Synthesis and Characterization of Amorphous Cycloaliphatic Copolyesters with Novel Structures and Architectures

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ABSTRACT

A series of random and amorphous copolyesters containing different cycloaliphatic rings within the polymer chains were prepared by melt polycondensaton of difunctional monomers (diesters and diols) in the presence of a catalyst. These polyesters were characterized by nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile tests and/or dynamic mechanical analysis (DMA). The copolyester based on dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2) was observed to have a higher T_g, about 115 ºC, than the other copolyesters with the same compositions in this study. For copolyesters containing different compositions of dimethyl-1,4-cyclohexane dicarboxylate (DMCD) and DMCD-2, the T_g increased linearly with the increase of DMCD-2 mole content. DMA showed that all of the cycloaliphatic copolyesters had secondary relaxations, resulting from conformational transitions of the cyclohexylene rings. The polyester based on DMCD-3 in the hydrolytic tests underwent the fastest hydrolytic degradation among these samples.

A new triptycene diol (TD) was synthesized and incorporated into a series of cycloaliphatic copolyester backbones by melt condensation polymerization. Straight chain aliphatic spacers, including ethylene glycol (EG), 1,4-butanediol (BD) and 1,6-hexanediol (HD), were used as co-diols to explore their effects on polyester properties.

An analogous series of non-triptycene copolyesters based on various hydroxyethylated bisphenols were also prepared for comparison. The results revealed that the TD-containing polymers had higher thermal stability and higher T_g's than the corresponding non-TD analogs. For TD-containing copolyesters, the mechanical properties were found to be dependent on the types and compositions of the co-diols. A 1,4-butanediol-based triptycene copolyester was observed to have a significantly increased T_g and modulus while maintaining high elongation at ambient temperature. Furthermore, it was demonstrated that the triptycene polyester exhibited higher T_g and modulus than those containing bisphenol derivatives. However, all of the 1,4-butanediol based copolyesters were brittle and had comparable moduli at low temperatures (-25 ^oC or -40 ^oC).

Melt polycondensation was also used to prepare a series of all-aliphatic block and random copolyesters including the following aliphatic monomers: *trans*-DMCD, DMCD-2, neopentyl glycol (NPG), diethylene glycol (DEG) and dimethyl succinate (DMS). The polymer compositions were determined by ^1H NMR, and the molecular weights were determined using SEC. The polyesters were also characterized by TGA, DSC, DMA and tensile tests. Phase separation was not observed in these block copolyesters. However, the block copolyester containing DMCD-2 and NPG was observed to have a higher T_g than the block copolyester based on *trans*-DMCD and NPG. In addition, these block copolyesters were found to have better mechanical properties than the corresponding random copolyesters.

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Table of Contents

List of Figures

List of Schemes

List of Tables

List of abbreviations

1,4-BDM	1,4-benzenedimethanol
BHPS	bis[4-(2-hydroxyethoxy)phenyl] sulfone
BHPC	1,1-bis[4-(2-hydroxyethoxy)-phenyl]cyclohexane
BHPT	1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane
BPA	bisphenol-A
BODO	bicyclo[2.2.2]octane-1,4-diol
BODM	1,4-bicyclo[2.2.2]octane dimethanol
BODA	1,4-bicyclo[2.2.2]octane dicarboxylic acid
BODC	1,4-bicyclo[2.2.2]octane dicarbonyl chloride
BNDM	1,5-bicyclo[3.2.2]nonane dimethanol
BNDA	1,5-bicyclo[3.2.2]nonane dicarboxylic acid
BD	1,4-butanediol
1,1-CHDM	1,1-cyclohexanedimethanol
1,4-CHDM	1,4-cyclohexanedimethanol
1,4-CHDA	1,4-cyclohexanedicarboxylic acid
1,3-CHDA	1,3-cyclohexanedicarboxylic acid
1,4-CHDC	1,4-cyclohexanedicarbonyl chloride
1,4-CHDO	1,4-cyclohexane diol
CPDA	1,3-cyclopentanedicarboxylic acid
CPDM	1,3-cyclopentanedimethanol
DEG	diethylene glycol
DETOSU	3,9-diethylidene-2,4,8,10-tetraoxaspiro[5.5]undecane
DMA	dynamic mechanical analysis
DMCD-1	dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate
DMCD-2	dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate
DMCD-3	dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate
DMBP	dimethyl biphenyl-4,4’-dicarboxylate
DMCD	dimethyl-1,4-cyclohexane dicarboxylate
DMCP	dimethyl-1,3-cyclopentane dicarboxylate

DMF	N,N-dimethylformamide
DMI	dimethyl isophthalate
DMN	dimethyl 2,6-naphthalate
DMCD-M	1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane
DME	1,2-dimethoxyethane
DMSHD	dimethyl spiro[3.3]heptanes-2,6-dicarboxylate
DMS	dimethyl succinate
DMT	dimethyl terephthalate
DMTP	dimethyl 4,4’-terphenyldicarboxylate
DSC	differential scanning calorimetry
EG	ethylene glycol
HBPA	hydrogenated bisphenol-A
HBE	hydroquinone bis(2-hydroxyethyl) ether
HD	1,6-hexanediol
HMPA	hexamethyl phosphoramide
IV	inherent viscosity
IPA	isophthalic acid
LED	light emitting diode
LDA	lithium diisopropylamide
LCP	liquid crystalline polymer
M_n	number average molecular weight
M_w	weight average molecular weight
NMR	nuclear magnetic resonance
N_2	nitrogen gas
NPG	neopentyl glycol
PBS	phosphate buffer saline
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCN	poly(1,4-cyclohexylenedimethylene 2,6-naphthalate)
PCT	poly(1,4-cyclohexylenedimethylene terephthalate)
PCTG	poly(1,4-cyclohexylenedimethylene terephthalate) glycol

PCTA	poly(1,4-cyclohexylenedimethylene terephthalate) acid
PCCD	poly(cyclohexylene dimethylene cyclohexane dicarboxylate)
PCPDT	poly (*cis*-1,3-cyclopentane dimethylene terephthalate)
PD	1,3-propane diol
PCL	polycaprolactone
PEA	poly(ethylene adipate)
PET	poly(ethylene terephthalate)
PETG	poly(ethylene terephthalate) glycol
PEN	poly(ethylene naphthalate)
PEIT	poly(ethylene-*co*-isosorbide) terephthalates
P(EN-*co*-CN)	poly(ethylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate)
P(BN-*co*-CN)	poly(butylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate)
P(BT-*co*-CPDT)	poly(butylene terephthalate-*co*-1,3-cyclopentylene dimethylene terephthalate)
PBSU	poly (butylenes succinate)
PBSA	poly(butylene succinate-*co*-adipate)
P(HN-*co*-CN)	poly(hexamethylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate)
PLLA	poly (L-lactic acid)
PNPIP	poly (neopentyl isophthalate)
PTT	poly(trimethylene terephthalate)
PIDA	phenylindan dicarboxylic acid
PMMA	poly(methyl methacrylate)
RI	refractive index
RT	room temperature
SEC	size exclusion chromatography
SHDA	spiro[3.3]heptanes-2,6-dicarboxylic acid
SHDAC	spiro[3.3]heptanes-2,6-dicarboxylic acid chloride
TPA	terephthalic acid

TMCBD	1,1,3,3-tetramethylcyclobutane-2,4-diol
TMS	tetramethylsilane
TGA	thermogravimetric analysis
T_c	temperature at which polymer was crystallized
T_m	melting transition temperature
T_g	glass transition temperature
THF	tetrahydrofunan
TD	triptycene diol
UV-Vis	ultraviolet/visible
YI	yellowness index

Chapter 1: Dissertation Overview

This dissertation is focused on the synthesis and characterization of polyesters with novel structures/architectures. It begins with a literature review (Chapter 2) on the synthesis and properties of polyesters containing cycloaliphatic rings. Chapter 3 is focused on the synthesis and characterization of linear amorphous polyesters with different cyclic diesters in the polymer backbones and the investigation of relationships between structure and properties. Chapter 4 describes the synthesis and characterization of polyesters containing other cyclic units in the polymer backbones. Future work on photooxidative stability of amorphous cycloaliphatic polyesters is also discussed. Chapter 5 and 6 discuss the melt-phase synthesis and properties of novel amorphous polyesters containing triptycene units or bisphenol units in the polymer backbones. These polymers differ from those in Chapter 3 and 4 because triptycene units or bisphenol units are rigid aromatic cyclic structures compared to the cycloaliphatic structures in Chapter 3 and 4. The properties of copolyesters containing different bisphenol derivatives are compared with the corresponding triptycene polyesters in these two chapters. Chapter 7 discusses an investigation of synthesis and properties of thermoplastic all-aliphatic block copolyesters containing dicyclic units and the neopentyl glycol (NPG) unit in the backbones. In this work, cyclic diesters were incorporated into the polyester backbones and their effects on the thermal and mechanical properties were studied. All polyesters in this dissertation were prepared by high temperature melt polycondensation of difunctional monomers—diesters and diols. Chapter 8 exhibits the overall summary and Chapter 9 shows ongoing experiements and our possible future work on the new project – high T_m polyesters for LED applications.

Chapter 2: Literature Review on Cycloaliphatic Polyesters

Partially taken from: S. Richard Turner; Yanchun Liu. Chemistry and Technology of Step-Growth Polyesters. In *Comprehensive Polymer Science (2nd)*, Elsevier, Inc., Vol. 5, Chapter 14, 2011, *in press*.

2.1 Introduction

This chapter discusses the rationale, synthetic processes most commonly used to prepare polyesters, general structure-property relations, and sections on different polyesters containing cycloaliphatic rings. Each section will describe specific cycloaliphatic monomers and corresponding polyesters, briefly highlight useful properties and suggest some applications.

2.1.1 Rationales for polyesters containing cycloaliphatic rings

Aliphatic polyesters were among the first, if not the first, intentionally prepared synthetic polymers in the pioneering work of Carothers.[1, 2] He and his research group synthesized many aliphatic polyesters from the melt condensation of aliphatic alcohols and aliphatic carboxylic acids. However, these aliphatic polyesters were abandoned as useful fibers because of their low glass transition temperatures (T_g), low melting points (T_m), and sensitivity to hydrolysis. The inclusion of aromatic terephthaloyl groups from dimethyl terephthalate by Winfield and Dickson to form poly(ethylene terephthalate) (PET) in the early 1940s led to a semicrystalline polyester with acceptable T_g's and T_m's for fiber applications.[3] PET was first commercialized by ICI (Imperial Chemical Industries, Ltd) as "Terylene," and it is now the most important polyester in terms of production volume and sales value.[4] PET finds many uses with principal applications in fibers and beverage packaging. Other leading semicrystalline polyesters include poly(butylene terephthalate) (PBT) and poly(1,4-cyclohexanedimethylene terephthalate) (PCT). A large number of aromatic polyesters display a wide variety of properties and have been used as important thermoplastic materials in industry today. Many excellent books and reviews have been written on these polyesters.[5, 6]

Despite their utility and ubiquity, aromatic group-containing polyesters do not exhibit good stability in outdoor applications because of the UV light absorption of the aromatic functionalities. Therefore, there has been a renewed effort in recent years in studying the polymerization chemistry and properties of all-aliphatic polyesters.[7] Many linear aliphatic polyesters from aliphatic diacids with different numbers of carbon atoms (2 to 19) and various diols have been widely synthesized and characterized.[8-12] Ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-butanediol, etc. are typical linear aliphatic diols used for polyester preparation.[10, 13] In general, linear aliphatic polyesters are crystalline with low melting points. They possess excellent UV stability,[14-16] but they often have very low T_g's and poor hydrolytic and/or enzymatic stability. Thus their commercial applications as general plastics have been severely limited.[17] Aliphatic copolyesters with diol end groups are widely used as coatings or intermediates for polyurethanes. More detailed discussion of the applications of linear aliphatic polyesters has been reviewed in various books.[10, 18-22] Introduction of alicyclic units to the main chain of the polymer can impart enhanced T_g's due to the rigidity of the cyclic structures.[19] Higher T_g all-aliphatic polyesters are expected to have important applications as UV protective cap layers for extruded sheet products, as stable substrates for flexible displays and solar cells, and as substrates for microfluidic devices. Therefore, this chapter discusses the information available on various cycloaliphatic monomers, synthetic methods of polyesters, and the effect of cycloaliphatic monomers on the various properties of polyesters.

2.1.2 Cycloaliphatic monomers for synthesis of polyesters

Table 2.1 Structures of cycloaliphatic diols for synthesis of polyesters

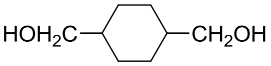
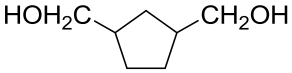
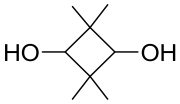
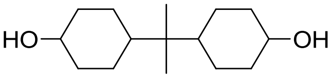
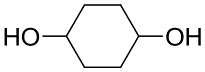
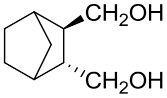
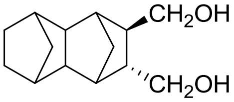
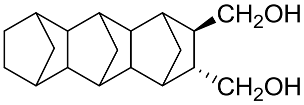
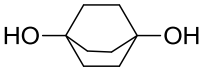
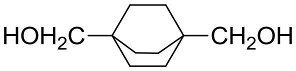
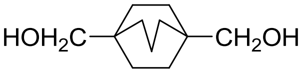
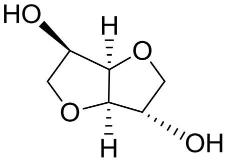
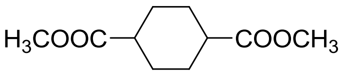
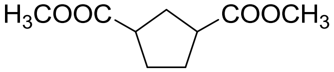
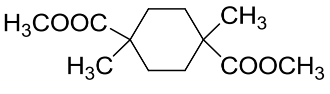
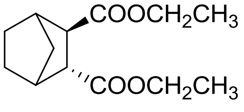
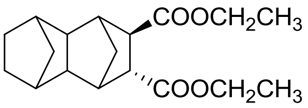
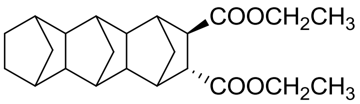
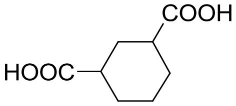
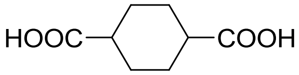
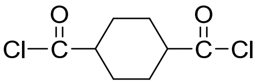
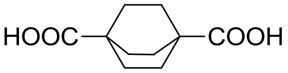
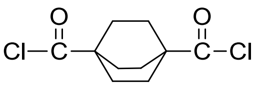
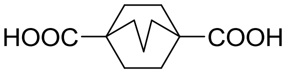
Structures	Name or Abbreviations	Ref.
	1,4-cyclohexanedimethanol (1,4-CHDM)	23
	1,3-cyclopentanedimethanol (CPDM)	24
	1,1,3,3-tetramethylcyclobutane-2,4-diol (TMCBD)	25
	2,2-bis(4-hydroxycyclohexyl)propane (HBPA)	26
	1,4-cyclohexanediol (CHDO)	27
	norbornane-2,3-*trans*-dimethanol (NDM)	28
	perhydro-1,4:5,8-dimethanonaphthalnene-2,3-*trans*-dimethanol (PDMNDM)	
	perhydro-1,4:5,8:9,10-trimethanoanthracene-2,3-*trans*-dimethanol (PTMADM)	
	bicyclo[2.2.2]octane-1,4-diol (BODO)	29
	1,4-bicyclo[2.2.2]octanedimethanol (BODM)	30
	1,5-bicyclo[3.2.2]nonanedimethanol (BNDM)	31
	isosorbide	32

Table 2.2 Structures of cycloaliphatic diacids and derivatives for synthesis of polyesters

Structures	Name or Abbreviations	Ref.
	dimethyl cyclohexane-1,4-dicarboxylate (DMCD)	33
	dimethyl cyclopentane-1,3-dicarboxylate (DMCP)	24
	1,4-dimethyl-1,4-di(methoxycarbonyl) cyclohexane (DMDMCH)	34
	diethyl norbornane-2,3-*trans*-dicarboxylate (DENDC)	28
	diethyl perhydro-1,4:5,8-dimethano naphthalene-2,3-*trans*-dicarboxylate (DEPDMNDC)	
	diethyl perhydro-1,4:5,8:9,10-trimethano-anthracene-2,3-*trans*-dicarboxylate (DEPTMADC)	
	1,3-cyclohexanedicarboxylic acid (1,3-CHDA)	23
	1,4-cyclohexanedicarboxylic acid (1,4-CHDA)	
	1,4-cyclohexanedicarbonyl chloride (1,4-CHDC)	35
	1,4-bicyclo[2.2.2]octanedicarboxylic acid (BODA)	30
	1,4-bicyclo[2.2.2]octanedicarbonyl chloride (BODC)	29
	1,5-bicyclo[3.2.2]nonanedicarboxylic acid (BNDA)	31

Various cycloaliphatic diols, diacids and their derivatives have been used for the synthesis of polyesters in the literature. Their structures are summarized in **Table 2.1** and **Table 2.2.** Their corresponding polyesters are discussed in later sections.

