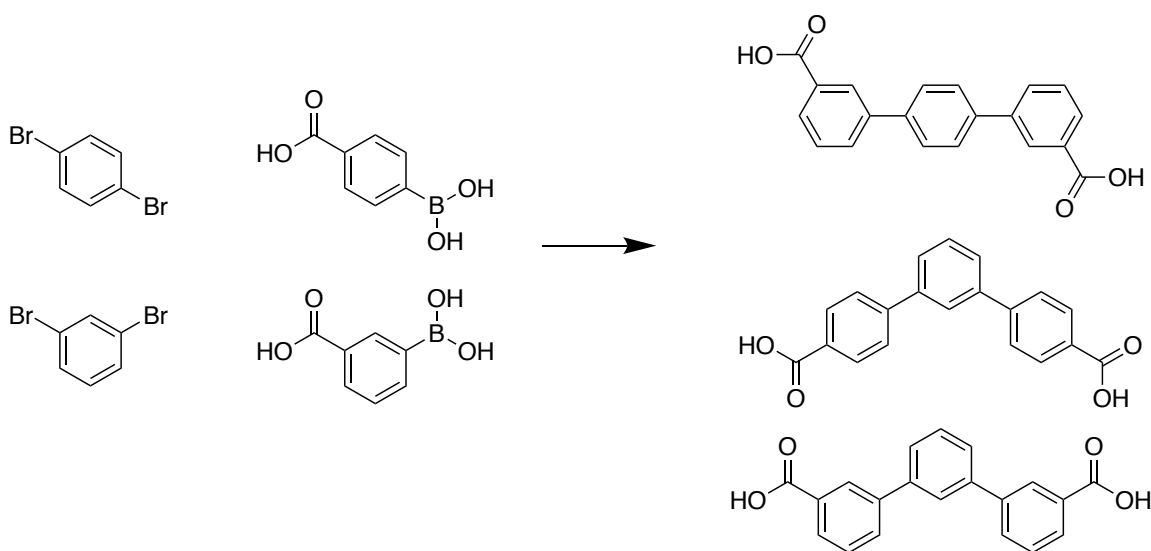
12.2 Synthesis and characterization of terphenyl diacid/diester regioisomers targeting high performance polyesters

To further understand the influence of backbone regiochemistry on polyester structure-property relationships, the synthesis of terphenyl-based polyesters would enable more complex regiochemical possibilities as well as more aromatic polymers. As seen in **Scheme 12.2.1**, utilizing similar methods to synthesize the BB-based diacids/diesters could be used to produce terphenyl regioisomers. Reacting 1,4-dibromobenzene with 4-methoxycarbonylphenylboronic acid or 4-Carboxyphenylboronic acid would produce the *meta-para-meta* terphenyl diacid/diester. Reacting the 1,3-dibromobenzene with 4-methoxycarbonylphenylboronic acid or 4-Carboxyphenylboronic acid would produce the *para-meta-para* terphenyl diacid/diester. Last, reacting the 1,3-dibromobenzene with 3-methoxycarbonylphenylboronic acid or 3-Carboxyphenylboronic acid would produce the *meta-meta-meta* terphenyl diacid/diester.

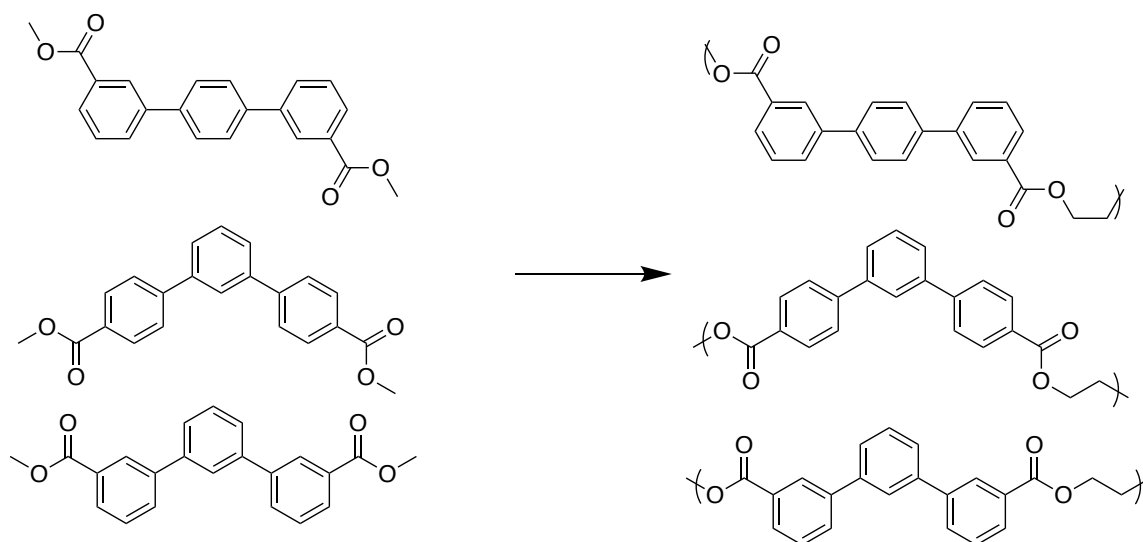
As seen in **Scheme 12.2.2**, these monomers could be polymerized with various diols (EG shown in **Scheme 12.2.2**) to produce various polyester regioisomers. The *meta-para-meta* and *para-meta-para* polyesters would most likely have a hard time packing, thus compromising mechanical properties, although the high aromatic character could balance

the lack of entanglement and chain packing. The *meta-meta-meta* polyester is the most interesting potential composition due to its completely kinked structure as well as linear and symmetric nature. This polyester could possess improved mechanical, barrier, and thermal properties compared to the BB-based polyesters due to the higher aromatic character as well as ability to pack. The symmetry could also promote a semi-crystalline morphology, though the kinked nature could hinder the crystallization rates.

Other diols of interest would be similar to the monomers proposed in **Scheme 12.1.1**. The longer alkyl diols such as butane or hexane diol could help promote crystallinity. The HER/HEH monomers could improve barrier performance. CHDM will raise the T_g , reduce crystallinity, and improve impact resistance. CBDO will raise the T_g but could compromise the mechanical properties, especially with the terphenyl regioisomers which will have difficulty packing. Changing the diol out for aromatic diols, such as hydroquinone or resorcinol could impart a liquid crystalline morphology due to the large aspect ratio of the diacid/diester.



Scheme 12.2.1. Synthesis of terphenyl diacid regioisomers (*meta-para-meta*, *para-meta-para*, and *meta-meta-meta*)



Scheme 12.2.2. Synthesis of polyesters based on terphenyl diester regioisomers (*meta*-*para*-*meta*, *para*-*meta*-*para*, and *meta*-*meta*-*meta*)

12.3 Determining relationship between monomer regiochemistry and cyclic formation and impact of cyclics on thermal, mechanical, and barrier properties

Cyclic formation is well known in step-growth polymerizations.¹³ Commonly, the amount of cyclics formed is determined by monomer regiochemistry and polymerization technique.¹⁴⁻²² Cyclics are at an equilibrium in the melt, commonly used to produce polyesters, and are thermodynamically produced due to entropy. Typically, PET possesses up to 3 wt % cyclic trimer and a little more than that for total cyclic wt %s. PET's *meta*-isomer, PEI, possesses up to 10 wt % cyclics. Other polymers cyclic contents have been quantified, yet limited understanding of the influence of these cyclic species size as well as wt % on bulk polymer properties has yet to be analyzed. Incorporating small molecules such as caffeine, dihydroxybenzenes, and naphthalates, as well as the dimethyl terephthalate or dimethyl isophthalate improved barrier properties up 10x.²³⁻²⁶ Thus, the origin of the improved barrier properties for PEI compared to PET could be due to the

increased amount of cyclics formed during polymerization. Since cyclics are in equilibrium with linear polymer chains, extracting and melt processing the extracted polymer results in reformation of the cyclics. Thus, to adequately quantify the cyclics as well as process the polymers into films for barrier, thermomechanical properties, and tensile properties requires solution processing, limiting the thermal energy needed for the cyclics to reform.