2.1.3 Synthetic methods of cycloaliphatic polyesters

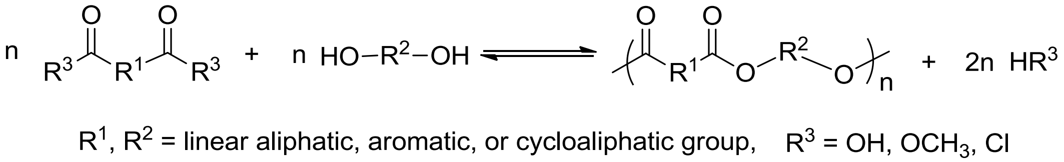
In theory any synthetic reactions to form an ester can be used to prepare cycloaliphatic polyesters. However, high conversions are necessary to achieve high molecular weight according to the well-known Carothers equation **(2.1)**,[36, 37] thus practical synthetic processes of polyesters are limited to direct esterification, transesterification and reaction of alcohols with diacyl chlorides and other activated esters (**Scheme 2.1**).[19, 20, 38, 39]

$$X_n = 1/(1-p)$$

Where X_n = number average degree of polymerization

p = the degree of conversion for functional groups

Equation 2.1 The Carothers equation



Scheme 2.1 Synthesis of polyesters based on different difunctional monomers

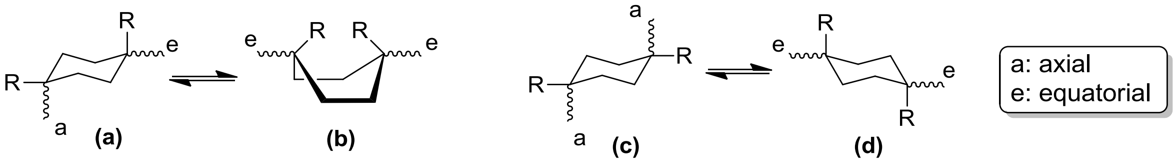
Direct esterification is the reaction of a diacid and diol or the self-condensation of a hydroxycarboxylic acid. It is a slow process and an acid catalyst is needed to increase the reaction rate. Furthermore, high temperature is required to remove the water by-product and achieve high molecular weight polymers. Direct esterification can be practical if the diacids are first converted to diesters, which, with a proper catalyst, operate as a transesterification polymerization as discussed later. A second method, the reaction of an acyl chloride with an alcohol (Schotten-Baumann reaction) does not usually require a high temperature due to the high reactivity of the acyl chloride. The reaction is essentially complete and irreversible. This method is useful for aromatic ester synthesis where phenol is used. It can be carried out interfacially by using a bisphenol dissolved in aqueous base and then adding the diacyl chloride in a water-immiscible solvent. The interfacial polycondensation procedure can give high molecular weight polyesters. One disadvantage is that large amount of solvents are necessary. Furthermore, the high reactivity of diacyl chloride necessitates purification and storage prior to use since these compounds are reactive with ambient moisture. Also, partially hydrolyzed diacid chloride could upset the stoichiometry and lower the degree of polymerization.

Melt transesterification is often the most practical route and is readily adapted to large scale industrial processes. It involves two distinct steps, namely the ester exchange stage and the polycondensation stage.[6] One advantage of this route over other methods is that the absence of any solvents leads to lower production costs and fewer environmental issues. Another attractive feature is that it is not necessary to worry about the solubility of reactants and products in the solvent. Moreover, the product can be directly used after the polymerization reaction. Finally, it is not necessary to exactly control the stoichiometric balance of the two functional groups at the start of the polymerization if the diol is readily volatile. The volatile diol may be used in excess. Stoichiometric balance is inherently achieved at the end of the second stage of the process. However, melt polymerization also has some drawbacks. For example, it requires relatively high temperatures to overcome the activation energy of the transesterification between diesters and diols. A partial or high vacuum is necessary to remove low molecular weight byproducts (such as methanol, ethylene glycol or oligomers), and to push the equilibrium toward the formation of the high molecular weight polyesters. Catalysts, such as titanium alkoxides or antimony oxide, are also required to accelerate the reaction. In addition, high molecular weight and amorphous cycloaliphatic copolyesters can be prepared by incorporating volatile comonomers, such as ethylene glycol, 1,3-propanediol, or 1,4-butanediol.[25] The excess volatile diol can drive the esterification to completion and can then be removed under high vacuum in the later stage of polymerization. In general, the number average molecular weight of cycloaliphatic polyesters is typically located in the range of 10,000 to 100,000 g/mol and their polydispersities are 2.0 - 2.5 as for most step-growth polymerizations.

2.1.4 Overall structure-property relationship of cycloaliphatic polyesters

The properties of polyesters are highly dependent on the monomer composition in the backbone and on the geometry, polarity and segmental mobility of their repeating units. Since the intermolecular interactions of polyesters are not as strong as those of polyamides or polyurethanes, the properties of polyesters are more sensitive to structures than these polar materials, which can also form hydrogen bonds. The characteristics of cycloaliphatic ring-containing polyesters are determined by the structure, symmetry, and conformational features of the cyclic units. Also, they are dependent on the relative contents of cyclic and acyclic components in the repeating units. Generally, polyesters with predominantly cyclic components have higher melting temperatures and glass transition temperatures than acyclic polyesters. The thermal properties of cycloaliphatic polyesters fall between those of aromatic and linear aliphatic polyesters. Cycloaliphatic polyesters can exhibit higher T_g's and T_m's than their non-cyclic counterparts.[18] This is because chain motion in the ring is restricted and chain rigidity is increased when methylene units are replaced by cyclic groups in the polymer backbones.

The thermal properties of polyesters can be greatly affected by the stereochemistry of the cycloaliphatic residues. Thermal *cis*/*trans* isomerization of the 1,4-cyclohexylene rings in the presence of certain catalysts during the polymerization greatly affects the physical state of polyesters. When a methylene group is inserted between carboxyl groups and the cyclohexane ring, the monomers do not isomerize during thermal polycondensation. Many papers about the synthesis of cycloaliphatic polyester study the *cis/trans* conformation and the isomerization between the two cyclohexane-containing isomers.[40-43] There are three possible low energy conformations (chair, boat, and twist) for the cyclohexane ring. The chair conformation has the lowest energy among three forms. In the case of 1,4-disubstituted cyclohexanes, *cis* isomers are obtained if one substitution is equatorial and the other is axial; the *cis* configuration can exist in the chair **(a)** or boat **(b)** conformation,[44] whereas the *trans* isomers result from two equatorially **(c)** or two axially **(d)** substituted forms.[45] In the latter case, the diequatorial chair conformation is preferred (**Scheme 2.2**).



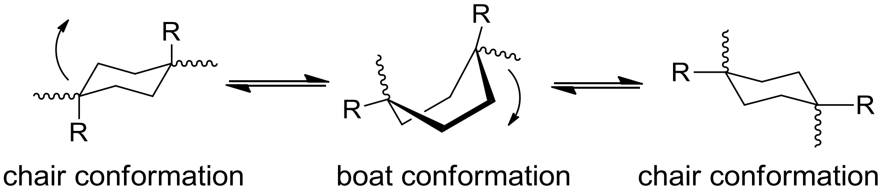
Scheme 2.2 Conformations for *cis*-1,4-cyclohexylene (left) and *trans*- units (right)[44]

High solubility of polymers in many organic solvents is an advantage in processing and is greatly affected by chain structure properties, such as geometry, symmetry, polarity, and segmental mobility. Most aromatic polyesters are insoluble in common organic solvents, but the incorporation of alicyclic structures into the polymer backbone can enhance solubility due to the decrease of polymer–polymer interactions.[46] The solubility of polymers also depends on the crystallinity and the molecular weight. Solubility is reduced when the molecular weight increases for the same type of polymer. Higher solubility of polymers may be related to low crystallinity.

When a cycloaliphatic group with possible *cis*/*trans* isomers is introduced into the polymer backbone, the *cis*/*trans* isomer ratio can greatly affect the crystallinity of the polymer.[47] The *trans* isomers favor the formation of crystalline or liquid crystalline phases due to more regular packing. Compared to the *trans* isomer, *cis* cyclohexane rings introduce kinks into the main chain and these kinks tend to hinder crystallinity. Polymers with high *trans* isomer content are usually crystalline, while polymers with fully *cis* isomer are amorphous. These amorphous characteristics of the polymers based on *cis* materials can be reflected in their appearance. The fibers from c*is* monomer are transparent, while those based on the *trans* monomer are translucent.[48]

The mechanical properties of a polymer are important attributes for many applications. Polyesters find end use as engineering thermoplastics and fibers, hence mechanical properties like tensile yield strength, flexural modulus and impact strength play a key role in suitability for specific applications. These mechanical properties are dependent on the polymer composition, molecular weight, and crystallinity. The impact strength of a polymer depends greatly on the polymer backbone structures, the position of the T_g and degree of crystallization.[49] Amorphous polymers can undergo brittle fracture significantly below their T_g, but they become tougher when the temperature is close to T_g. When the temperature increases well above the T_g, a rubbery state is formed and the impact strength does not have significance. Crystallizability is an important factor which affects the physical properties of polymers. In the case of crystalline polymers, both degree of crystallinity and the size of the spherulitic structures can influence the toughness. However, the degree of crystallinity of the polymer is partially determined by the molecular weight of the polymer and the processing procedures, such as time permitted for cooling. Fast quenching often results in lower crystallinity material, while very slow cooling produces higher crystallinity. Generally, a large degree of crystallinity will result in inflexible structures, which will produce moderate impact strength. Similarly, low impact strength also results from large spherulitic structures.[49]

The impact strength of polymers can also be affected by low temperature relaxations. Many studies have been focused on the secondary relaxation of polymers in the past several decades.[44, 50, 51] A major motive of these studies was to find a relationship between these secondary relaxations and mechanical properties. Ductile materials show a distinct low-temperature secondary loss peak in their DMA spectra. The mode of failure varies from ductile to brittle at the ductile-brittle transition temperature, which was often related to secondary relaxation peak temperatures. The incorporation of the cyclohexyl group increases the intensity of the secondary relaxation, which is due to the conformational transition between the two stable chair conformations of the main chain cyclohexylene group (**Scheme 2.3**).



Scheme 2.3 Conformational transition of the cyclohexylene ring.[52]

When the cyclohexylene content increased, the yield stress was found to decrease. [53] Because of conformational changes of the cyclohexylene rings, the barriers between chain segments are reduced and result in the ease of chain motion. Furthermore, the conformational transition of the cyclohexylene ring can interact with the motions of neighboring segments. This interaction further facilitates the molecular motion of neighboring segments and influences the mechanical properties of polymers. The mechanical properties of some specific cycloaliphatic polyesters will be discussed and compared in later sections.

The optical properties of polymers are related to light transmission and light reflection. Ultraviolet/visible spectroscopy (UV-Vis) can be used to study certain optical properties of polymers. These optical properties are sensitive to chain structures. In the case of the aromatic polymers, the aromatic groups strongly absorb ultraviolet light and, depending on specific aromatic groups, absorb visible light. Aromatic group-containing polymers usually undergo serious yellowing and chain degradation as a result of the absorbed energy. Semi-crystalline polyesters, such as PBT, poly(ethylene naphthalate) (PEN) and PET, when the crystallites are larger than the wavelength of visible light, are also opaque due to the scattering of light by the semi-crystalline morphology. As far as transparency is concerned, it is the ability of a sample to transmit light and it can be quantified as the ratio of the intensity of the light directly transmitted through the sample to the intensity of the incident light, [54] as shown in **Equation 2.2**.

$$\text{Transparency (\%)} = I_t / I_i \times 100 \qquad \textbf{(Equation 2.2)}$$

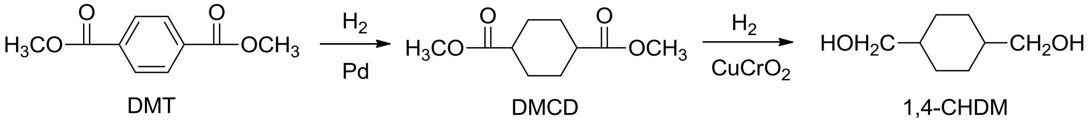
Where: I_t = intensity of unscattered transmitted light; I_i = intensity of incident light.

The transparency of crystalline polymers increases when the degree of crystallinity decreases. In general, amorphous polymers are more transparent than semi-crystalline polymers. Compared to similar polymers having aromatic rings in their main chain, the alicyclic polymers are also more optically homogeneous due to lower crystallinity. Polyesters with different isomers of alicyclic structures often have lower crystallinity and are transparent. Due to the excellent transparence of cyclic aliphatic polyesters, they can be used as optical articles and weatherable materials, which together with the photooxidative stability will be discussed later.