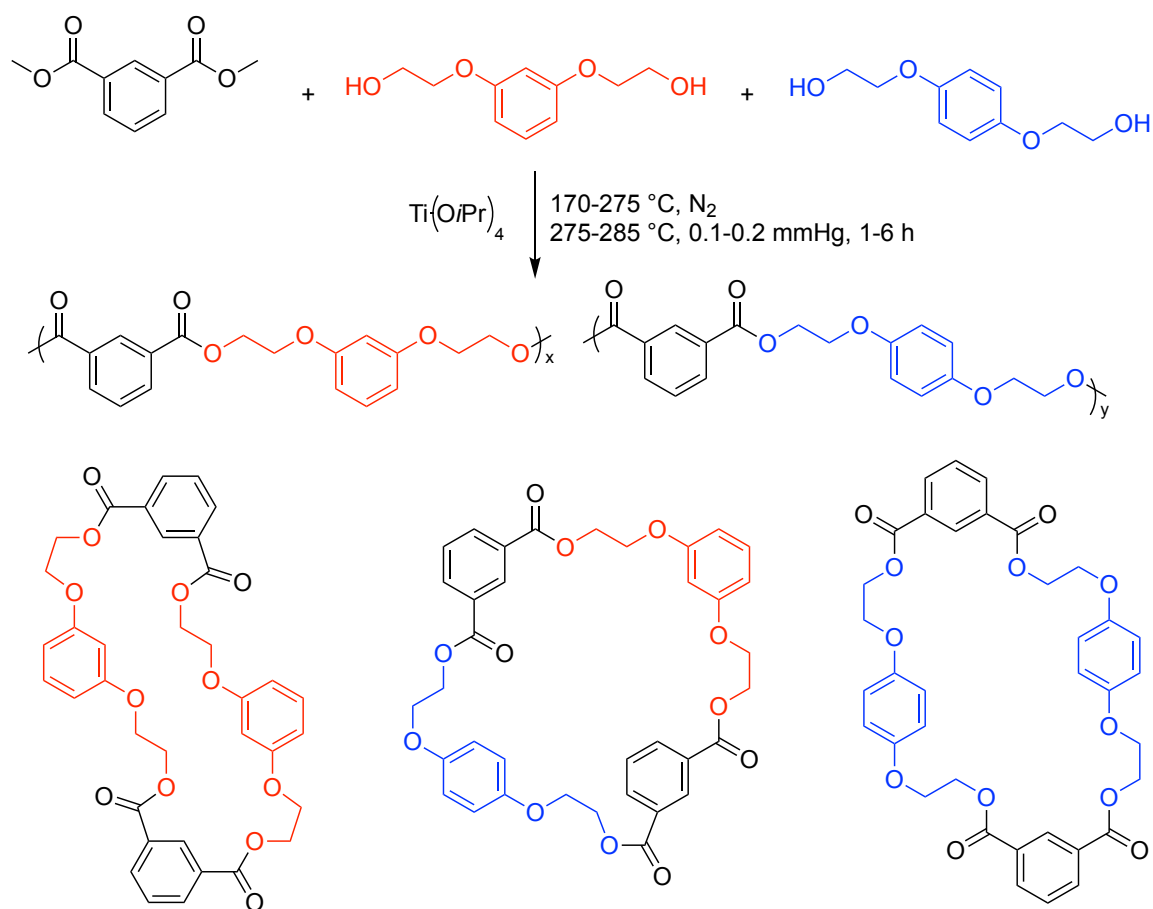
Previous attempts at making polyesters utilizing dimethyl terephthalate and hydroxyethylresorcinol/hydroxyethylhydroquinone (HER/HEH) proved difficult to dissolve in common SEC solvents such as THF and CHCl_3 for compositions with high HEH incorporation. The cyclics were extracted and quantified using APC analysis, but the lack of high molecular weight polymer made extraction of just cyclics difficult. Also, the lack of solubility in common solvents prohibited solution processing films for barrier/tensile analysis. Thus, polymers which systematically change regiochemistry while affording solubility is important to study the influence of cyclic wt % and size on bulk polymer properties.

As seen in **Scheme 12.3.1**, the synthesis of HER/HEH-based polyesters using dimethyl isophthalate rather than dimethyl terephthalate should improve solubility due to the less ordered polymers. High molecular weight must be achieved in order to limit low molecular weight linear chains. Successful extraction of only cyclic species will ensure separation of high molecular weight linear chains and cyclics. Solution processing films with cyclics extracted and without the cyclics removed will enable direct comparison of thermal, mechanical, and barrier properties. Cyclic wt % can be determined utilizing the APC with an RI detector to determine the concentration of individual peak populations. With the concentration of the individual cyclic populations as well as the main chain peak,

the wt % of cyclics can be determined. The presence of cyclics can be determined by MS, ideally MALDI-TOF.

The influence on T_g may be minimal if the cyclics are approaching trimer/tetramer sizes and have sufficient molecular weight to not lower the T_g drastically. If the polyesters are semi-crystalline, the removal of the cyclics could change the crystallization kinetics drastically, since removing the cyclics would remove defects, thus improving crystallizability as well as crystallization kinetics. If the cyclics act more as a plasticizer, mechanical properties would be expected to increase for the extracted samples. The most interesting property would be barrier performance.

Typically, for semi-aromatic polyesters, the improvement in barrier properties for *meta*-substituted polyesters is attributed to the *meta*-substitution's ring rotation being hindered compared to the linear *para*-substitution as well as higher amorphous density. This hindered ring rotation lowers gas diffusivity and thus improves the barrier performance while the denser amorphous phase restricts short range motions, similarly to the ring rotation, also improving barrier performance. If the cyclics are filling free volume, while possessing hindered short range motions, such as ring rotation, the barrier performance of the extracted polyesters would be decreased. Thus, testing barrier performance of the extracted polyesters as well as unextracted polyesters would quantify the influence of cyclics on barrier properties as well as investigate the cyclics behaviors as filling free volume, plasticization, anti-plasticization, etc. Low temperature DMA of these same samples would probe the short range relaxations by comparing the intensity and area of the $\tan \delta$ β -relaxation.



Scheme 12.3.1. Synthesis of hydroxyethylresorcinol (HER)- and hydroxyethylhydroquinone (HEH)-based polyesters with isophthalate as the diester. Potential cyclic dimer regioisomers shown.

12.4 Utilizing DABA-PEIs for improved interlayer adhesion of FDM additive manufacturing and shape fidelity of SLA 3D printing of organogels

12.4.1 Improved FDM interlayer adhesion

Technological innovations resulting from revolutionary manufacturing techniques, i.e. 3D printing, have led to major growth of capabilities and rapid innovation over the past decade.²⁷ Aided by computational design, voxel by voxel control of material placement enables production of custom 3D objects of novel engineering structures. Spatial control of architecture and resolution has led to innovative new products in medical

devices/implants, consumer goods (shoes and car parts), electronic storage devices, and aerospace parts (**Figure 12.4.1.1**).²⁸⁻³² Despite rapid advances in 3D printing capabilities, the field has been hampered by the lack of functional polymeric materials. Herein, we propose novel, functional, and temperature resistant ($\sim 600\text{ }^{\circ}\text{C}$) high-performance engineering polymers to enable fabrication of light-weight, multifunctional 3D structures with applications in the aerospace industry ranging from electrical insulation to light-weight engineering parts. Understanding structure-property-processing relationships of these novel polymers will enable application-specific formulations, targeting advanced technological needs.

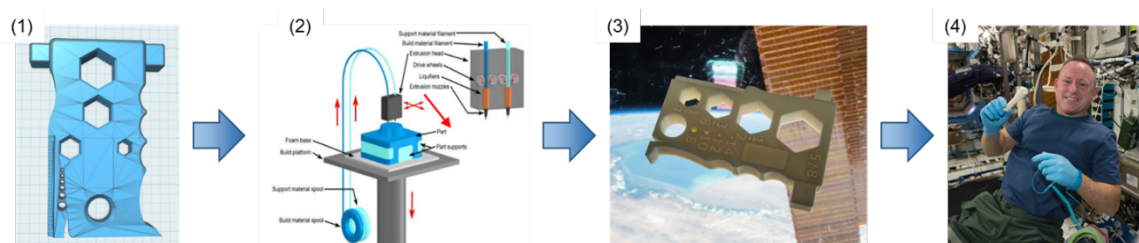


Figure 12.4.1.1: (1) 3D multipurpose precision maintenance tool design³ printed using (2) FDM methods¹⁰ affording (3) multifunctional tool⁴ for use by (4) astronauts on the International Space Station³

Recently developed 3D printing methods offer novel avenues to fabricate unprecedented high-performance polyimide parts.³³ Highly aromatic polyimides possess exceptional high-temperature, radiation, and oxygen stability, chemical resistivity, electrically insulating capability, and low flammability.³⁴⁻³⁶ The most common thermoplastic 3D printing method is material extrusion (Fused Deposition Modeling (FDM)), typically using ABS, polysulfones, polycarbonates, and polyetherimides.²⁸ A nozzle extrudes a melted thermoplastic filament, depositing material at precise locations in the x-y plane. Once a layer is completed, the nozzle head is raised, and places material on top of the previous layer, resulting in an interface between layers. Although intricate and

challenging designs are obtained using this process, issues pertaining to layer interfaces result in anisotropy of material properties. The weak interface reduces the constructs mechanical properties compared to injection molded or extruded parts.³⁷⁻⁴² Post-printing methods such as chemical crosslinking,⁴³⁻⁴⁵ annealing, electrostatic interactions between layers,⁴⁴ and surface modifications⁴⁶⁻⁴⁷ have all been attempted to improve inter-layer adhesion. However, such methods lengthen already undesirably long fabrication times compared to conventional manufacturing techniques. Furthermore, chemical crosslinking is typically accomplished using oligomers above flow temperatures, thereby sacrificing mechanical properties and potentially part resolution due to thermal deformation. In order to advance the utility of FDM, novel chemistry must be developed to enable 3D printed structures to maintain engineering polymer properties. Thus, can polymer design facilitate layer-less 3D printed polyimide structures?

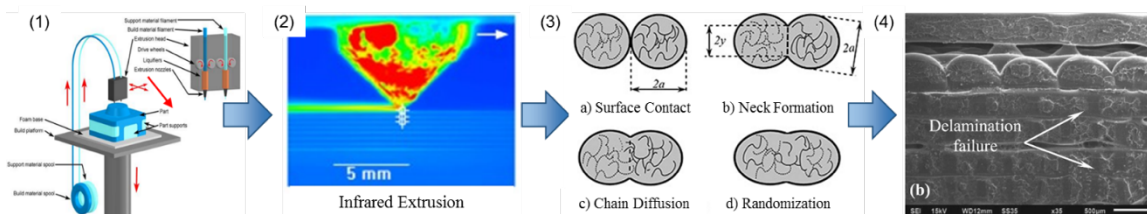


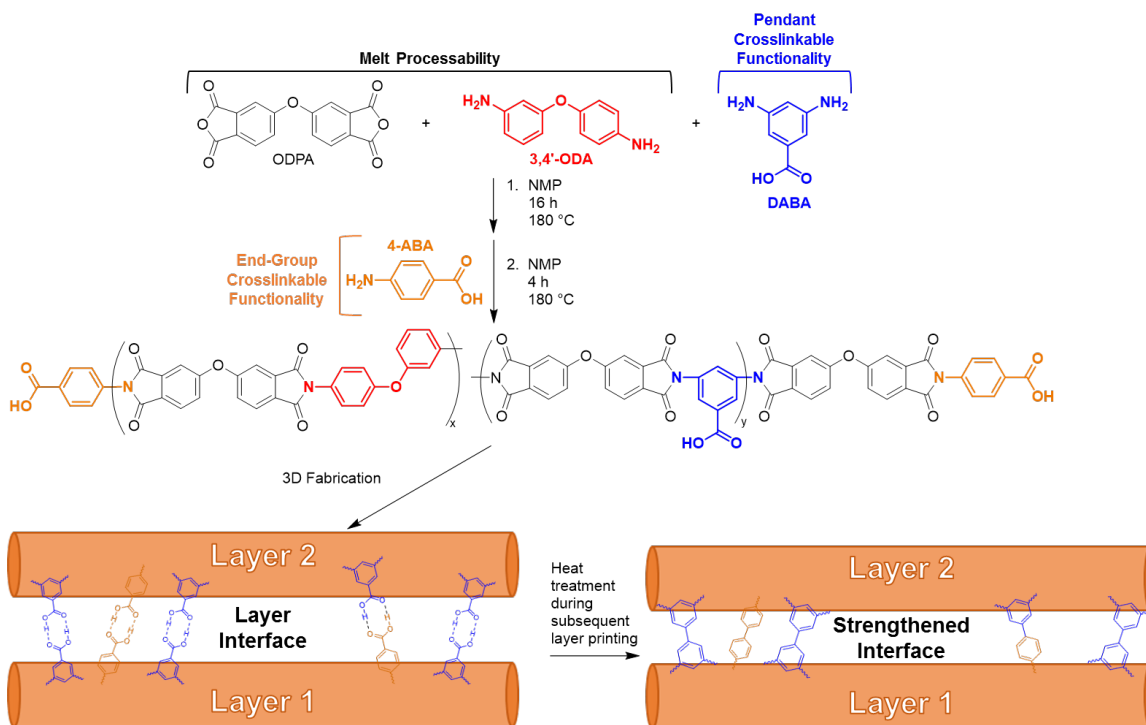
Figure 12.4.1.2: (1) FDM printing³ (2) extrudes melted thermoplastic layer-by-layer,⁸ but limits (3) chain entanglement across filament layers,¹¹ leading to (4) delamination failure in the z-print direction¹²

A radical approach towards accomplishing this goal relies on controlling the interfacial covalent crosslinking time and temperature. 3,5-diaminobenzoic acid (DABA) and 4-aminobenzoic acid (4-ABA) facilitate covalent crosslinking over timeframes longer than extruding a layer (<15 min), minimalizing the risk of the polymer thermosetting in the extruder.⁴⁸ The crosslinking also occurs at temperatures lower than the typical flow temperatures for extrusion,⁴⁹ thus enabling layer elimination in the chamber bed and

prohibiting thermal deformation of the part. Moreover, the products of crosslinking are stable at high-temperatures. The utilization of kinked monomers such as 3,4'-oxydianiline (3,4'-ODA), along with the flexible 4,4'-oxydiphthalic anhydride (ODPA), affords flow properties crucial for filament preparation.⁴⁵ An added advantage is that high crosslink densities can be achieved even with high molecular weights.

Thus, the need exists to develop 3D printable polyimide thermoplastics that form a thermoset during subsequent layer printing, to strengthen/eliminate interfaces. Structure-property-processing relationships of these polyimides will enable computational design of high-temperature parts for aerospace applications. The goal is to develop polyimides with tunable flow temperatures and the ability to strengthen/eliminate interfaces during printing, through inter-layer covalent bond formation. The synthesis focuses on functional polyimides, utilizing the vast array of commercially available monomers as well as industrially practiced methods, offering easy property tunability and scalability. Based on literature precedent, the initial synthesis (**Scheme 12.4.1.1**) will focus on incorporating 3,4'-ODA, DABA, and 4,4'-oxydiphthalic anhydride (OPDA) in the polyimide backbone and end-capping with 4-aminobenzoic acid. End-groups have been shown to migrate to the surface and alter surface energies.⁵⁰ Carboxylic acid end-groups are expected to increase surface wettability and increase crosslinking functionality at the interface. Methods to control the melt flow temperature as well as crosslinking behavior include varying the 3,4'-ODA to DABA mol ratio and altering the molecular weight. Isolating soluble poly(amic acid) intermediates enables compositional and molecular weight analysis using ¹H NMR spectroscopy and size exclusion chromatography (SEC). Unlike previous crosslinking filaments,⁴³⁻⁴⁵ incorporating pendant crosslinking functionality along the polymer

backbone as well as at the end-groups, offers a higher probability these groups will interact across layers, enabling tunable crosslinking through monomer incorporation. Homopolymers of 3,4'-ODA and OPDA should be synthesized as un-crosslinkable controls.



Scheme 12.4.1.1: Proposed synthetic strategy to afford layer-less polyimide 3D structures

Before 3D printing, polyimide processability will be required to optimize monomer ratios and molecular weight. First, thermal transitions should be characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA would confirm high thermal stability (>500 °C) and DSC would reveal transition temperatures including crosslinking. Then, high molecular weight samples containing various monomer ratios should be fabricated into films and held at temperatures mimicking previously determined crosslinking temperatures. Dynamic mechanical analysis (DMA) would probe thermomechanical properties and tensile testing would determine mechanical

properties. DMA plateau moduli analysis will offer insight into extent of crosslinking as a function of time and temperature. Tensile testing would determine variation in mechanical properties. Fourier transform infrared spectroscopy (FTIR) and contact angle hysteresis will examine compositional and crosslinking influences on surface properties. Melt rheology should be performed on compositions that crosslink near complete print times. Several rheological methods, including time-sweeps, shear-sweeps, and temperature-sweeps, will help reveal the influence of molecular weight and composition on shear modulus and printability. Melt flow temperatures would be optimized to create a sufficient window between the flow and crosslinking temperature. 3D structures will be made using compositions that show ideal flow properties.

Extrusion based 3D printers employ filament to produce parts. A Filabot extruder could be used to fabricate filament and a Hyrel 3D: System 30M could 3D print initial constructs to verify selected compositions and molecular weights translate from rheological testing to printing. An extrusion 3D printer with a temperature controlled printing chamber would fabricate advanced parts for property testing. Optimization of the chamber temperatures will enable subsequent layers of the print to crosslink and form strong interfaces during printing. Minimal post-cure times are expected to be needed to induce uniform thermosetting. Optimal chamber temperature will be determined from previous characterization.

T-peel analysis, for interfacial strength determination, will use single-nozzle wide constructs (1 wide x 10 high) to directly test the strength between two layers.⁵¹ Single-nozzle wide samples are ideal due to fracture propagating along the typically weaker interface, reducing random fracture propagation and increasing testing repeatability.