2.2 Polyesters based on monocyclic monomers

2.2.1 Monocyclic diol: 1,4-cyclohexanedimethanol (1,4-CHDM)

1,4-Cyclohexanedimethanol (1,4-CHDM) **(1)** is an important commercial cycloaliphatic diol that is used in a variety of important commercial polyesters.[55] 1,4-CHDM **(1)** is synthesized commercially by the hydrogenation of dimethyl terephthalate (DMT) under high pressure to dimethyl cyclohexane-1,4-dicarboxylate (DMCD) and further reduction with copper chromite to the primary diol 1,4-CHDM. The synthetic process is shown in **Scheme 2.4**.[56, 57]

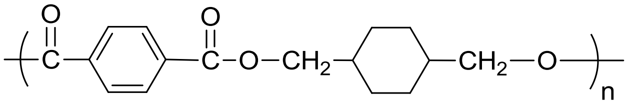


(1)

Scheme 2.4 Synthesis of 1,4-CHDM

1,4-CHDM can exist as the *cis* or *trans* isomer and most commercial 1,4-CHDM is an equilibrium mixture of isomers with an approximately 70/30 *trans*/*cis* ratio. It is readily incorporated into polyester backbones by conventional high-temperature, melt-phase polymerization. For example, poly(1,4-cyclohexylenedimethylene terephthalate)

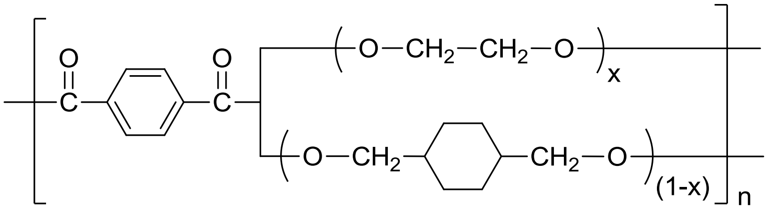
(PCT) **(2)** prepared from 1,4-CHDM and DMT was first produced by Eastman Kodak as a semicrystalline polyester fiber and was successfully marketed in the fiber industry for many years until it was discontinued in the 1980s.[55]



(2)

Then PCT was introduced as a molding resin with specific uses such as connectors for both the electronic and automotive markets. PCT has a high heat deflection temperature (~260 °C) and is much cheaper than liquid crystalline polymers. One specific advantage of PCT is that it has similar flow characteristics during molding as that of PET and PBT even at high temperatures, thus it can be used in conventional injection molding equipment. In addition, PCT has low moisture uptake and is not affected by humidity changes. PCT has a high melting point (about 300 °C for the homopolymer) and a high melt viscosity allowing high processing temperatures of up to 300 °C. Brittle parts are produced at such high temperatures due to thermo-oxidative degradation and a severe drop in viscosity during molding.[58] One source of structural weakness is the presence of two tertiary hydrogen atoms; both in the *β*–position to the ester group. Common PCT commercial polyester are modified with small amount of isophthalate to lower the melting point so that the polyester can be melt proceeded at lower temperature.[59]

The usual commercial form of PCT has a similar isomer ratio (70/30 *trans*/*cis*) with the monomer diol 1,4-CHDM produced at the reduction stage. The melting point of PCT is dependent on the *cis*/*trans* ratio of 1,4-CHDM and it is approximately 315 °C for *trans* 1,4-CHDM and 250 °C for *cis* 1,4-CHDM.[55] The T_g also increases from 60 °C (*cis*) to approximately 90 °C (*trans*). However, there is little difference in the degree of crystallinity or the crystallization rates over the entire isomer range for PCT.[60] PCT does not crystallize as rapidly as PBT but its crystallization behavior is similar to that of PET. Crystalline PCT from 70/30 *trans*/*cis* mixture has a higher T_m than PET (300 vs 260 ^oC) and a higher T_g (88 vs 80 ^oC). Furthermore, PCT has improved stability and better heat-distortion temperature characteristics compared to PET. 1,4-CHDM has found considerable use in PET container resins. Low levels of 1,4-CHDM (< 5 mol %) incorporated into PET improve the molding characteristics of PET and enhance clarity to stretch blow-molded bottles by modifying the crystallization characteristics of the PET backbone. PETG name **(3)** is applied to the copolyester of PET that is modified with up to 50 % of 1,4-CHDM. When 1,4-CHDM is contained in the compositional range from 20 to 50 mol%, PETGs are typically amorphous and tough.



Structure represents PETG **(3)** when EG is the major glycol component
Structure represents PCTG **(4)** when 1,4-CHDM is the major glycol component

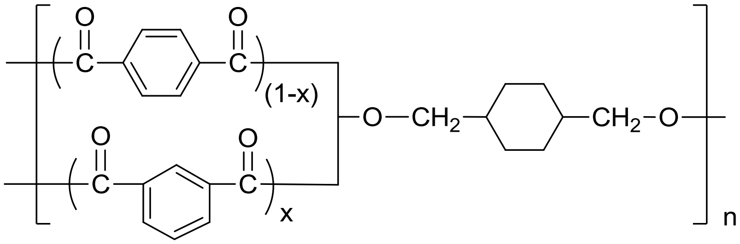
PETG polyester has been widely applied in specialty packaging areas due to its higher clarity and impact resistance compared to PET and other transparent resins, such as poly(methyl methacrylate) (PMMA).[61] PETG's trade name Spectar^{TM}, based on proprietary manufacturing technology, was introduced by Eastman Chemical Company in the last decade. Spectar^{TM} copolyesters possess excellent color, optical and physical properties and are extruded into heavy gauge sheeting widely used for point-of-purchase displays.[61] Furthermore, the copolymer PETG has relatively low cost, high impact strength and is readily melt processed, thus it is available for many transparent plastic applications. Many articles formed from PETG have increased hardness and/or heat resistance. Examples of these articles include molded polyester exterior panels used in automobiles and small molded polyester appliance parts. The terephthalate copolyesters of EG and 1,4-CHDM have T_gs below 100 ^{o}C, but they exhibit high Izod impact at room temperature (e.g., > 1000 J/m) for PCTG with high content (> 50 mol%) of 1,4-CHDM. The high impact of 1,4-CHDM copolymer results from the conformational changes of the cyclohexylene rings and their effects on chain motion.[52, 62] In order to achieve a balance between the stiffness of PET and the toughness of 1,4-CHDM polyesters, EG is used to modify the glycol component of PETG copolyesters. Increasing EG content in PETG copolyesters often results in increased hardness (Rockwell L hardness) and, concurrently, decreased impact strength. However, in the case of PETG copolyesters, it is difficult to achieve high hardness. A PETG sample based on TPA with about 70 mol% of EG and 30 mol% 1,4-CHDM possesses a high flexural modulus, as shown in **Table 2.3**.[61]

Table 2.3 Physical Property comparison of amorphous PETG, PCTG and PCTA[61]

Property	PETG	PCTG	PCTA
T_g (^{o}C)	81	84	88
Stress at break (MPa)	28	52	51
Elongation at break (%)	110	330	300
Flexural modulus (MPa)	2100	1900	1800
Flexural yield strength (MPa)	70	66	69
Izod impact strength---Notched at 23 ^{o}C (J/m)	101	No break	80
Izod impact strength---Notched at -40 ^{o}C (J/m)	37	64	40

PCTG **(4)** refers to the modification of PCT with ≤ 50 mol% ethylene glycol (EG). When the EG content is increased, the melting points of PCTG decrease dramatically and thus the crystallization rate is reduced. Although the normally amorphous PCTG copolyester could be intentionally induced to crystallize using a specific heat treatment process, the inclusion of EG in the PCT backbone renders these copolyesters amorphous under standard processing conditions.[61] PCTG copolyesters can be processed into various articles with desirable properties. Particularly, PCTG copolyester prepared with about 40 mol% of EG has superior clarity and toughness and is used for injection molding thin-wall medical components. PCTG is well-suited for molding such components due to its excellent resistance to gamma-ray sterilization and its ability to maintain its high elongation to break.[63] A PCTG sample based on TPA with 65 mol% of CHDM and 35 mol% of EG exhibits enhanced impact strength when compared to those of a PETG and PCTA sample. This is due to the existence of a high concentration of CHDM units in the backbone.[61]

PCTA **(5)** refers to PCT compositions modified with up to 50 mol% isophthalic acid (IPA) and has the following structure:



(5)

As mentioned before, PCT has a high T_m (up to 300 ^oC), thus a higher processing temperature (above 300 ^oC) is required to process the homopolymer. However, the high temperature could lead to the occurrence of thermal decomposition.[61] When IPA is incorporated at a low level (5-10 mol %), the processing window can be enlarged by lowering the melting point of the polyester while retaining the crystallinity and toughness of the PCT homopolymer. At higher IPA incorporation levels, the copolyesters do not crystallize.[59, 64, 65]

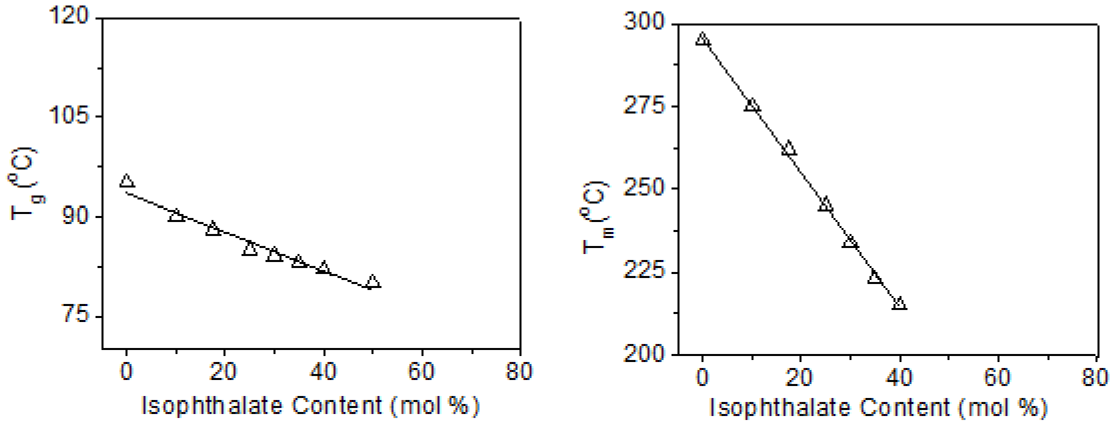
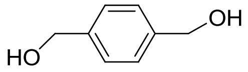
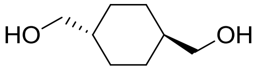
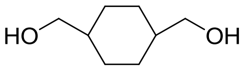


Figure 2.1 Effect of isophthalate content on the T_g and T_m of PCT copolyesters.[59]

Figure 2.1 shows how both the T_g and T_m decreased with increasing isophthalate content when isophthalate was incorporated into PCT. However, the T_m decreased at a faster rate than T_g did. There was no T_m observed on a DSC scan after a modification level of 40 mol%.[59] This phenomenon suggests that high levels of isophthalate (>40 mol%) disturbed chain packing, and thus, totally amorphous copolyesters were obtained. Amorphous PCTA compositions are transparent, tough and have good hydrolysis and chemical resistance. The PCTA can be used for precision molded parts and can also be extruded into clear sheeting, pipe, and shaped products.[61] PCTA can be melt processed without extensive pre-drying processes. This attractive feature is a result of the presence of hydrophobic 1,4-CHDM in the backbone and the absence of hydrophilic EG. PCTA prepared from about 70 mol% of TPA and 30 mol% of IPA has a T_g of 88 °C and other physical properties are comparable to PETG and PCTG.[61]

A series of polyesters from *trans*-1,4-CHDM or *cis*-1,4-CHDM with various aromatic diacids was synthesized.[66] Melting transition temperatures were compared with an analogous series of polyesters prepared from 1,4-benzenedimethanol (1,4-BDM), as shown in **Table 2.4**.

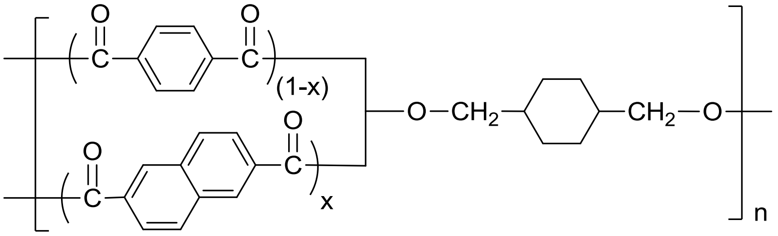
Table 2.4 The T_ms (°C) of polyesters from 1,4-BDM, *trans* and *cis*-1,4-CHDM[67]

Diol (right) Diacid (below)	1,4-BDM 	*trans*-1,4-CHDM 	*cis*-1,4-CHDM 
trans-1,4-CHDA	106	246	205
Isophthalic	100	197	-
Terephthalic	272	318	256
2,6-Naphthalene dicarboxylic	280	341*	287

* prepared from a *cis*/*trans* mixture containing 68 % *trans* isomer.

Polyesters prepared from aromatic diacids and *trans*-1,4-CHDM or 1,4-benzenedimethanol (1,4-BDM) combine rigidity and symmetry in their diacid and diol components. In such cases the polyesters of *trans*-1,4-CHDM appear to have higher T_m's than the analogous polyesters from 1,4-BDM. Thus the *trans*-1,4-CHDM is even better than 1,4-BDM to provide high melting points to the polyesters.[67] However, the polyesters prepared with *cis*-1,4-CHDM have lower T_m than the *trans* derivatives due to the reduced symmetry of the polyesters based on *cis*-1,4-CHDM.

Hoffman and Pecorini[59] studied the effect on the thermal properties of PCT (1,4-CHDM with a *cis*/*trans* ratio of 70/30 was used) by replacing varying amounts of the dimethyl terephthalate (DMT) unit with dimethyl 2,6-naphthalene dicarboxylate (DMN). The copolyester can be named PCTN **(6)** and has the following structure:



(6)

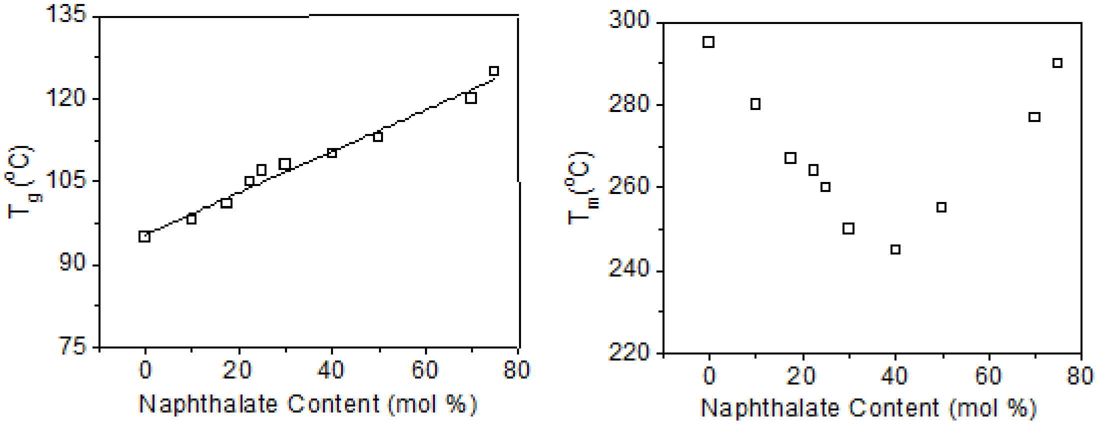
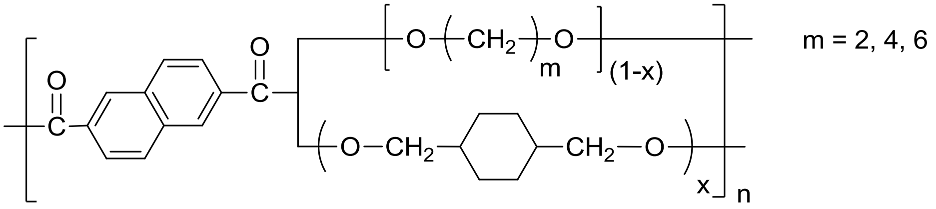


Figure 2.2 Effect of naphthalate content on the T_g and T_m of PCT copolyesters.[59]

Figure 2.2 shows the T_g and T_m of PCTN with increasing incorporation levels of DMN. From the above graph, we can see that the T_g increases with increasing naphthalate content in a linear trend. The T_m of the naphthalate-modified PCT copolyesters decreases initially, then begins to increase with enhanced naphthalate levels when an eutectic point reaches at about 40 mol% naphthalate.[59] At the eutectic composition, PCT-type and PCN-type crystals coexist in the copolyester. These results suggest that the naphthalate unit imparts rigidity to the polyester backbone.