Dogbone tensile specimens will be fabricated in multiple spatial orientations to probe interfacial strength along different axes. Fracture surfaces from T-peel and tensile testing will be analyzed using scanning electron microscopy (SEM) to understand failure modes. All of these tests should be repeated on polyimide samples with no DABA/4-ABA crosslinking functionality. To ensure printed parts maintain properties required for the harsh environmental conditions experienced in aerospace applications, thermal and chemical stability testing is essential. Characterizing a parts resistance to swelling, due to exposure of solvents, expands targeted applications to include energy storage and insulating devices. Flammability testing and isothermal aging will offer advanced stability testing. Overall, the synthesis and characterization of these polymeric materials will provide a full understanding of the structure-property-processing relationships necessary to design next-generation 3D printing materials.

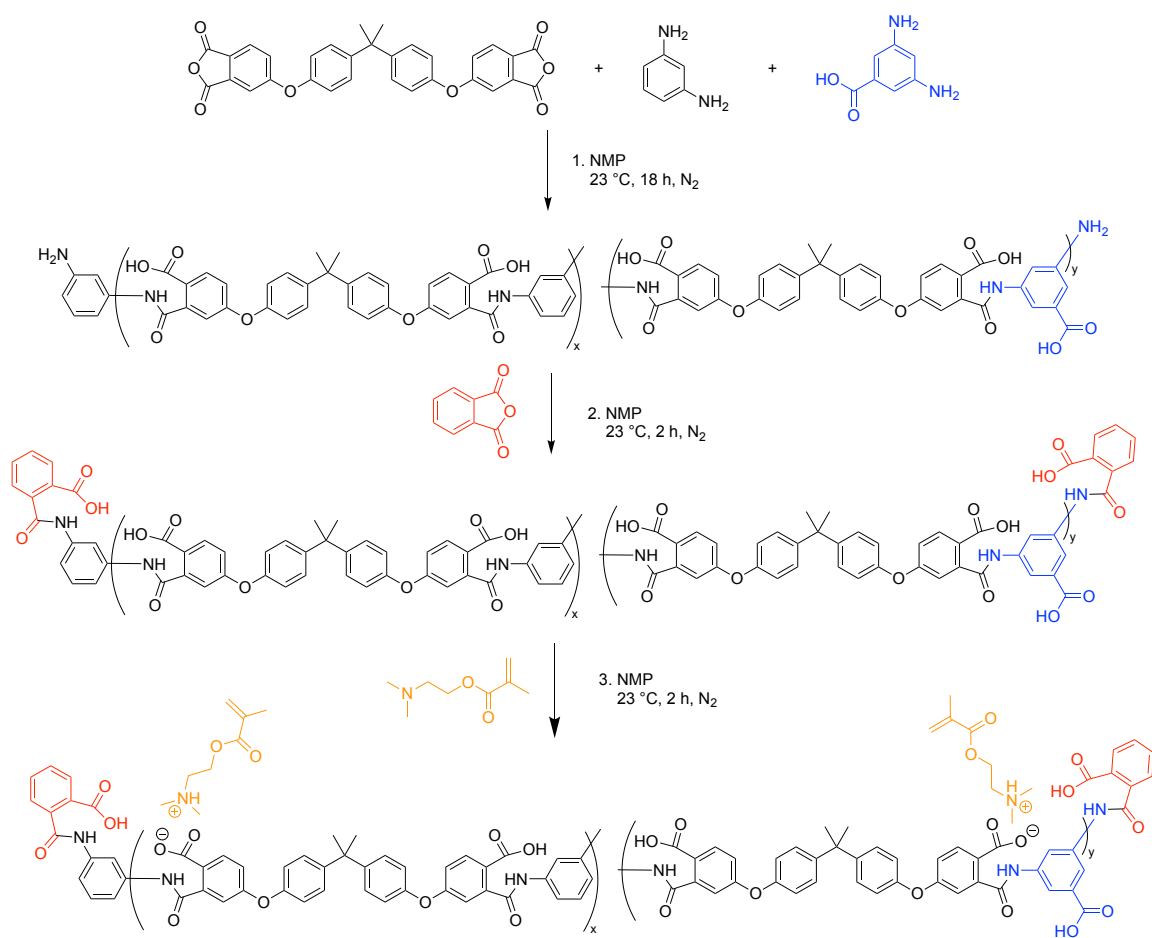
12.4.2 Improved shape fidelity of SLA-printed PEIs containing DABA

Similar to FDM 3D printing, SLA offers difficulties with respect to processing high performance polymers such as polyimides. Kapton® polyimides printed utilizing an SLA 3D printing of an organogel, with subsequent imidization, scaffold degradation/volatilization, and drying, produced 3D structures with properties similar to Kapton® film. Kapton®'s lack of flow before degradation around 600 °C allows the printed shapes to retain their shape fidelity during imidization and drying, which requires high temperatures (>300 °C). When trying to SLA 3D print PEIs that are melt processable, such as ULTEM™ PEI, the high temperatures required for imidization and degradation of the scaffold also results in the PEI to begin to flow. This ability to flow compromises the

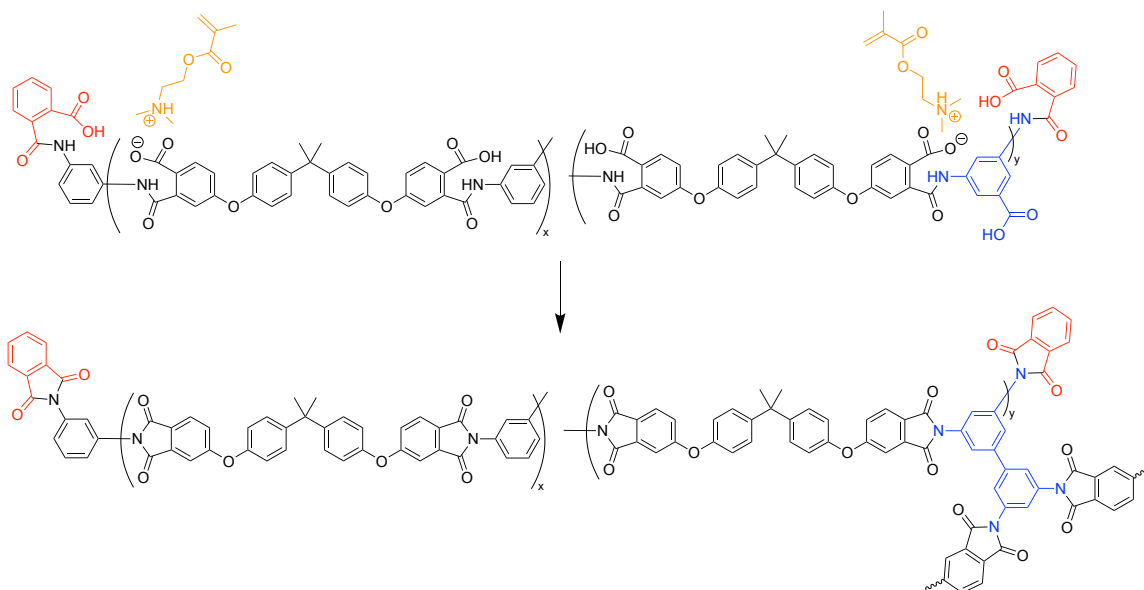
shape fidelity and resolution imparted by the printing technique. Thus, chemistry to lock in the 3D printed shape is required to overcome the onset of flow for these polymers.

Incorporating DABA into PEIs affords a crosslinking mechanism at 300 °C, the same temperature required to begin imidization as well as scaffold degradation. As seen in **Scheme 12.4.2.1**, the synthesis of poly(amic acid)s incorporating DABA into the backbone, with subsequent acid/base chemistry to put photocrosslinkable methacrylates ionically off the backbone, affords multifunctional PEI precursors, which should maintain shape fidelity and resolution throughout the fabrication process with SLA 3D printing.

As seen in **Figure 12.4.2.2**, high temperatures will imidize the poly(amic acid) intermediate, releasing the crosslinked scaffold based off of DMAEMA as well as decarboxylate the pendant carboxylic acid, leading to crosslinking. The crosslinking imparted by the decarboxylation and crosslinking will reduce the flow of the polymer during post-printing processing and afford parts with the desired shape and resolution. This crosslinking strategy can be implemented with all PEI structures to obtain thermosets rather than thermoplastics and could be interesting in the automotive, aerospace, and microelectronic industries.