The random copolyesters poly(*m*-methylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate) **(7)** (*m* denotes the number of methylene groups) were also synthesized and their crystallization behavior was studied by Jo *et al.*[68] Poly(ethylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate) (P(EN-

co-CN)) **(7)** (m = 2) was found to be amorphous in the middle of copolymer composition.[68]



(7)

Poly(butylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate) (P(BN-*co*-CN)) **(7)** (m = 4) and poly(hexamethylene 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate) (P(HN-*co*-CN)) **(7)** (m = 6) exhibited clear melting and crystallization peaks in DSC and sharp diffraction peaks in WAXD for entire copolyester compositions. It indicates that both of polyesters showed cocrystallization behavior. Furthermore, P(BN-*co*-CN) also exhibited an eutectic melting point, as shown in **Figure 2.3**. The typical eutectic behavior suggested that the cocrystallization was isodimorphic in nature.[68] On the other hand, T_g increased linearly with increasing CN content (**Figure 2.3**).

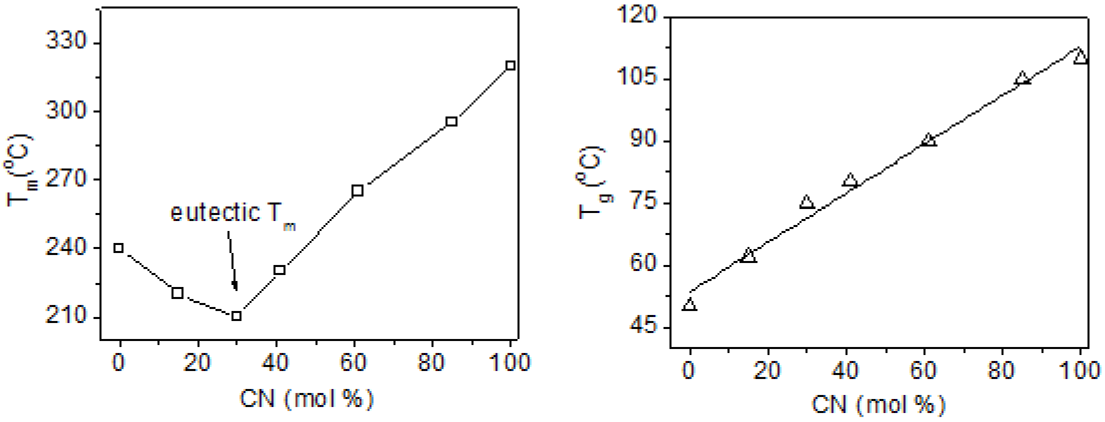
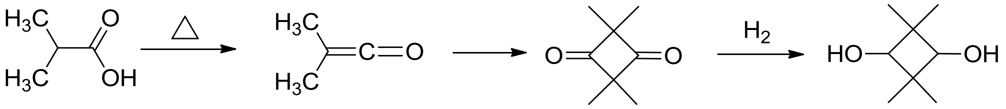


Figure 2.3 T_m and T_g of (P(BN-*co*-CN)) copolyesters as a function of composition

However, unlike P(BN-*co*-CN), the T_m of P(HN-*co*-CN) copolyester increases with increasing CN content, without showing an eutectic behavior. The absence of eutectic composition indicates that the cocrystallization of P(HN-*co*-CN) copolyester is isomorphic in nature.[68] From this study, we can conclude that EN unit cannot cocrystallize with CN unit, whereas BN and HN units can. This is possibly due to the fact that the lengths of the repeating units, the densities and the volumes of BN and HN units are comparable to those of CN units in their individual lattice crystal. However, it is not the case for those of EN units and CN units in that they are not comparable.[68]

2.2.2 Monocyclic diol: 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD)

2,2,4,4-Tetraalkyl-1,3-cyclobutylenes, such as *cis*/*trans*-2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD) **(8)**, are one class of rigid, thermally stable and symmetrical alicyclic diols, and are suitable for the preparation of polyesters. TMCBD can be prepared in high yield by the pyrolysis of isobutyric acid to produce dimethylketene, which dimerizes to form the cyclic diketone, as shown in **Scheme 2.5**. Hydrogenation of diketone using catalysts like ruthenium[69] produces *cis*/*trans*-TMCBD in high yield (up to 98 %) **(8)**. The monomer has usually been used as a *cis*/*trans* mixture in polymerization because isolation of the pure isomers is tedious and expensive.[70]



(8)

Scheme 2.5 Synthesis of TMCBD **(8)**

The TMCBD hydroxyl groups are secondary and sterically hindered by adjacent methyl groups, as shown in **Figure 2.4** (All 3-D structures in this dissertation were obtained from geometry optimization in the augmented MM3 force field contained in a Scigress Explorer Ultra version 7.7.0.47), so they are more difficult to polymerize than primary diols. However, there has still been considerable work on different polyesters based on TMCBD by melt polymerization.[25, 71]

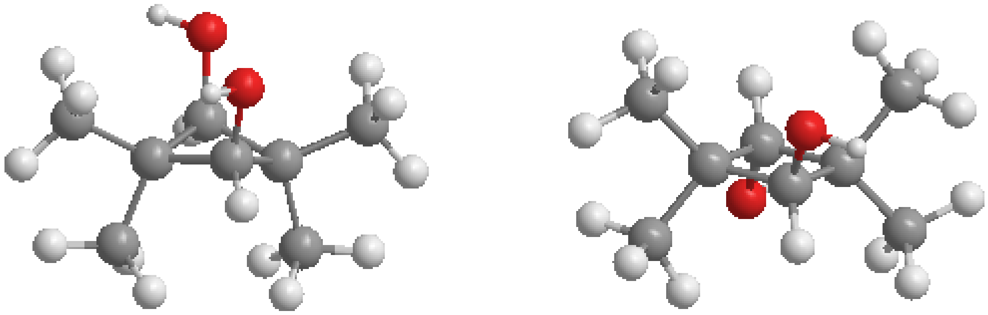
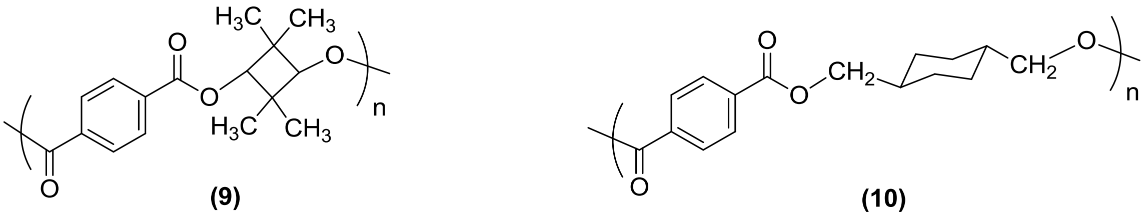


Figure 2.4 3-D structures of *cis*-TMCBD (left) and *trans*-TMCBD (right)

Tin[72] and lead catalysts are used successfully for TMCBD polymerization, although the latter tends to produce gray polymer. Tin compounds like dibutyltin oxide are good catalysts for transesterification of TMCBD with DMT at 240 °C, but it is still not clear why tin catalysts are so much better in this case than other typical polyester catalysts, such as titanium alkoxides.[73] Aromatic polyesters of TMCBD are primarily high melting and semicrystalline materials.[72, 74, 75] Melting points for the homopolyesters based on DMT and TMCBD are 316 – 319 °C (38/62 *cis*/*trans*),[72] 269 -308 °C (*cis*), and > 350 °C (*trans*) **(9)**.[73] The terephthalate polyester with 60 % of the *trans*-TMCBD has a very high T_g value, up to 184 °C.[75] The chain properties of polyester **(9)** from *trans*-TMCBD were compared to those of PCT **(10)** from *trans*-1,4-CHDM by Sulatha *et al.*[76, 77] The structures of two polyesters in the *trans*-conformation are exhibited in **Scheme 2.6**.

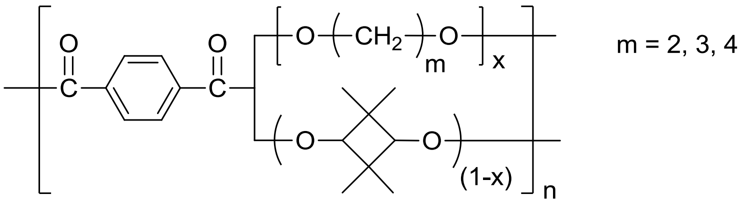


(9) **(10)**

Scheme 2.6 Geometry of the repeat units of the polyesters in the *trans* configuration

It was found that polyesters **(9)** with cyclobutylene groups were much more rigid than polyesters **(10)** with *trans*-cyclohexylene groups in the backbone by using RIS Metropolis Monte-Carlo (RMMC) simulations.[76] The spatial length of the cyclobutyl group is shorter than that of the cyclohexyl group, thus the intramolecular repulsive interactions within the chain are not well separated. Also, van der Waals energy of the chains in the polyester **(9)** is higher than that of PCT **(10)**. RMMC simulations show that the incorporation of cyclobutylene rings in the backbone could increase the chain dimensions, such as the characteristic ratio (C_n) and the persistence length (L_p), thus contributes rigidity to the single chains. Higher values of chain dimensions result from the conformational preferences of the various bonds in the repeat unit of the polyester **(9)** containing cyclobutylene rings. An analysis of torsional distributions shows that the oxy-cyclobutylene bond prefers a conformation corresponding to torsional values of about 5^o and 95^o. This preferred conformation can minimize the steric interactions resulting from the proximity of carbonyl oxygen and the methyl groups on the cyclobutylene ring. Other conformations are not energetically favorable.

Many semicrystalline copolyesters based on DMT, TMCBD and other diols were also reported. Examples include the TMCBD/1,6-hexanediol (HD) terephthalate copolyester (T_m = 180-190 ^oC) and the TMCBD/ 1,4-CHDM terephthalate copolymer (T_m = 192-204 ^oC).[72] A segmented copolyester (T_m = 248 ^oC) of about 15 mol % TMCBD terephthalate and 85 mol % ethylene terephthalate was also reported.[78] Kelsey *et al.* synthesized random aromatic copolyesters **(11)** using rigid *cis*/*trans*-TMCBD and flexible aliphatic glycols (two to four carbon atoms) over a range of compositions.[73]



(11)

The morphology of the TMCBD/ diol terephthalate copolyesters **(11)** is governed by the composition of TMCBD and partially determined by the *cis*/*trans* isomer ratio. When the TMCBD (~50/50 *cis*/*trans*) content is 40 – 90 mol % of total diols, the copolyesters are amorphous and transparent.[25, 79] When TMCBD content is below about 40 mol %, terephthalate copolyesters such as TMCBD/1,3-propanediol (PD) became semicrystalline. At 25 mol % TMCBD, this copolyester exhibited crystallization and a distinct melting transition on heating. A higher *trans*/*cis* TMCBD isomer ratio may increase crystallinity since *trans* isomer is more symmetrical than *cis* isomer.[25] The rigidity of TMCBD unit is comparable to that of common aromatic groups and it can decrease the degree of freedom in the polymer and thus increase their T_g's. For example, the T_g of a copolyester prepared from a 78/22 mole ratio of TMCBD/1,4-butanediol (BD) with DMT is 145 ^{o}C, an increase of nearly 100 ºC compared to the homopolymer made from 1,4-butanediol (BD) with DMT.[73] The T_g's of copolyesters made from TMCBD/PD with DMT are in the range of 80 – 168 ^{o}C and dependent on the proportion of rigid TMCBD units. **Figure 2.5** shows that T_g is enhanced with increasing content of alicyclic TMCBD units, suggesting the effectiveness of TMCBD group to increase T_g of polyesters. Surprisingly, it was found that compositions of TMCBD in the range of about 50-80 mol % have excellent toughness (> 250 J/m) together with T_g's > 100 ^{o}C.[25]

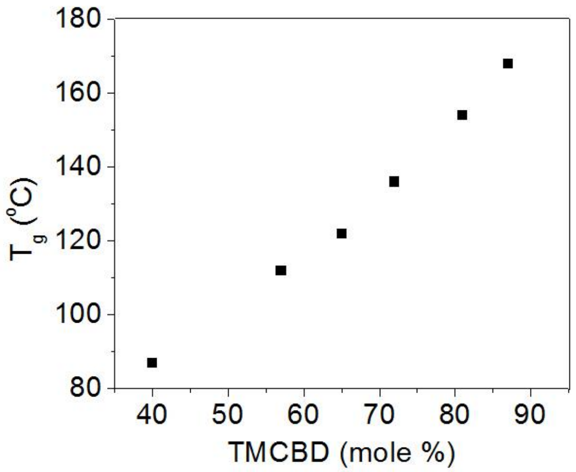
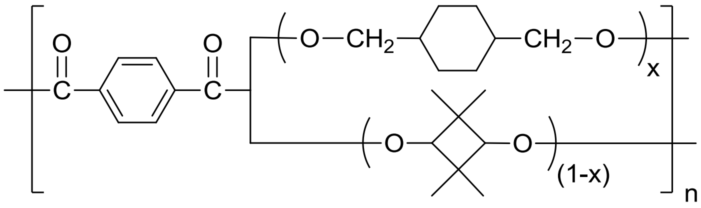


Figure 2.5 Effect of TMCBD content on T_g for terephthalate copolymers with PD.[73]

Amorphous TMCBD-containing copolyester materials have been found to exhibit excellent physical properties, including thermal stability, UV stability, clarity, low color and high T_g, therefore, they can be used in such applications as lenses, packaging and compact disks. They also have potential outdoor applications due to their high impact resistance combined with good resistance against weathering.

Recently copolyesters based on PCT modified with TMCBD were commercialized by Eastman Chemical Company under the trade name "Tritan^{TM} copolyesters" **(12)**, which have the following structures:

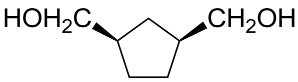


(12)

These copolyesters **(12)** have T_g values greater than 100 ^oC and have found large applications in kitchenware, signs, etc.[80] Other high T_g copolyesters prepared from TMCBD and bisphenols with diacid chlorides, such as terephthaloyl chloride, have been reported to possess T_g values in the 200 ^oC range.[81]

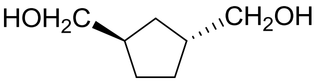
2.2.3 Monocyclic diol: 1,3-cyclopentane dimethanol (CPDM)

1,3-Cyclopentane dimethanol (CPDM) is commercially available and has two isomers **(13a and 13b)**. The cyclopentyl ring has a non planar structure (**13c**), which can contribute flexibility to polymer chains.