Scheme 12.4.2.1. Synthesis of photo-crosslinkable poly(amic acids) incorporating 3,5-diaminobenzoic acid (DABA) and DMAEMA ionic pendant groups



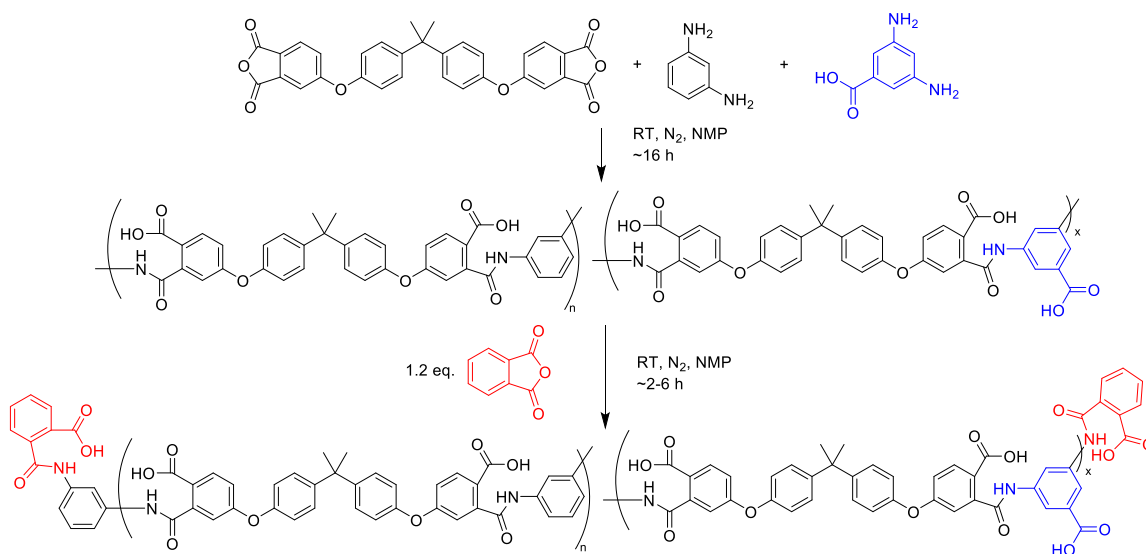
Scheme 12.4.2.2. Thermal imidization and crosslinking of printed DABA-poly(amic acid) resulting in polyetherimide thermoset

12.5 DABA-PEIs as high temperature hot melt adhesives/thermosets with improved adhesion and cohesion through carboxylic acids

Similar to the targeted improvement of FDM 3D printed parts, utilizing the pendant DABA PEIs functionality could be used to improve structural adhesives. PEIs are used as structural adhesives due to their high thermal resistance, mechanical integrity, and easy melt processing as the PEI and solution processing as either the poly(amic acid) intermediate or PEI. Improving PEIs adhesive properties is desirable for construction, automotive, and aerospace applications.

The pendant carboxylic acid will preferentially interact with hydrophilic surfaces, common in metal and glass surfaces. These surface interactions will improve the substrate adhesive adhesion. Similarly, the carboxylic acids ability to dimerize through cooperative hydrogen bonding will strengthen the cohesive strength of the adhesive. Improving both the adhesion to the substrate as well as the cohesion of the adhesive itself will improve the

overall adhesives performance. Synthesis of the poly(amic acids) incorporating DABA is seen in **Figure 12.5.1**. These PEIs can be chemically imidized and melt processed or solution cast from the poly(amic acid) intermediate and thermally imidized. Solution processing is typically preferred due to the ability of the polymer to fill the crevices of the typically rough surfaces or for the chains to preferentially align to maximize adhesion to the substrate surface.



Scheme 12.5.1. Synthesis of DABA-poly(amic acids) (DABA-PAA) with phthalic amic acid end-groups.

As seen in **Figure 12.5.1** and summarized in **Table 12.5.1**, initial 90° peel testing resulted in improved adhesive performance for the DABA-PEIs between stainless steel plates and Kapton® film. The Kapton® film was required as a flexible component to attached to the peel tester. All samples failed adhesively between the DABA-PEI and the stainless steel plates. Increases in average load and maximum load for the compositions with higher DABA mol % indicates the carboxylic acid pendant groups are improving the adhesive and cohesive forces.

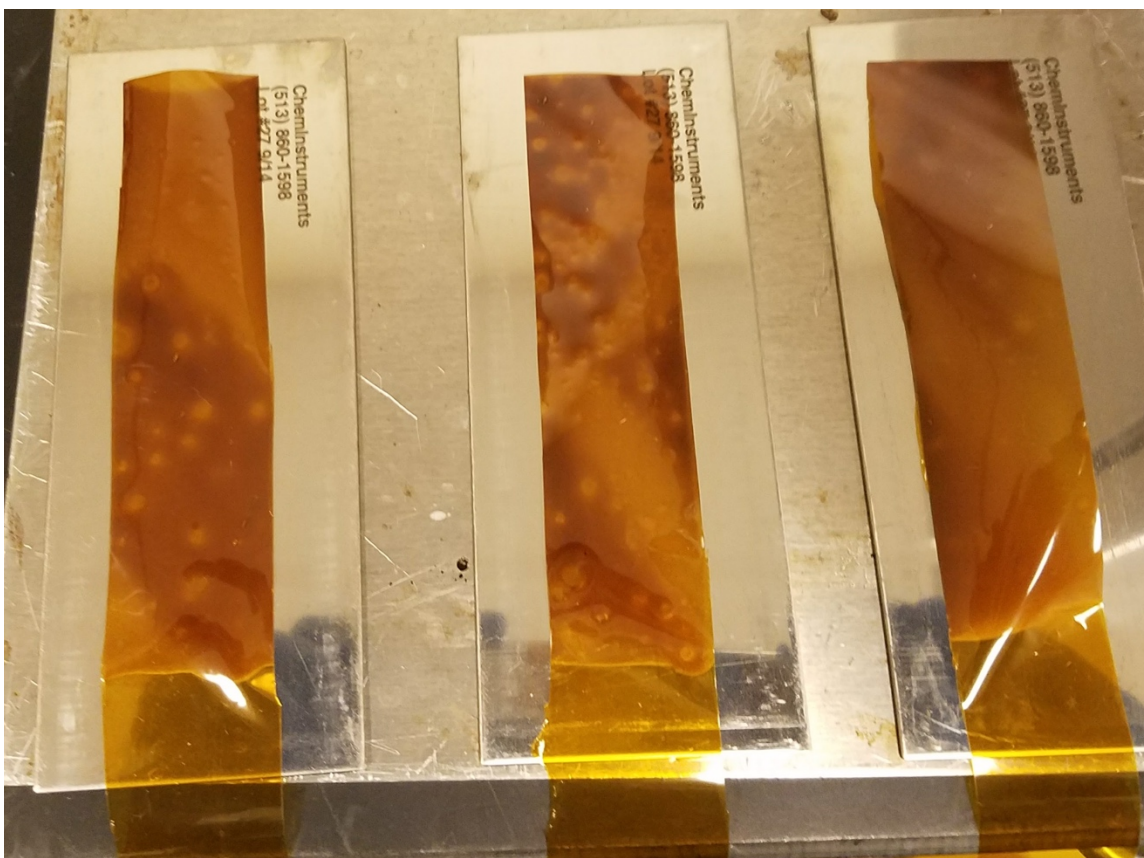


Figure 12.5.1. DABA-PAAs coated on Kapton® film and adhered to stainless steel plates for peel testing

Table 12.5.1. Preliminary 90° peel tests suggest carboxylic acids improve adhesive properties

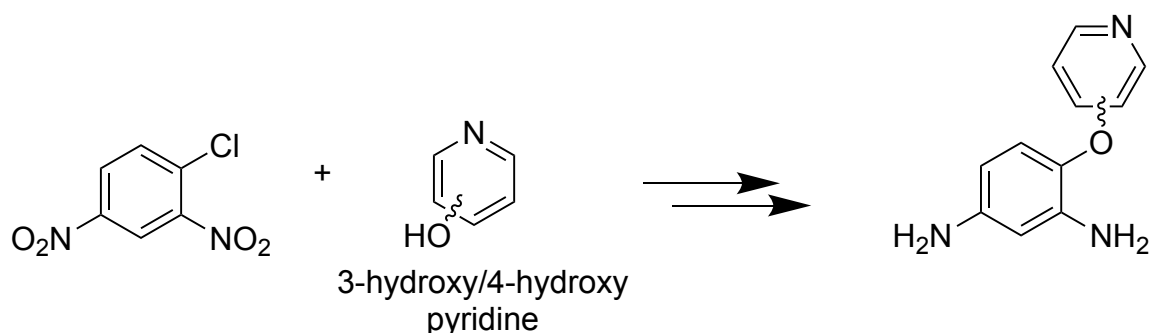
	Average Load (g)	Max Load (g)	Failure Mode	Failure Side
Ultem	213 ± 107	546 ± 137	Adhesive Material	Metal/Kapton
50 % DABA	250 ± 61	704 ± 582	Adhesive Material	Metal/Kapton
100 % DABA	387 ± 76	843 ± 193	Adhesive Material	Metal/Kapton

Another potential use of the pendant carboxylic acid is to use the decarboxylation and subsequent crosslinking that is known to produce adhesive thermosets. The thermoset should improve the cohesion of the adhesive, though could compromise the improved

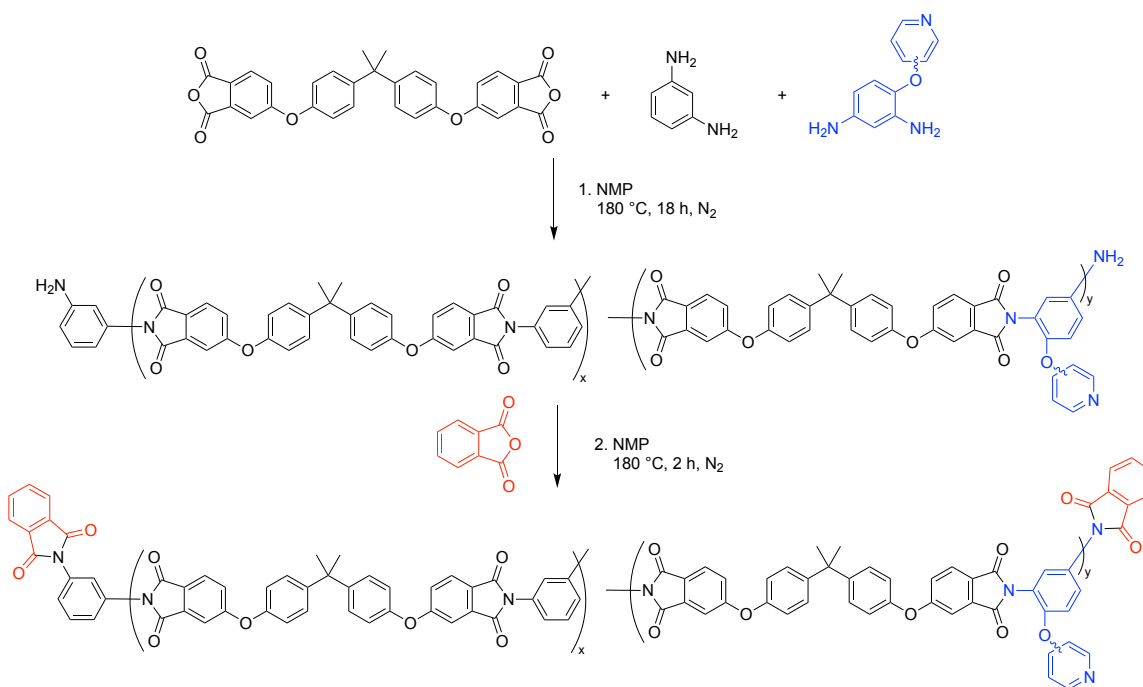
adhesion to the substrate due to loss of the carboxylic acids interacting with the substrate surface. If the adhesive is applied but not decarboxylated and crosslinked when originally set, the decarboxylation and crosslinking could be used later to potentially “heal” the adhesive. If there are signs of the adhesive weakening, heating the adhesive could induce the crosslinking and thus reset or regain the desired adhesive performance.

12.6 Synthesis and characterization of pyridinyl pendant polyetherimides

Increasing functionality of PEIs is desirable to improve processability as well as applicability. Pyridinyl pendant functionality is desirable due to its ability to participate in weak hydrogen bonding as well as metal-chelating ability. As seen in **Scheme 12.6.1**, the reaction of 1-chloro-2,4-dinitrobenzene with 3/4-hydroxypyridine and subsequent reduction of the nitro groups to amines, produces an aromatic diamine with pendant pyridinyl functionality. The ether linkage ensures thermal stability. Replacing common diamines used in PEI synthesis produces pyridinyl pendant functional PEIs, as seen in **Scheme 12.6.2**.



Scheme 12.6.1. Synthesis of pendant pyridinyl diaminobenzene



Scheme 12.6.2. Synthesis of PEIs with pendant pyridinyl functionality

The incorporation of the pendant pyridinyl groups could be used to access reversible supramolecular PEIs. As seen in **Figure 12.6.1**, multiple pyridinyl groups from the same chain or different chains could chelate to a metal element such as zinc or copper. This chelating could enable easier to process PEIs. If the chelating disassociation temperature coincides with the melt processing window, low molecular weight PEIs could be used to lower the melt viscosity, while the final bulk properties could resemble high molecular weight polymer due to the supramolecular interactions. Alternatively, these PEIs could act as water purification membranes to purify out undesired metals in water. The water transmission rate of these PEIs would most likely be low but incorporation of ionic pendant groups could increase the water flow for reverse osmosis type membranes, where the pyridinyl groups could coordinate with the metals; thus acting as purification membranes.

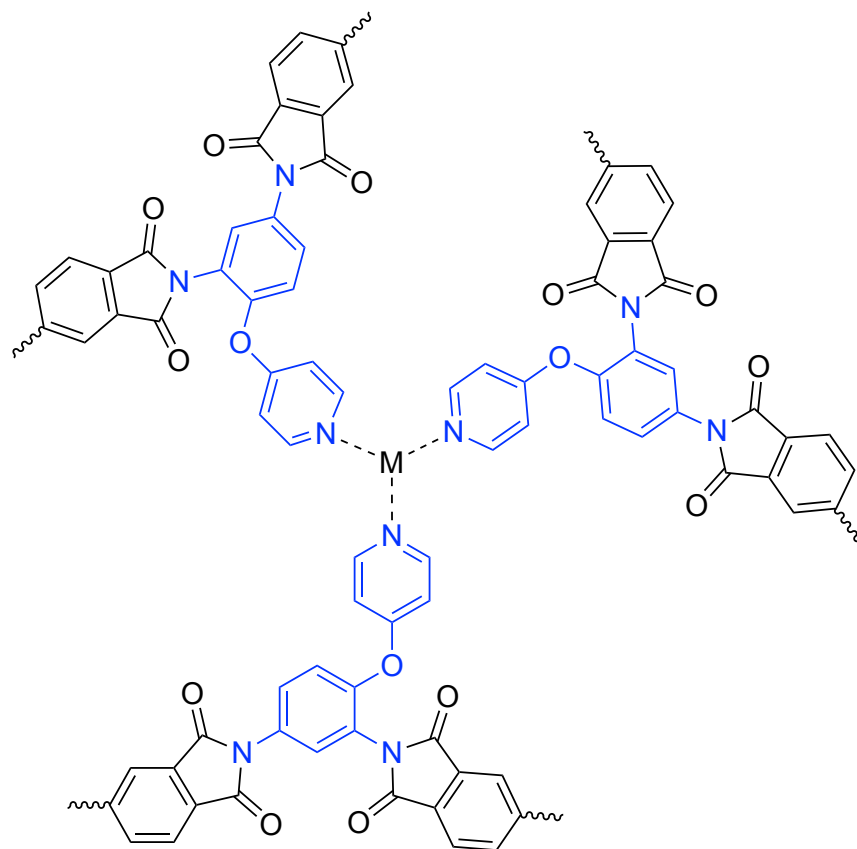
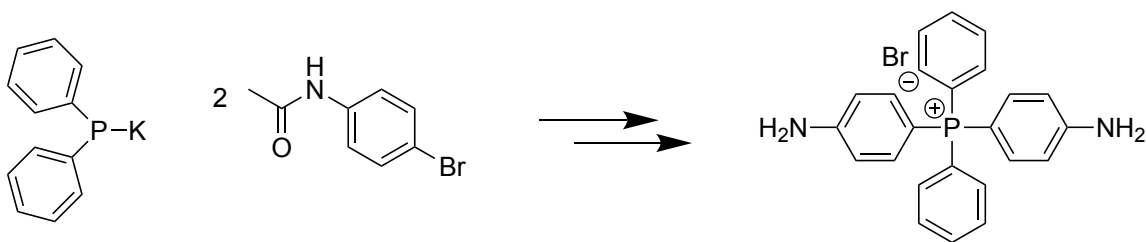


Figure 12.6.1. Inter-/intra-molecular metal binding of polymer chains with pendant pyridinyl functionality

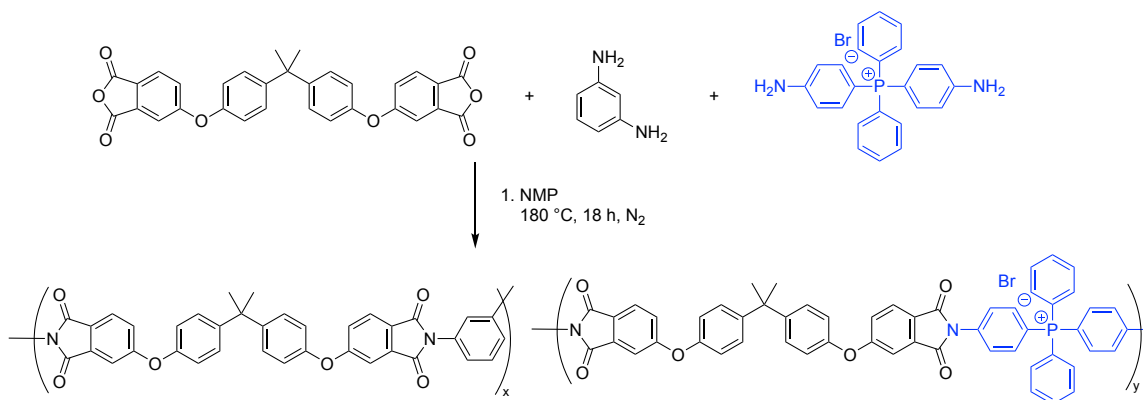
12.7 Synthesis and characterization of phosphonium ionene PEIs

Another method to incorporate functionality and alter properties is to install charged monomers into the polymer backbone. Phosphonium ionenes are interesting polymers due to the systematic placement of the phosphonium charge along the backbone as well as the phosphoniums relatively high thermal stability compared to nitrogen-based counterparts, such as ammonium, pyridinium, and imidazolium. The higher thermal stability enabled melt rheological analysis including TTS and WLF analysis. The stability in the melt at elevated temperatures makes these compositions attractive candidates for incorporation into high performance polymers such as PEIs.