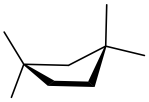
cis

(13a)



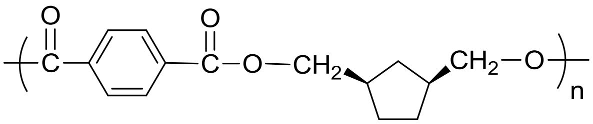
trans

(13b)



(13c)

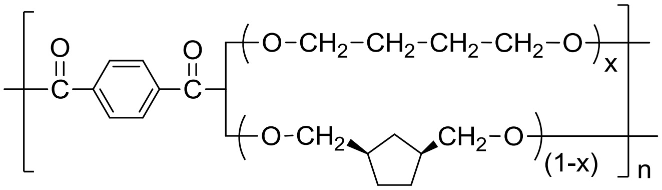
Some polyesters and copolyesters containing cyclopentyl rings in their main chains were synthesized and the effects of cyclopentyl rings on the thermal and crystallization behavior were studied.[24] Poly (*cis*-1,3-cyclopentanedimethylene terephthalate) (PCPDT) **(14)** is a semicrystalline polyester and exhibits well-defined crystallization with a crystallization temperature upon cooling (T_c) of 140 ^oC. The T_g is about 60 ^oC and the melting point appears at 207 ^oC.



(14)

Optical microscopy shows that PCPDT **(14)** exhibits well-defined big-banded spherulites, which are highly birefringent when it crystallizes from the melt. However, PCPDT **(14)** has a lower T_m and a lower crystallization rate compared to PBT or PCT. The crystallization half-time of PCPDT **(14)** is 6 min at 130 ^oC, at which the maximum crystallization rate is reached. The non planar structure of the cyclopentyl group (**13c**) inhibits the easy packing of the chains into a lattice and thus results in slower crystallization rates.

Random copolyesters poly(butylene terephthalate-*co*-1,3-cyclopentylene dimethylene terephthalate) (P(BT-*co*-CPDT)) **(15)** were also synthesized from the *cis*-1,3-CPDT, BD and DMT.



(15)

The T_g of the copolyester P(BT-*co*-CPDT) **(15)** increased with enhancing CPDT content from 40 ^oC for homopolyester PBT to 60 ^oC for pure PCPDT, as shown in **Figure 2.6**.

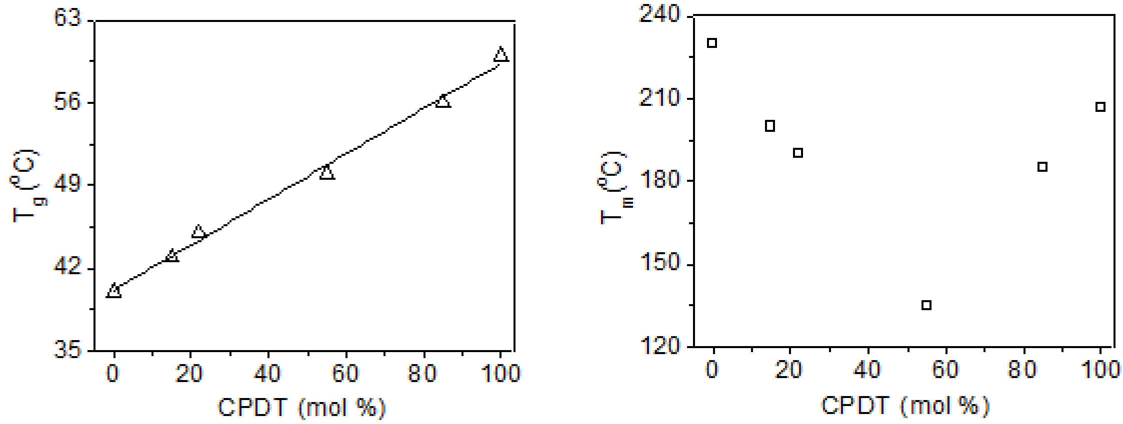
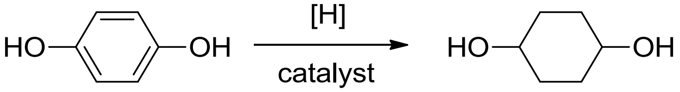


Figure 2.6 Dependence of T_g and T_m of P(BT-*co*-CPDT) on copolymer compositions.

The P(BT-*co*-CPDT) **(15)** copolyester showed a melting endotherm on heating and a crystallization exotherm on cooling throughout all composition ranges, indicating that this copolyester showed cocrystallization behavior over all composition ranges. The change of T_m with the CPDT content in **Figure 2.6** exhibited a typical eutectic behavior, which suggested that the cocrystallization was isodimorphic. The eutectic composition of the P(BT-*co*-CPDT) was $PBT_{45}CPDT_{55}$.[24] A similar isodimorphic crystallization behavior was mentioned in the case of P(BN-*co*-CN) earlier in this chapter.[68]

2.2.4 Monocyclic diol: 1,4-cyclohexanediol (1,4-CHDO)

1,4-Cyclohexanediol (1,4-CHDO) **(16)** is also commercially available and can be prepared by the catalytic hydrogenation of hydroquinone, as shown in **Scheme 2.7**.[82, 83] Ruthenium (Ru/C) was found to exhibit higher activity and selectivity in catalytic hydrogenation of hydroquinone than platinum, palladium, rhodium and nickel.[83]

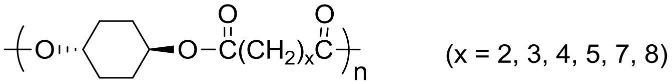


(16)

Scheme 2.7 Synthesis of 1,4-cyclohexanediol (1,4-CHDO) **(16)**

1,4-Cyclohexanediol (1,4-CHDO) **(16)** is a secondary diol and possesses *cis*/*trans* isomers. *Trans*-1,4-CHDO has an equal ability with 1,4-benzenedimethanol (1,4-BDM) to provide high T_m to the polyesters due to its rigidity and symmetry.

Echeverria *et al.*[84] studied the polymerization kinetics of *trans*-1,4-CHDO and succinic diacid or succinic anhydride in bulk in protic and aprotic catalytic systems. It was observed that polyester **(17)** (x = 4), when prepared with a copper (II) acetylacetonate (a non-proton donating catalyst), had better morphology characteristics and higher molecular weights than that obtained using *p*-toluenesulfonic acid (a proton donating catalyst) although they have comparable catalytic activity. Metal coordination was indicated to play a key role. The polyester **(17)** (x = 4) was typically liquid crystalline polymer and had a lyotropic and thermotropic molecular order.[84] A series of homopolyesters **(17)** based on *trans*-1,4-CHDO and the aliphatic diacids were synthesized and their T_ms were reported in **Table 2.5**.[85]



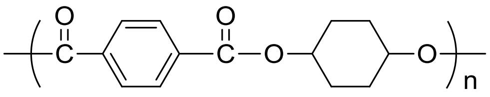
(17)

Table 2.5 T_m of poly(*trans*-1,4-cyclohexanediyl alkylene dicarboxylate) **(17)**[85]

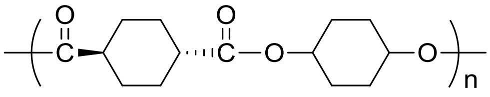
Repeating unit with x =	2	3	4	5	7	8
T_m, (^oC)	268	212	225	163	127	144

As can be seen in **Table 2.5**, polyesters **(17)** based on *trans*-1,4-CHDO and the aliphatic diacids with an even number of carbon atoms (x = 2, 4, 8) have higher melting temperatures than analogous polyesters of *trans*-1,4-CHDO and aliphatic diacids with an odd number of carbon atoms (x = 3, 5, 7). This is due to considerable differences in their rates of crystallization, which varies with the number of methylene groups. Crystallization is rapid from the melt when x = 2 and 4, and is slower for x = 5 and 7.[85]

Also, Osman[86] studied the effect of incorporating *cis*-1,4-CHDO into rigid polyesters (**18) and (19**) on the T_m and mesophase stability of polyesters (**Table 2.6**).



(18)



(19)

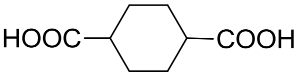
Table 2.6 Effect of *cis*/*trans*-1,4-CHDO on the thermal behavior of rod like polyesters[87]

Cis/*trans* ratio of **(16)**	Thermal behavior of **(18)** or **(19)**	Remarks/solubilities (TCE: *sym*-tetrachloroethane ClPh: 2-chlorophenol)
0:1	Nontractable **(18)**	Decompose above 300 ^oC
1:1	Crystalline, 290-300, nematic **(18)**	Soluble in TCE and ClPh
3:2	Crystalline, 230-250, isotropic **(18)**	Soluble in TCE and ClPh
7:3	Crystalline, 210-230, isotropic **(18)**	Soluble in TCE and ClPh
6:1	Crystalline, 180-190, isotropic (**18)**	Soluble in TCE and ClPh
0:1	Nontractable **(19)**	Decompose above 300 ^oC, soluble in ClPh
1:1	Crystalline, 295-300, nematic **(19)**	Soluble in TCE
6:1	Crystalline,140-160, isotropic **(19)**	Soluble in THF

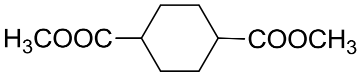
Poly(1,4-cyclohexene terephthalate) **(18)** based on *trans*-1,4-CHDO was infusible, however, the corresponding polyester based on a mixture of *cis*/*trans* cyclohexyl moieties (*cis*/*trans* molar ratio is 1/1) melted above 290 °C to give a nematic phase. This was different from the behavior of the *trans* isomer. The melting point was further lowered as the content of the *cis* isomer of 1,4-CHDO increased, but no subsequent mesophase was observed (**Table 2.6**). The same situation was found in poly(1,4-cyclohexene 1,4-cyclohexanedicarboxylate) **(19)**: the mesophase disappeared with high *cis* content because the *cis* isomer is nonlinear and has low symmetry.[86] Therefore, *cis*-cyclohexyl units of 1,4-CHDO lower the T_m and destabilize the mesophase, although nematic phases could be still observed at a low content of *cis* isomer.[86]

2.2.5 Monocyclic diacids: 1,4-cyclohexanedicarboxylic acid and its derivatives

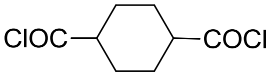
Cyclohexyl groups have been incorporated into a wide variety of polyesters to impart desirable physical properties.[88-90] In the early 1990s, cyclohexane isomeric diacid monomers such as hexahydrophthalic anhydride (HHPA), 1,3-cyclohexanedicarboxylic acid (1,3-CHDA), and 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) **(20a)** were typically used in the preparation of polyester polyols.[91-93] 1,4-CHDA, its diester dimethyl-1,4-cyclohexanedicarboxylate (DMCD) **(20b)**, and 1,4-cyclohexanedicarbonyl chloride **(20c)** are especially important monomers for raising the T_g in all-aliphatic polyesters and have found wide applications in coating resins.



(20a)



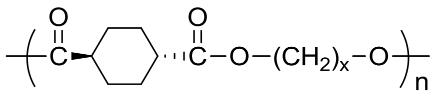
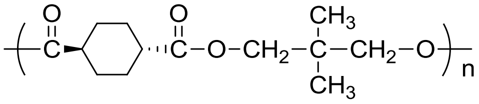
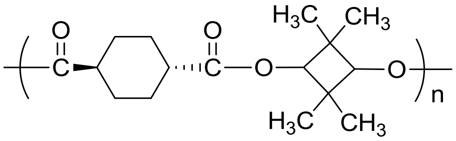
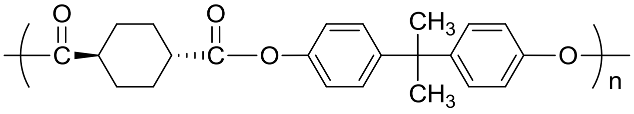
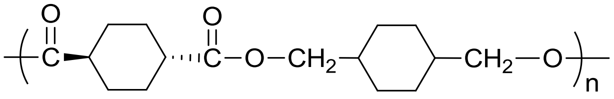
(20b)



(20c)

DMCD **(20b)** is commercially available with > 95 % *trans* content and the thermodynamic equilibrium for DMCD is about 66/34 *trans*/*cis* ratio. It is desirable to have *trans*-enriched DMCD as a starting component above the thermodynamic equilibrium. Jackson *et al.*[75] prepared cycloaliphatic polyesters of *trans*-1,4-CHDA with various diols (**Table 2.7**). Polyesters **(21)** (x = 2, 3, 4) and **(22)** synthesized from straight chain diols have low T_g's, while the polyesters **(23)** and **(24)** from rigid cyclic diols possess very high T_g values. Poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate) (PCCD) **(25)** prepared from *trans*-1,4-CHDA and 70 % *trans* of 1,4-CHDM has a moderate T_g and it will be discussed in detail later.

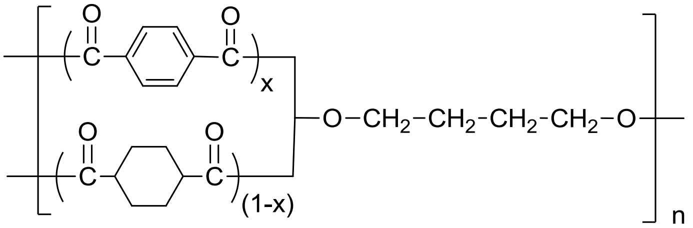
Table 2.7 Polyesters of *trans*-1,4-CHDA with various diols[75, 87]

Series #	Polyester structures		$[\eta]^a$	T_g, (°C)	Relative cryst., %
(21)		x = 2	0.84	18	0
		x = 3	0.91	-6	0
		x = 4	1.13	-10	19.5
(22)			1.06	30	5
(23)	 (60% *trans* of TMCBD)		0.77	169	0
(24)			1.09	150	0
(25)	 (70 % *trans* of 1,4-CHDM)		0.52	52	0

[a] IV were measured in a 60/40 (w/w) phenol/tetrachloroethane mixture at 25 °C (2.5 g/L)

Poly(butylene-1,4-cyclohexane dicarboxylate) (PBCD) **(21)** (x = 4) is easily prepared by standard melt phase polycondensation, it shows a melting temperature at 56

^{o}C.[24] However, PBCD exhibits an extremely low crystallization rate compared to that of PBT since PBCD does not crystallize on cooling from the melt or on the second heating. PBCD with a *trans*/*cis* ratio of 70/30 of DMCD may be treated as an amorphous polyester with a T_g value of -10 ^{o}C and is rubbery at room temperature.[24] The PBCD prepared from *trans*-DMCD is a semicrystalline polyester with a T_g of 31 ^{o}C, a T_c of 112 ^{o}C and a T_m of 163 ^{o}C.[75] The PBCD molecule is more flexible than PBT due to its non planar structure, which does not easily pack into a lattice for crystallization. However, the poly(butylene terephthalate-*co*-1,4-cyclohexane dicarboxylate) (P(BT-*co*-BCD)) **(26)** copolyester can be crystallized and shows a melting endotherm on heating over the entire composition range studied. Furthermore, the T_m and T_g values show a linear relationship with composition; they decrease as content of BCD is increased. P(BT-*co*-BCD) **(26)** does not exhibit an eutectic behavior, but an isomorphic crystallization behavior from WAXS patterns was observed.[24]