As seen in **Scheme 12.7.1**, reaction an protected-amino bromoaniline with potassium diphenylphosphine would produce a bromo-triphenylphosphine. A second quaternization with the same protected-amino bromoaniline and subsequent deprotection produces the diamino tetraphenyl phosphonium bromide monomer. This monomer could then replace standard PEI diamines to make PEI copolyimides with targeted amounts of the phosphonium in the backbone. The installed positively charged phosphonium would promote ionic interactions. Placing the charge in the backbone compared to pendant would limit pushing chains apart and could help maintain the desired chain packing compared to the pendant functionality pushing chains apart. Comparing to a pendant functionalized PEI with a phosphonium is interesting to study the influence of phosphonium placement on structure-property relationships of high performance polymers such as PEIs.



Scheme 12.7.1. Synthesis of phosphonium-containing diamino monomer

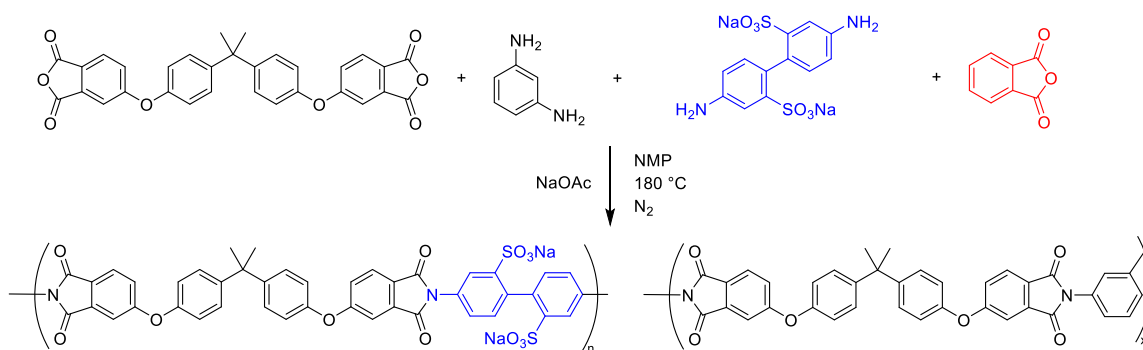


Scheme 12.7.2. Synthesis of poly(ether imide-co-phosphonium ionene)

12.8 Synthesis, fabrication, and characterization of thin film BDSA-PEI actuators incorporating PILs

Incorporation of sulfonate groups into high performance polymers is common due to the thermal stability and functionality. Sulfonates are thermally stable above 300 °C, uncommon for many positively or negatively charged functionality. They also provide ionic interactions, reinforcing mechanical properties through physical crosslinking and ionic aggregation. They are also of interest due to their ability to help with ion and water transfer, important properties required in energy storage applications and water purification membranes. Incorporating the sodium 2,2'-benzidinedisulfonate (BDSA) into the polymer backbone places multiple charges along the backbone, increasing the overall wt % of charged functionality. This increase is interesting for the aforementioned applications as well as changes in solubility.

Incorporating BDSA into polyamides resulted in robust ionic gels when combined with ionic liquids (IL) and water.⁵²⁻⁵³ Thus, incorporating these functional groups into PEIs to improve thermal stability and mechanical properties is interesting for purification membranes as well as electromechanical devices. As seen in **Scheme 12.8.1**, incorporating BDSA into PEIs controls the amount of sulfonate functionality in the polymer. The amount of BDSA will dictate flow behavior and solubility. The potential to incorporate ionic liquid is interesting for electromechanical applications.



Scheme 12.8.1. Synthesis of PEIs containing 2,2'-benzidinedisulfonate

Finding the right amount of BDSA incorporation to swell the PEI with ILs rather than dissolve them is key to making robust devices. Once the right mol % of BDSA is determined, thin films can be fabricated by either casting the PEIs with IL in the casting solvent or swelling the thin films in ILs. Once swollen and incorporated into the BDSA-PEI, the ionic film could be used for electromechanical devices such as actuators. IL composition as well as film fabrication is crucial to obtain high-performing actuators, though actuators based on PEIs will offer superior mechanical strength and thermal stability compared to commonly utilized polymers. These actuators could be used in harsh environment sensing applications including the aerospace, automotive, and microelectronic fields. If incorporating ILs yields actuating thin films, added functionality could come from incorporating polymerizable ionic liquids (PIL)s.

Incorporating PIL monomers into the BDSA-PEI thin films offers the ability to control the morphology of the BDSA-PEI-PIL film using lithography. A photo-mask and UV light can be utilized to polymerize the PILs swollen in the films. Utilizing the mask, different shapes could be selectively polymerized into the films. The varying shapes could then influence the actuation behavior and potentially the bending/movement

direction/shape. This added level of functionality would enable new applications for sensing applications and robotics.

12.9 References

1. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R.; Sirrine, J. M.; Weiseman, T. F.; Nazarenko, S.; Colby, R. H.; Turner, S. R.; Long, T. E., Influence of Bibenzoate Regioisomers on Cyclohexanedimethanol-based (Co)polyester Structure-Property Relationships. *Macromolecules* **2018**, *Submitted*.
2. Mondschein, R. J.; Dennis, J. M.; Liu, H.; Ramakrishnan, R. K.; Nazarenko, S.; Turner, S. R.; Long, T. E., Synthesis and Characterization of Amorphous Bibenzoate (Co)polyesters: Permeability and Rheological Performance. *Macromolecules* **2017**, *50* (19), 7603-7610.
3. Asrar, J., High performance polyesters based on 4,4'-biphenyl dicarboxylic acid. In *Specialty polyesters*, Shotland Business Research, Skillman, NJ: 1995.
4. Dennis, J. M.; Fazekas, N. A.; Mondschein, R. J.; Ramakrishnan, R.; Nazarenko, S.; Long, T. E., Influence of cyclobutane segments in cycloaliphatic decahydronaphthalene-containing copolyesters. *High Perform. Polym.* **2017**, *29* (6), 750-756.
5. Edling, H. E.; Liu, H.; Sun, H.; Mondschein, R. J.; Schiraldi, D. A.; Long, T. E.; Turner, S. R., Copolyesters based on bibenzoic acids. *Polymer* **2018**, *135*, 120-130.
6. Polyakova, A.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A.; Baer, E., Oxygen-barrier properties of copolymers based on ethylene terephthalate. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (16), 1889-1899.
7. Scheirs, J.; Long, T. E., *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*. John Wiley & Sons, Ltd: 2003.
8. Turner, S. R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *J Polym Sci Pol Chem* **2004**, *42* (23), 5847-5852.
9. Turner, S. R.; Seymour, R. W.; Dombroski, J. R., Amorphous and Crystalline Polyesters based on 1,4-Cyclohexanedimethanol. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Scheirs, J.; Long, T. E., Eds. John Wiley & Sons, Ltd: 2003.
10. Booth, C. J.; Kindinger, M.; McKenzie, H. R.; Handcock, J.; Bray, A. V.; Beall, G. W., Copolyterephthalates containing tetramethylcyclobutane with impact and ballistic properties greater than bisphenol A polycarbonate. *Polymer* **2006**, *47* (18), 6398-6405.
11. Kelsey, D. R.; Scardino, B. M.; Grebowicz, J. S.; Chuah, H. H., High impact, amorphous terephthalate copolyesters of rigid 2,2,4,4-tetramethyl-1,3-cyclobutanediol with flexible diols. *Macromolecules* **2000**, *33* (16), 5810-5818.
12. Clary, R. S.; Lee, C. D.; Monroe Iv, W. G.; Vaughn, D. A.; Ragheb, R. T.; Erter Iii, J. W.; Brown, D. M.; Schiraldi, D. A., A Green, One-Pot Route to the Biphenyldicarboxylic Acids: Useful Intermediates in Polymer Synthesis. *International Journal of Organic Chemistry* **2013**, *03* (02), 143-147.
13. Carothers, W. H., Polymerization. *Chem. Rev.* **1931**, *8* (3), 353-426.
14. Berr, C. E., Isolation of a Cyclic Dimer during Synthesis of Polyethylene Isophthalate. *J Polym Sci* **1955**, *15* (80), 590-591.
15. Cooper, D. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 11. Cyclics in poly(ethylene terephthalate). *Polymer* **1973**, *14* (5), 185-192.