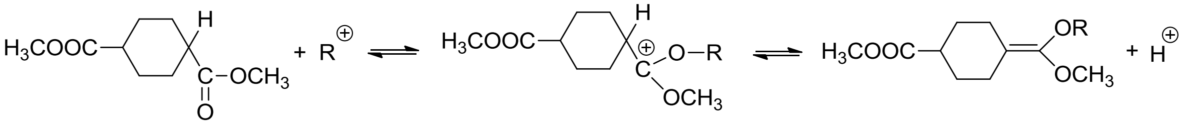


(26)

Crystallizable polyesters of cycloaliphatic diacids or diesters with cycloaliphatic diols have relatively high melting points and are ultraviolet (UV) resistant since they do not appreciably absorb light in the UV region.[75, 94] An example is the all cycloaliphatic polyester, poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate) (PCCD) **(25)**, with a T_g of around 40-70 °C depending on the *cis*/*trans* ratio of monomers. PCCD has many advantageous properties, such as resistance to weathering when exposed to UV radiation. Therefore, PCCD materials have potential applications in situations where UV stability is required.[95-97]

PCCD was typically synthesized by melt polymerization from 1,4-CHDA or DMCD and 1,4-CHDM in the presence of titanium(IV) isopropoxide catalyst.[98] It is relatively difficult to achieve high molecular weights for this type of fully cycloaliphatic polyesters because cycloaliphatic diols, such as 1,4-CHDM, are hard to volatilize (boiling point ~286 ^{o}C) and are difficult to be removed to drive the polymerization. Therefore, it has been necessary to polymerize 1,4-CHDM and DMCD in a one-step process and then tightly control the stoichiometry to obtain a high molecular weight product. US patent 6084055[99] described a synthetic method of PCCD with a high M_w in the range of 70,000 to 93,000 g/mol where the polyester crystallized rapidly from the melt. The T_m was observed to up to 234 ^{o}C and the T_c was about 175 ^{o}C. US patent 5986040[100] to Patel and Smith described that an improved process was used to obtain PCCD with enhanced crystallinity, good impact resistance, as well as good processability in combination with enhancing resistance to both solvent and UV light. DMCD is often used in about 0.5 mole percent excess.[99] These strict limitations on the process conditions to obtain high molecular weight polyesters are barriers for commercial application. Recent work indicates much progress for commercial use of PCCD as weatherable materials.[101, 102]

The T_m of crystalline PCCD is in the range of 220 – 235 ^{o}C and T_c is between 152 and 175 ^{o}C. The crystallinity and T_m of PCCD are greatly affected by the isomeric state; that is, the *trans*/*cis* ratio of the 1,4-CHDM and DMCD moieties in the polyester backbone. The content of the *trans* isomer in DMCD as supplied can be up to 99 %. Higher *trans* content typically results in a higher T_m, higher degree of crystallinity, and faster crystallization rates. However, isomerization of the high content *trans*-DMCD of the polymer backbone to the *cis* isomer can take place and results in an increase of the *cis* isomer concentration and a decrease of crystallinity. Generally, certain cationic substances can catalyze the isomerization of 1,4-cyclohexanedicarboxylic acid derivatives and a reaction mechanism is shown in **Scheme 2.8**.[103] Commercial 1,4-CHDM with 70 % *trans* does not undergo isomerization during polymerization.

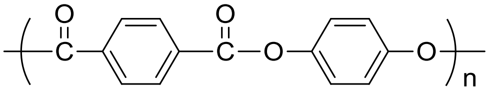
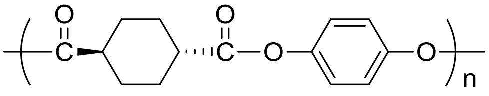
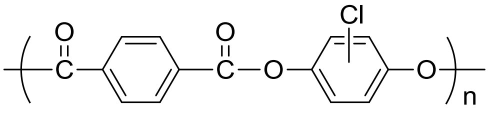
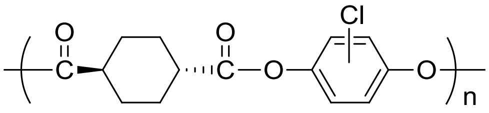
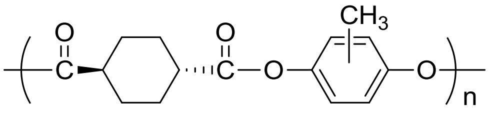
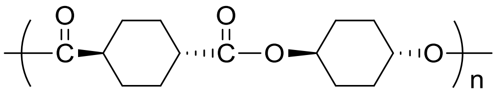


Scheme 2.8 An isomerization mechanism of DMCD[103]

US patent 6455664 [97] described the rate of isomerization vs. polymerization as an important parameter that was desirably controlled during the process of forming PCCD. It was claimed that the minimization of the reaction time period at high temperatures (below 270 °C) could prevent *trans*-to-*cis* isomerizatoin and the use of a slight stoichiometric excess of DMCD could increase the polymerization rate.[97]

Osman *et al.*[86] prepared a series of quasi-rigid polyesters (without aliphatic primary alcohols) containing cyclohexyl units by solution polymerization, which was carried out at low temperatures to minimize possible isomerization. In model systems, it was found that no isomerization occurred on esterification of 1,4-*trans*-cyclohexanoyl dichloride or of the *cis*/*trans* (1/1) mixture with cyclohexanol or phenol in the presence of pyridine at 0-80 °C.[86] The *trans* esters were also obtained through the esterification of 1,4-*trans*-CHDO with aliphatic or aromatic acid chlorides. Therefore, it was believed that the cyclohexyl units in quasi-rigid polyesters prepared by solution polymerization could keep the original configuration in the monomers.[86] Those rigid polyesters prepared by applying equimolar quantities of the monomers possessed low molecular weights, probably due to their limited solubilities. Their thermal properties are shown in **Table 2.8**.[86]

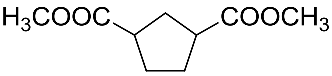
Table 2.8 Effect of *trans*-1,4-CHDA on the thermal properties of rod-like polyesters[86]

Sample #	Polyester structures	Thermal behavior
(27)		Nontractable Decompose above 350 °C
(28)		Nontractable Decompose above 350 °C
(29)		Nontractable Decompose above 300 °C
(30)		Crystalline, 260-280, nematic
(31)		Crystalline, 290-300, nematic
(32)		Nontractable Decompose above 300 °C

The average number of repeating units was still higher than ten, thus it was safe to compare their thermal properties. Poly(1,4-phenylene terephthalate) **(27)** in **Table 2.8** was reported to be nontractable, and the corresponding polyester with replacement of terephthalic acid by *trans*-1,4-CHDA **(28)** did not improve this property and decomposed before its T_m was reached.[86] The completely aromatic polyester **(29)** with a lateral substituent is also nontractable. However, the polyester **(30)** based on *trans*-1,4-CHDA and chlorohydroquinone resulted in a thermotropic nematic polymer and the corresponding methyl derivative **(31)** also gave a nematic phase above 290 °C. Therefore, the *trans*-1,4-cyclohexyl moieties could increase the flexibility of the polymers, keep their linearity, and decrease their packing density.[86] However, a lateral substituent is necessary to help depress the melting point below 300 °C. The full cycloaliphatic polyester **(32)** based on *trans* monomers is nontractable, probably due to the absence of lateral substituents and because its symmetrical geometry leads to high packing density.[86]

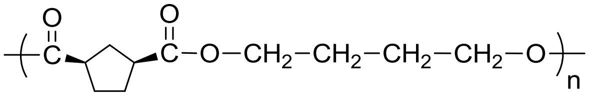
2.2.6 Monocyclic diacids: 1,3-dimethylcyclopentane dicarboxylate (DMCP)

Similar to 1,3-cyclopentanedimethanol (1,3-CPDM), dimethyl 1,3-cyclopentane dicarboxylate (1,3-DMCP) **(33)** also contains a cyclopentyl ring, which is non planar and can provide flexibility to polymer chains. Some polyesters based on 1,3-DMCP **(33)** were studied to investigate the role of the molecular structure on polymer properties.



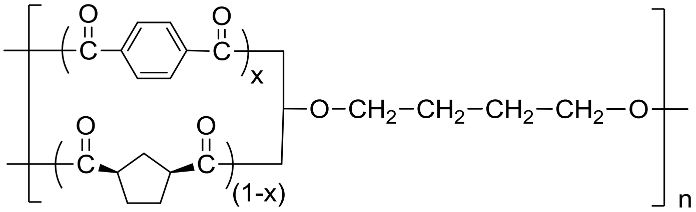
(33)

Poly(1,4-butylene 1,3-cyclopentanedicarboxylate) (PBCP) **(34)** is an amorphous polyester with a T_g of -44 °C and thus it is rubbery at room temperature. PBCP is more flexible than PBCD with a T_g of -10 °C discussed earlier due to the non planar structure of 1,3-DMCP.[24]



(34)

Poly(butylene terephthalate-*co*-1,3-cyclopentane dicarboxylate) (P(BT-*co*-PBCP)) **(35)** showed similar thermal behavior with poly(butylene terephthalate-*co*-1,4-cyclohexane dicarboxylate) (P(BT-*co*-BCD)) **(26)** discussed earlier. Both T_g and T_m decreased with increasing composition of PBCP linearly in the range studied (up to 50 %).[24]



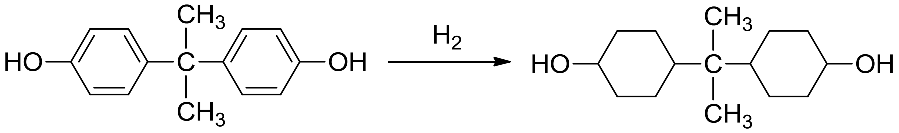
(35)

When more than 50 % of BCP is incorporated, the copolyester does not crystallize due to the chain packing disruption of BCP. For example, the homopolyester PBCP **(34)** is amorphous.

2.3 Polyesters based on bicyclic/multicyclic monomers

2.3.1 Bicyclic diol--2,2-bis(4-hydroxycyclohexyl)propane

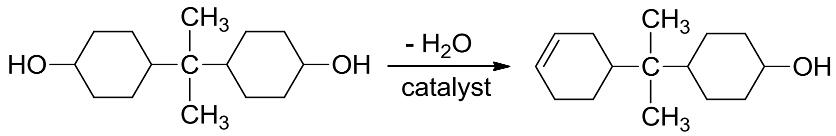
Hydrogenated bisphenol-A (HBPA) **(36)** can be prepared by the catalytic hydrogenation of bisphenol A (**Scheme 2.9**) as a mixture of three isomers: *cis*, *cis* (a, a); *cis*, *trans* (a, e); *trans*, *trans* (e, e).



(36)

Scheme 2.9 Synthesis of HBPA **(36)**

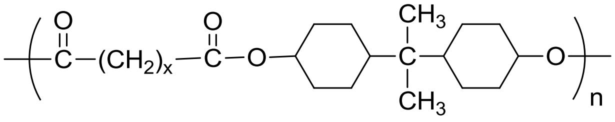
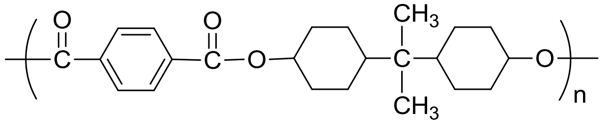
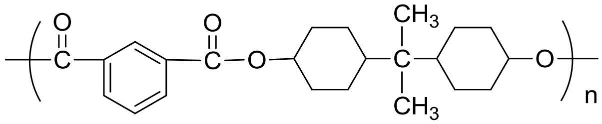
HBPA is a useful diol for the preparation of polyesters; its isomeric composition is important in determining the thermal and mechanical properties of the polyesters. However, the polymerization catalysts need to be selected carefully since the use of strong acidic or strong basic catalysts can result in the occurrence of side reactions, such as dehydration of HBPA to olefin, as shown in **Scheme 2.10**. In order to minimize the dehydration reaction, very weak Lewis acids are required to catalyze the polymerization.[26]



Scheme 2.10 Dehydration of HBPA to olefin

Gaughan *et al.*[26] synthesized high molecular weight polyesters from HBPA with various aliphatic acids under the presence of tin catalyst (**Table 2.9**). n-Butylhydroxyoxostannane is a very weak Lewis acid and thus was used to prevent catalytical elimination of water from the secondary cyclic alcohol of HBPA **(36)**.

Table 2.9 Thermal properties of 2,2-bis(4-hydroxycyclohexyl)propane polyesters[26]

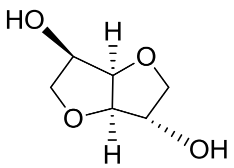
Series #	Polyester structures	Repeat unit with x=	T_g (°C)	T_m (°C)
(37)		2	113	180
		4	75	200
		8	25	Noncrystalline
(38)			135	350*
(39)			127	267

*the polymer decomposed on melting

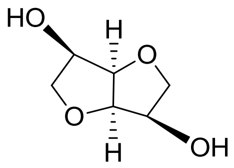
From the table, we can see that long chain acids, from succinic diacid to sebacic diacid, afforded polyesters **(37)** (x = 2, 4, 8) with low T_g and T_m. The all-aliphatic polyester prepared from HBPA and adipic acid had a higher T_m than the polymers prepared from succinic acid. Low molecular weight polyesters **(38)** and **(39)** were obtained from HBPA with isophthalic and terephthalic acids due to the sublimation of starting materials and the non-volatility of secondary cyclic diol---HBPA. The polyester poly[2,2-bis(4-hydroxycyclohexyl)propane adipate] **(37)** (x = 4) possesses enhanced physical properties than some other engineering plastics like PBT, PC and Nylon 66.[26] For example, this polyester **(37)** (x = 4) exhibited excellent notched impact strength (21.6 ft. lbs/in.) compared to PBT (only 1.0 ft. lbs/in.) and PC (Lexan 121) (12-16 ft. lbs/in.). This is due to the higher degrees of freedom of the two cyclohexyl rings, which is believed to dissipate energy through molecular motions. Furthermore, **(37)** (x = 4) possessed greater elongation at break (287 %) than PC (Lexan 121) (110 %), probably due to its conformational flexibility.[26]

2.3.2 Bicyclic diol----isosorbide and its isomers

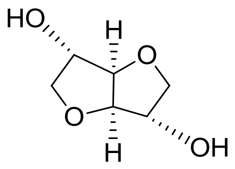
Isosorbide is a commercially available "sugar diol" produced commercially from renewable resources. The stereochemistry structures of isosorbide **(40a)** and its two isomers---isomannide **(40b)** and isoidide **(40c)** are shown as following.