16. Harrison, A. G.; Taylor, M. J.; Scrivens, J. H.; Yates, H., Analysis of cyclic oligomers of poly(ethylene terephthalate) by liquid chromatography/mass spectrometry. *Polymer* **1997**, *38* (10), 2549-2555.
17. Heath, R., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 16. Theoretical and experimental investigations of cyclics prepared from poly(decamethylene fumarate) and poly(decamethylene maleate) ring-chain equilibrium reactions. *Polymer* **2000**, *41* (4), 1487-1495.
18. Holland, B. J.; Hay, J. N., Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate). *Polymer* **2002**, *43* (6), 1797-1804.
19. Kricheldorf, H. R., Cyclic polymers: Synthetic strategies and physical properties. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (2), 251-284.
20. Peebles, L. H.; Huffman, M. W.; Ablett, C. T., Isolation and identification of the linear and cyclic oligomers of poly(ethylene terephthalate) and the mechanism of cyclic oligomer formation. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1969**, *7* (2), 479-496.
21. Ross, S. D.; Coburn, E. R.; Leach, W. A.; Robinson, W. B., Isolation of a cyclic trimer from polyethylene terephthalate film. *J Polym Sci* **1954**, *13* (70), 406-407.
22. Walker, G. R.; Semlyen, J. A., Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 4. Calculation of cyclic trimer content of poly(ethylene terephthalate). *Polymer* **1970**, *11* (9), 472-485.
23. Shi, Y. Polyester Composition with Enhanced Gas Barrier, Articles Made Therewith, and Methods. 2005.
24. Shi, Y. S., R. J.; Walters, C.; Kriegel, R.; Huang, X. Polyester Container with Enhanced Gas Barrier and Method. 2006.
25. Shi, Y. S., F. M.; Weemes, D. A.; Weemes, M. K. Container and Composition for Enhanced Gas Barrier Properties. 2010.
26. Zekriardehani, S.; Joshi, A. S.; Jabarin, S. A.; Gidley, D. W.; Coleman, M. R., Effect of Dimethyl Terephthalate and Dimethyl Isophthalate on the Free Volume and Barrier Properties of Poly(ethylene terephthalate) (PET): Amorphous PET. *Macromolecules* **2018**, *51* (2), 456-467.
27. de Gans, B. J.; Duineveld, P. C.; Schubert, U. S., Inkjet printing of polymers: State of the art and future developments. *Adv. Mater.* **2004**, *16* (3), 203-213.
28. Huang, S. H.; Liu, P.; Mokasdar, A.; Hou, L., Additive manufacturing and its societal impact: a literature review. *International Journal of Advanced Manufacturing Technology* **2013**, *67* (5-8), 1191-1203.
29. Students Selected for Winning Designs of 3-D Printed Tools for Astronauts. <https://www.nasa.gov/content/students-selected-for-winning-designs-of-3-d-printed-tools-for-astronauts>.
30. Anderson, J. Building the Future: Space Station Crew 3-D Prints First Student-Designed Tool in Space. https://www.nasa.gov/mission_pages/station/research/news/multipurpose_precision_maintenance_tool.
31. Buck, J. M., T.; Huot, D. Space Station 3-D Printer Builds Ratchet Wrench To Complete First Phase Of Operations. https://www.nasa.gov/mission_pages/station/research/news/3Dratchet_wrench.

32. International Space Station's 3-D Printer.
<https://www.nasa.gov/content/international-space-station-s-3-d-printer>.
33. Hegde, M.; Chartrain, C.; Williams, C. B.; Long, T. E., 3D Printing All-Aromatic, High Performance Polyimides and Polybenzoxazoles Using Stereolithography (SLA): Processing the Unprocessable. VTIP: 2016.
34. Finckenor, M. M.; de Groh, K. K. *A researchers guide to: International Space Station: Space Environmental Effects*; NASA ISS Program Science Office, 2016.
35. Kapton® for Aircraft Thermal/Acoustic Insulation Systems.
<http://www.dupont.com/products-and-services/membranes-films/polyimide-films/brands/kapton-polyimide-film/case-studies/kapton-for-aircraft-insulation-systems.html>.
36. Kapton® Used as the Primary Electrical Insulation in Aerospace Applications.
<http://www.dupont.com/products-and-services/membranes-films/polyimide-films/brands/kapton-polyimide-film/uses-and-applications/kapton-for-aerospace-electrical-insulation.html>.
37. Aubart, M. A.; Jain, S.; Liu, D.; Pedicini, A.; Serpe, S., Enhancing Part Properties in Additive Manufacturing Through Material Design and Print Process Optimization. *Microsc. Microanal.* **2016**, 22 (S3), 1758-1759.
38. Seppala, J. E.; Migler, K. D., Infrared thermography of welding zones produced by polymer extrusion additive manufacturing. *Additive Manufacturing* **2016**, 12, 71-76.
39. Sun, Q.; Rizvi, G. M.; Bellehumeur, C. T.; Gu, P., Effect of processing conditions on the bonding quality of FDM polymer filaments. *Rapid Prototyping Journal* **2008**, 14 (2), 72-80.
40. Chuang, K. C. G., J. E.; Draper, R. D.; Shin, E.-S. E.; Patterson, C.; Santelle, T. D. In *Additive Manufacturing and Characterization of ULTEM Polymers and Composites*, The Composites and Advanced Materials Expo., Dallas, TX, Dallas, TX, 2015.
41. N. Turner, B.; Strong, R.; A. Gold, S., A review of melt extrusion additive manufacturing processes: I. Process design and modeling. *Rapid Prototyping Journal* **2014**, 20 (3), 192-204.
42. Garg, A.; Bhattacharya, A., An insight to the failure of FDM parts under tensile loading: finite element analysis and experimental study. *International Journal of Mechanical Sciences* **2017**, 120, 225-236.
43. Davidson, J. R.; Appuhamillage, G. A.; Thompson, C. M.; Voit, W.; Smaldone, R. A., Design Paradigm Utilizing Reversible Diels-Alder Reactions to Enhance the Mechanical Properties of 3D Printed Materials. *Acs Applied Materials & Interfaces* **2016**, 8 (26), 16961-16966.
44. S., S. M. Improving and Understanding Inter-filament Bonding in 3D-printed. The University of Tennessee, Knoxville, 2016.
45. Chuang, K. C. H., T. W.; Avakian, R.; Hu, L. *Reactive Extrusion of High Temperature Resins for Additive Manufacturing*; 2012.
46. Narahara, H.; Shirahama, Y.; Koresawa, H., Improvement and Evaluation of the Interlaminar Bonding Strength of FDM Parts by Atmospheric-Pressure Plasma. *18th Cirp Conference on Electro Physical and Chemical Machining (Isem Xviii)* **2016**, 42, 754-759.

47. Shaffer, S.; Yang, K. J.; Vargas, J.; Di Prima, M. A.; Voit, W., On reducing anisotropy in 3D printed polymers via ionizing radiation. *Polymer* **2014**, *55* (23), 5969-5979.
48. Kratochvil, A. M.; Koros, W. J., Decarboxylation-Induced Cross-Linking of a Polyimide for Enhanced CO₂ Plasticization Resistance. *Macromolecules* **2008**, *41* (21), 7920-7927.
49. Qiu, W. L.; Chen, C. C.; Xu, L. R.; Cui, L. L.; Paul, D. R.; Koros, W. J., Sub-T-g Cross-Linking of a Polyimide Membrane for Enhanced CO₂ Plasticization Resistance for Natural Gas Separation. *Macromolecules* **2011**, *44* (15), 6046-6056.
50. Orlicki, J. A.; Viernes, N. O. L.; Moore, J. S.; Sendjarevic, I.; McHugh, A. J., Roles of molecular architecture and end-group functionality on the surface properties of branched polymers. *Langmuir* **2002**, *18* (25), 9990-9995.
51. Duranty, E.; Spradlin, B.; Stark, M.; Dadmun, M., Understanding and Improving the Quality of Inter-Layer Interfaces in FDM 3-D Printing. In *American Physical Society March Meeting*, Baltimore, MD, 2016.
52. Wang, Y.; Chen, Y.; Gao, J.; Yoon, H. G.; Jin, L.; Forsyth, M.; Dingemans, T. J.; Madsen, L. A., Highly Conductive and Thermally Stable Ion Gels with Tunable Anisotropy and Modulus. *Adv. Mater.* **2016**.
53. Wang, Y.; Gao, J. W.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions. *Macromolecules* **2014**, *47* (9), 2984-2992.