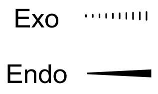
(40a)



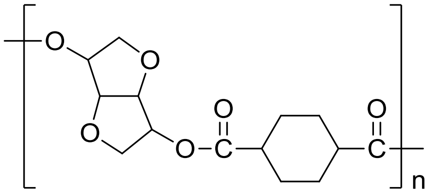
(40b)



(40c)



Various aliphatic and aromatic polyesters were prepared from isosorbide.[104-108] The bulky chemical structure of isosorbide does not facilitate crystallization, but it possesses relatively high thermal stability and limited molecular mobility; therefore, isosorbide is useful to synthesize high T_g polyesters. For example, poly(isosorbide terephthalate) was reported to have a T_g around 190 ^oC and exhibit excellent thermal stability.[109] In fact, the T_gs of polyesters derived from isosorbide also depend on its comonomers and can be altered in a wide range. As we mentioned, heat distortion temperatures above 100 °C are desirable for many potential applications. A recent paper by Kricheldorf and coworkers[32] reported the synthesis of the homopolyesters based on *cis*/*trans*-1,4-cyclohexanedicarboxylic acid (1,4-CHDA) or its derivative 1,4-cyclohexanedicarbonyl chloride (1,4-CHDC) and sugar diol isosorbide or its two isomers. Five different methods were studied for the preparation of the homopolyesters **(41)**. **Table 2.10** describes the detailed preparation conditions and the results from different synthetic approaches.



(41)

Table 2.10 Synthesis of polyesters from isosorbide and 1,4-CHDA or its derivatives[32]

Sugar diol	Reaction partner	Reaction medium	Catalyst	Final temp. (°C)	Yield (%)	T_g * (°C)
Isosorbide	DMCD	N/A	$Ti(OBu)_4$	240	No product	N/A
Isosorbide	1,4-CHDA	N/A	$Sn(OTf)_3$	100	No product	N/A
Isosorbide	1,4-CHDC	N/A	No	120	96	122
Isosorbide	1,4-CHDC	chlorobenzene	No	140	97	121
Isosorbide	1,4-CHDC	chlorobenzene	No	140	95	108
Isosorbide	1,4-CHDC	1,2-dichloro-benzene	No	185	94	109
Isosorbide	1,4-CHDC [@]	CH_2Cl_2	pyridine	20	96	145
Isomannide	1,4-CHDC [@]	CH_2Cl_2	pyridine	20	98	133
Isoidide	1,4-CHDC [@]	dioxane	pyridine	20	96	115

* T_g from the second heating cycle of DSC with a heating rate of 20 °C/min

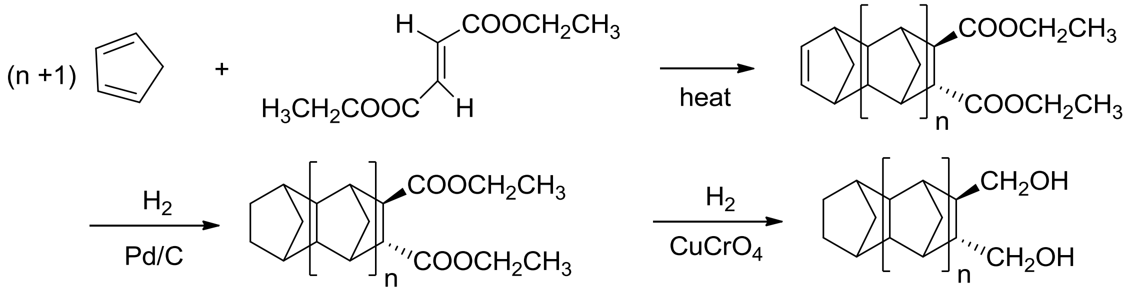
[@] An excess of 1 mol % 1,4-CHDC was used.

Table 2.10 indicates that polyesters were not obtained by the classical transesterification method in the presence of titanium tetrabutoxide at high temperature (240 ^{o}C) and samarium triflate catalyzed polycondensation at 100 ^{o}C.[32] This is because the secondary alcohol isosorbide has poor reactivity and is sensitive to acid. The best approach, shown in **Table 2.10**, is the polycondensation of sugar diol with 1,4-CHDC in solution at room temperature in the presence of pyridine, which is a catalyst and HCl acceptor. All homopolyesters are amorphous as expected and the T_g values are above 100 ^{o}C. Some T_g values are even more than 140 ^{o}C in certain cases if the relative average molecular weights are higher than 10,000 g/mol.[32] For the aliphatic polyester, T_g value of 145 ^{o}C is unusually high and almost equal to the T_g of poly(bisphenol A carbonate). Polyesters derived from isoidide or isomannide have relatively low molecular weights and thus it is hard to adequately compare their T_gs. However, the T_g values of the last three rows listed in **Table 2.10** suggest a trend that the T_gs increase in the following order: isoidide < isomannide < isosorbide, for polyesters with identical molecular weights (> 10,000 g/mol).

Succinic acid was also incorporated into the polyesters of isosorbide to adjust T_g and enhance the hydrolytic degradation rate. The T_g values may still remain above 100 ^{o}C for those copolyesters containing less than 40 mol% of succinyl units. Therefore, the homo- and copolyesters of isosobide are potentially useful transparent engineering plastics.[32] Unfortunately, it is difficult to find an inexpensive method to obtain high molecular weight polyesters of isosobide. Furthermore, the control and elimination of color in isosobide-containing polyesters still have problems.[110] In several patents of Charbonneau *et al.*,[111-113] isosorbide was incorporated into the PET backbone to make low color copolyesters—poly(ethylene-*co*-isosorbide) terephthalates (PEIT) with a low diethylene glycol (DEG) content. DEG, a typical impurity during traditional high temperature melt-phase synthesis of PET, can reduce the T_g of PET. It was claimed that these copolyesters (PEIT) with a T_g range of 80-118 ^{o}C could be used to make bottles, films, sheet, fiber, optical articles, and polymer blends.

2.3.3 Bicyclic diols containing bicyclo[2.2.1]heptane (norbornane) rings

Norbornane structures have not been widely incorporated into step-growth polymers. Initially, Jackson and Caldwell[114] found that polycarbonates from three-dimensional polycyclic bisphenols have T_g's that increase with the increasing size of the polycyclic side group. The increase of T_g is attributed to stiffness and bulk factors. Norbornane and norbornane-condensed diesters [**(42a), (42b) and (42c)** and dimethanols [**(43a), (43b) and (43c)]** were synthesized by Wilson and Hamb (**Scheme 2.11**).[28]



n = 0 **(42a)**
n = 1 **(42b)**
n = 2 **(42c)**

n = 0 **(43a)**
n = 1 **(43b)**
n = 2 **(43c)**

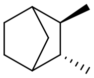
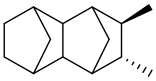
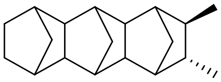
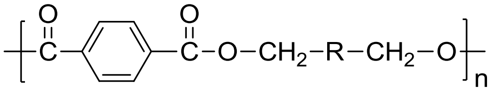
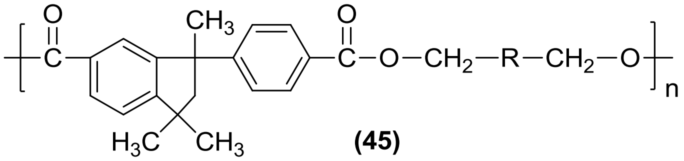
Scheme 2.11 Synthesis of **(42a), (42b), (42c), (43a), (43b) and (43c)**[115]

As shown in **Scheme 2.11**, the diethyl 2,3-*trans*-dicarboxylic esters of norbornane and norbornane condensed monomers [**(42a), (42b) and (42c)]** were synthesized by the Diels-Alder reaction, followed by reduction with hydrogen and palladium-on-carbon catalyst at a pressure of 1000 psi. The corresponding *trans*-dimethanols [**(43a), (43b) and**

(43c)] were obtained by the treatment of these esters with hydrogen and copper chromite under high pressure (above 4000 psi).[115]

Polyesters **(44)** and **(45)** were prepared by the standard melt-phase polymerization based on norbornane dimethanols with aromatic diesters --- DMT and phenylindan dicarboxylic acid (PIDA). In these polymerizations, zinc acetate dihydrate and either antimony(III) oxide or dibutyltin oxide were used as catalysts. The T_g values and inherent viscosities were reported in **Table 2.11**.

Table 2.11 T_g values and inherent viscosities (IV) of polyesters **(44)** and **(45)** based on norbornane dimethanols **(43a)**, **(43b)**, and **(43c)** [28]

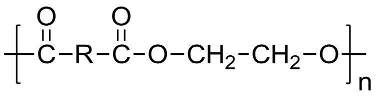
Polyester structures and series #	T_g (^{o}C) and IV (dl/g) with R =		
			
 **(44)**	117 (0.38)	154 (0.19)	197 (0.27)
 **(45)**	172 (0.38)	195 (0.28)	227 (0.20)

The polyesters in **Table 2.11** have low molecular weights but have very high T_gs (>100 ^{o}C). Increasing the number of norbornane residues significantly increases the bulkiness of the monomer unit and results in increase in T_g from 117 to 197 ^{o}C in the case of terephthalate polyesters and from 172 to 227 ^{o}C for polyesters prepared from phenylindan dicarboxylic acid (PIDA). T_g increases linearly with the increase of the number of norbornane residues in polymer side chains. This increase is an apparent function of the length and size of the norbornane moiety. The stiffness and bulkiness of the polymer chain are increased due to the increase in the size of the norbornane moiety relative to the size of the polymer repeat unit. In addition, the bulky three-dimensional norbornane ring leads to a reduced segmental mobility; this effect becomes increasingly important with additional norbornane residues.

2.3.4 Bicyclic diesters containing bicyclo[2.2.1]heptane (norbornane) rings

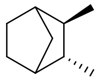
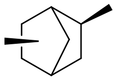
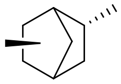
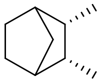
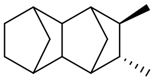
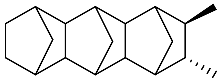
The synthesis of norbornane condensed diesters [**(42a), (42b) and (42c)]** was discussed in a previous section and a series of polyesters based on these diesters were also studied by Wilson and Hamb.[28] Polyesters **(46)** prepared from various isomers of diethyl norbornanedicarboxylate **(42a)** and ethylene glycol (EG) exhibited T_g values from 23 to 41 ^oC, as shown in **Table 2.12**. These data indicate that the mode of substitution in the norbornane moiety has little effect on the T_g of these polyesters containing isomers of **(42a)**. However, when **(42b)** and **(42c)** were incorporated into polyester **(46)** chains, the T_g was enhanced greatly (more than 150 ^oC, as shown in **Table 2.12**) due to the increased number of norbornane rings.

Table 2.12 T_g values and inherent viscosities (IV) for polyesters **(46)** with EG [28]



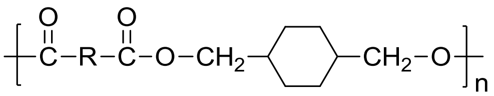
$\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O \right]_n$

(46)

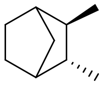
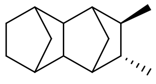
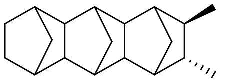
R						
T_g (°C)	41	40	23	36	95	156
IV (dl/g)	0.98	Partially crosslinked	0.79	0.63	0.56	0.27

The norbornane moieties **(42a)**, **(42b)** and **(42c)** were also introduced as polymer side chains for the polyesters **(47)**, as shown in **Table 2.13**. Once again, the table exhibits the effect of increasing the concentration of the norbornane moiety on the T_g of polyesters.[28] The T_g was increased by increasing the number of norbornane residues in the respective monomer units. It confirmed the positive effects of chain bulk on the T_g of these polyesters.

Table 2.13 T_g values and inherent viscosities (IV) for polyesters **(47)** with 1,4-CHDM [28]

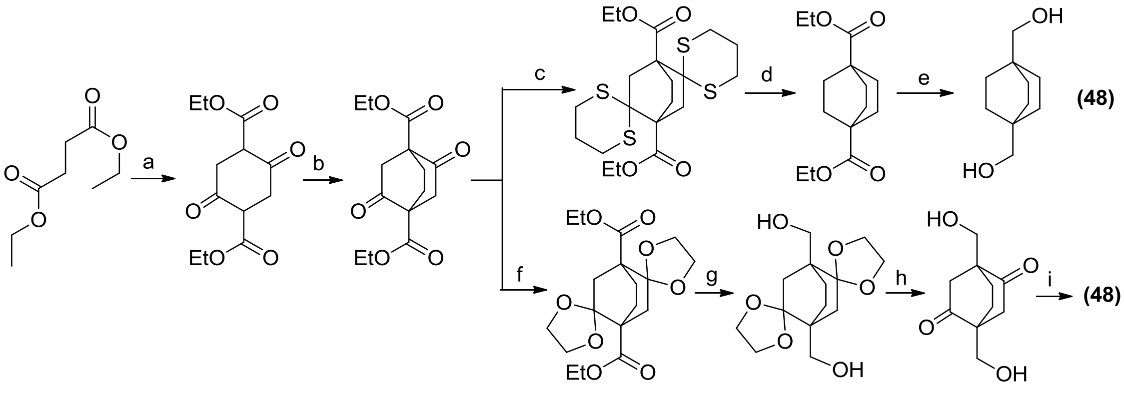


(47)

R	$—CH_2CH_2—$			
T_g (°C)	-4	67	111	146
IV (dl/g)	0.29	0.34	0.38	0.27

2.3.5 Bicyclic diols containing bicyclo[2.2.2]octane or bicyclo[3.2.2]nonane rings

The bicyclo[2.2.2]octane ring and the bicyclo[3.2.2]nonane ring systems are interesting due to their high rigidity. Bicyclo[2.2.2]octane-1,4-dimethanol (BCODM) **(48)** is not commercially available, however its synthesis is documented in the literature.[116-118] Generally, it can be obtained by a five or six step synthesis, as shown in **Scheme 2.12**.



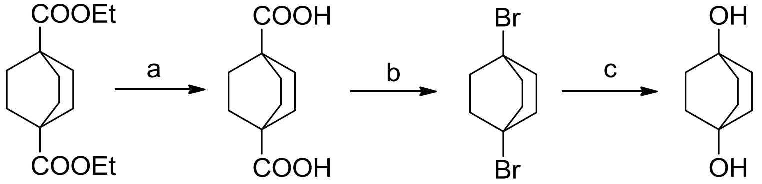
Scheme 2.12* Five-step or six-step synthesis of BCODM **(48)**[119, 120]

* Reagents include: (a) NaH, dimethoxyethane, 60 °C, 15 h, 78% yield; (b) NaH, 1,2-dibromoethane, 110 °C, 96 h, 85% yield; (c) $HS(CH_2)_3SH$, $BF_3·Et_2O$, $CHCl_3$, 80% yield; (d) Raney Ni, EtOH, 98% yield; (e) $LiAlH_4$, Et_2O, 89% yield; (f) *p*-TsOH, diethylene

glycol (DEG), toluene, reflux, 48 h, 71% yield; (g) $LiAlH_4$, Et_2O, reflux, 5 h, 93% yield; (h) HCl 0.1M, reflux, 24 h, quant.; (i) KOH, hydrazine monohydrate, DEG, reflux, 48 h, 41% yield.

Bicyclo[2.2.2]octane-1,4-dimethanol (BODM) **(48)** has a rigid and symmetrical structure similar to that of *trans*-1,4-CHDM. However, BODM has one advantage: that is, ring inversion cannot happen, whereas it could occur for 1,4-CHDM by converting the *trans*-diaxial form to the *trans*-diequatorial conformation.[31]

One more bicyclo[2.2.2]octane ring-containing diol is bicyclo[2.2.2]octane-1,4-diol (BODO) **(49)**, which has been widely studied.[121-123] It was prepared from the same starting materials as those for BODM **(48)**, as shown in **Scheme 2.13.** BODO **(49)** is a white crystalline solid with a melting point of 282 °C.



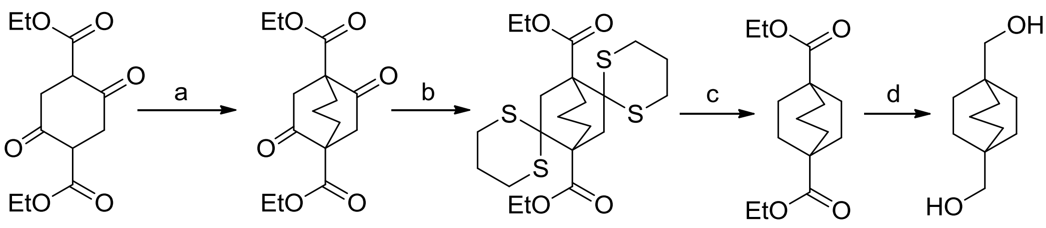
(49)

Scheme 2.13* Synthesis of **(49)**[122]

***** Reagents include: (a) KOH, EtOH, reflux, 12 h, 90 % yield; (b) HgO, Br_2 in 1,2-dibromoethane, 75 °C, 12 h, 44% yield; (c) CuO, Fe, H_2O, 215 °C, 24 h, 65% yield.

Bicyclo[2.2.2]octane-1,4-diol (BODO) **(49)** is more rigid than bicyclo[2.2.2]octane-1,4-dimethanol (BODM) **(48)** due to the absence of a methylene group. Polyesters prepared from bicyclo[2.2.2]octane-1,4-diol (BODO) **(49)** usually exhibit liquid crystalline behavior and will be discussed later.[27, 29]

The bicyclo[3.2.2]nonane-1,5-dimethanol (BNDM) **(50)** was also reported and its synthetic procedure, as shown in **Scheme 2.14**, generally followed that for BODM **(48)**.[124, 125]



(50)

Scheme 2.14* Synthesis of BNDM **(50)**[125]

* Reagents include: (a) NaH, $Br(CH_2)_3Br$, 130 °C, 22 h, 36% yield; (b) $HS(CH_2)_3SH$, $BF_3{\cdot}Et_2O$, $CHCl_3$, 56% yield; (c) Raney Ni, EtOH, 90% yield; (d) $LiAlH_4$, dry THF, 76% yield.

The rigidity of bicyclo[3.2.2]nonane ring system is the same as that of bicyclo[2.2.2]octane ring, but its symmetry is reduced due to an extra carbon on the bridge.

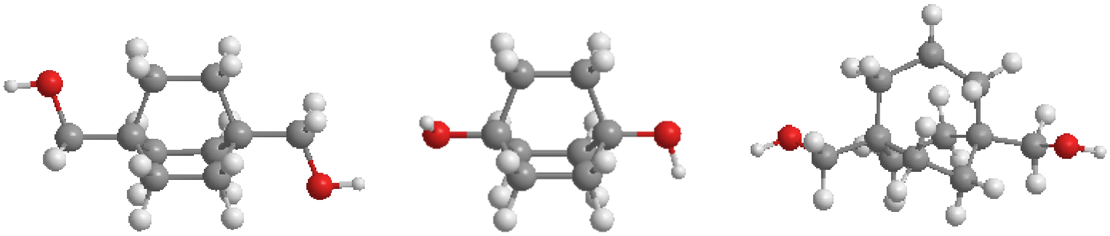
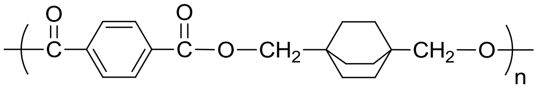
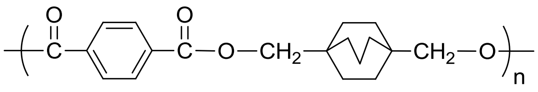


Figure 2.7 3-D models of **(48)** (left), **(49)** (middle) and **(50)** (right)

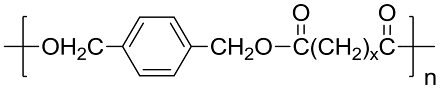
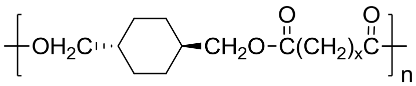
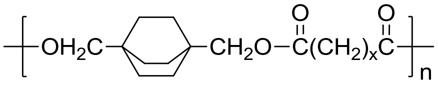
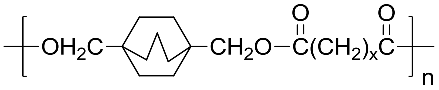
The 3-D model in **Figure 2.7** shows that two functional groups attached to the bridgehead carbons of the bicyclo[3.2.2]nonane ring of **(50)** form an angle of about 150^{o}, whereas these same groups in the bicyclo[2.2.2]octane ring of **(48)** and **(49)** are arranged in a linear pattern. Therefore, low melt temperatures of polyesters containing bicyclo[3.2.2]nonane ring systems could be expected. This result was confirmed by the studies of Taimr and Smith,[31] who synthesized terephthalate polyesters containing bicyclo[2.2.2]octane rings **(51a)** and bicyclo[3.2.2]nonane rings **(51b)** and then compared their thermal properties of. It was found that the terephthalate polyester **(51a)** has much higher melting temperature (> 300 °C) than the related polyester **(51b)** (160 °C).[31] This result suggests that their melting points are influenced considerably by symmetry.


(51a)

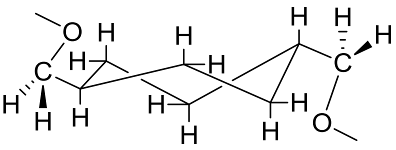

(51b)

When the acid segment of polyester is a flexible aliphatic acid, the melting point decreases sharply. Taimr et. al[31] also compared the melting points of a series of polyesters **(52---55)** containing linear aliphatic diacid units and different cyclic diol units in the repeating unit, i.e., 1,4-phenylene, *trans*-1,4-cyclohexylene, 1,4-bicyclo[2.2.2]octane and 1,5-bicyclo[3.2.2]nonane, as shown in **Table 2.14**.

Table 2.14 Melting points (°C) of polyesters **(52)---(55)** [31]

Series #	Polyester structures and series number	T_m, °C, for repeating unit with x=			
		4	6	7	8
(52)		81	82	66	93
(53)		124	96	50	78
(54)		101	77	37	65
(55)		82	Amorphous soft materials, No T_m was observed		

These data in **Table 2.14** indicate that polyesters **(53)** containing *trans*-1,4-CHDM show even a higher T_m than **(54)** containing bicyclo [2.2.2]octane rings. This was proposed to be due to the *trans*-1,4-CHDM moiety's slightly compressed conformation **(Scheme 2.15)**, which possesses a shorter oxygen-oxygen distance than does 1,4-benzenedimethanol.[66]

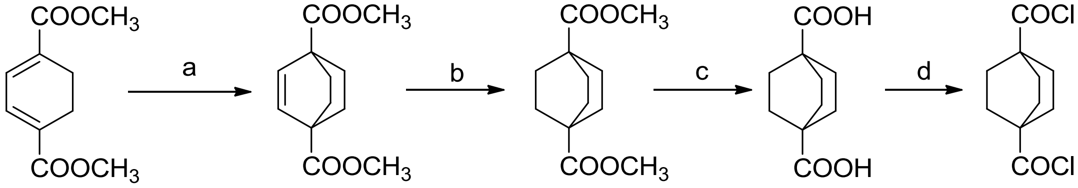


Scheme 2.15 The compressed conformation of *trans*-1,4-CHDM

A rigid bicyclo [2.2.2]octane ring does not have such a capability to compress. Polyesters **(55)** in **Table 2.14**, prepared from bicyclo[3.2.2]nonane-1,5-dimethanol and aliphatic dicarboxylic acids (x = 6, 7, 8), are amorphous (no T_m was observed) and soft materials, indicating the lower symmetry of the bicyclo[3.2.2]nonane ring.

2.3.6 Bicyclic diacids containing bicyclo[2.2.2]octane or bicyclo[3.2.2]nonane rings

Similarly, the rigid and symmetrical diacids containing bicyclo[2.2.2]octane rings, such as dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate **(56a)**, bicyclo[2.2.2]octane-1,4-dicarboxylic acid (BODA) **(56b)**, and bicyclo[2.2.2]octane dicarbonyl chloride (BODC) **(56c)**, can also be used to synthesize polyesters with high T_ms. The preparation of these diacids was widely reported, as shown in **Scheme 2.16**.[126-129]



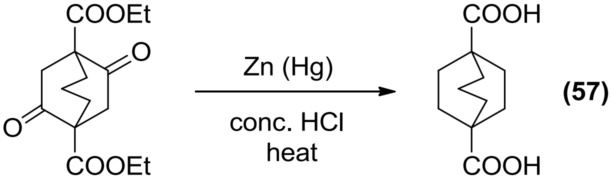
(56a) **(56b)** **(56c)**

Scheme 2.16* Synthesis of **(56a)**, **(56b)** and **(56c)**[126]

***** Reagents include: (a) $CH_2=CH_2$, 1000 atm, 165 °C, overnight, 90% yield; (b) 40 psi, platinum oxide, THF, 92% yield; (c) KOH, aqueous methanol, then acidification, quant.; (d) $SOCl_2$, one drop of DMF, reflux, overnight, 82% yield.

One advantage of polyesters from bicyclo[2.2.2]octane-1,4-dicarboxylic acids is that isomerization cannot happen during preparation, whereas *trans*-1,4-CHDA is known to isomerize during polymerization.

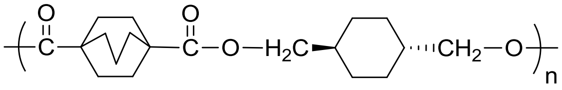
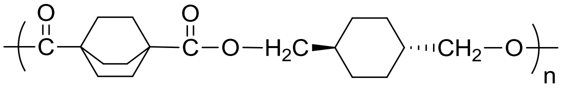
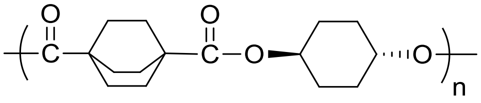
There are few studies on the synthesis of bicyclo[3.2.2]nonane-1,5-dicarboxylic acid **(57)**. An article by Guha reported that acid hydrolysis and Clemmensen reduction of 1,5-dicarboxyethoxybicyclo[3.2.2]nonane-6,8-dione could produce bicyclo[3.2.2]nonane-1,5-dicarboxylic acid (BNDA) **(57)** in a 30 % yield (**Scheme 2.17**).[130]



Scheme 2.17 Synthesis of **(57)**[130]

Polyester **(58)** prepared from bicyclo[3.2.2]nonane-1,5-dicarboxylic acid and *trans*-1,4-CHDM was compared to the analogous polyester **(59)** prepared from bicyclo[2.2.2]octane-1,4-dicarboxylic acid and *trans*-1,4-CHDM in **Table 2.15**.

Table 2.15 Melting points of various cycloaliphatic polyesters [27, 31]

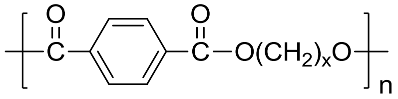
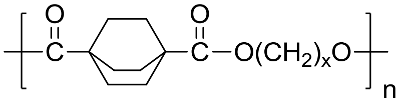
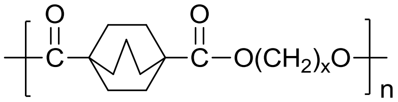
Series number	Polyester structures	T_m, °C
(58)		192
(59)		315
(60)		No melting before decomposition

Interestingly, a similar behavior is found: that is, the polyester **(59)** containing bicyclo[2.2.2]octane rings had a much higher melting temperature (> 310 ^oC) than the related polyester **(58)** containing bicyclo[3.2.2]nonane rings (< 200 ^oC).[31] This is still due to the lower symmetry of the bicyclo[3.2.2]nonane ring. However, the polyester **(60)** prepared by Polk *et al.* in **Table 2.15** showed no melting before decomposition.[27] This result indicates that *trans*-1,4-cyclohexanediol is more rigid than *trans*-1,4-

cyclohexanedimethanol, which has a flexible connecting methylene group between the ring and the oxygen atom.

Taimr and Smith also studied the polyesters prepared from the bicyclo diacids and various aliphatic diols; The T_ms of polyesters are listed in **Table 2.16**.[31]

Table 2.16 Melting points of various polyesters: comparison of the diacid ring system[31]

Series number	Polyester structures	T_m, °C Repeating unit with x=			
		3	4	5	6
(61)		233	232	134	154
(62)		143 (0.44)[a]	238 (0.56)	56 (0.22)	147 (0.54)
(63)		No T_m	130 (0.57)	No T_m	55 (0.56)

[a] Inherent viscosity η_{inh} in parentheses determined in 60:40 of phenol:tetrachoroethane

Again, the less symmetrical bicyclo[3.2.2]nonane ring results in lower T_m values of polyesters **(63)**, as shown in **Table 2.16**. There is little difference between **(61)** containing an aromatic ring and **(62)** containing a bicyclo[2.2.2]octane ring when the number (x) of carbon atoms in aliphatic diols is four or six. This fact implies that the bridge head carbonyl groups of bicyclo[2.2.2]octane-1,4-dicarboxylic acid probably possess the preferred orientation, shown in the 3-D model in **Figure 2.8**. The two carbonyl groups tend to be arranged in a similar manner with the terephthalate unit (**Figure 2.8**).[31] The high melting points of the terephthalate polymers probably result from the π-orbital overlap of the aromatic ring and the carbonyl groups in the rigid and symmetrical structures.

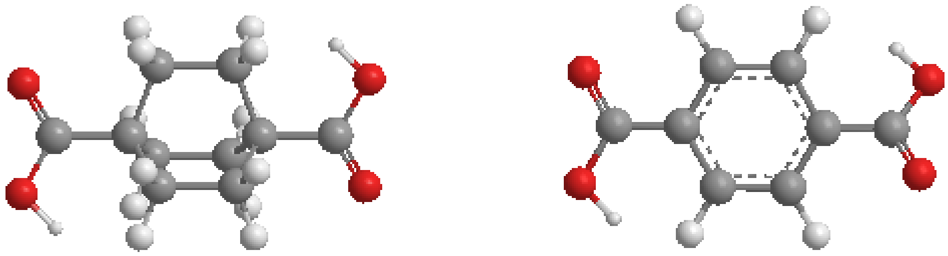
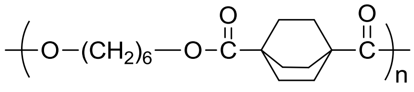
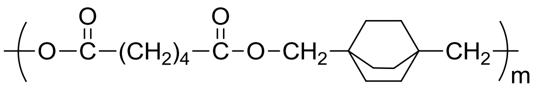


Figure 2.8 3-D models of **(56b)** (left) and terephthalic acid (TPA) (right)

However, polyesters **(61)** prepared from terephthalic acid (TPA) and aliphatic diols with an odd number of carbon atoms (x = 3 and 5) possess higher T_m values than the analogous bicyclo[2.2.2]octane ring polyesters **(62)** (x = 3 and 5). The molecular interaction of the two carbonyl groups connected to bicyclo rings is not an effective orienting influence, when compared to the aromatic system. Therefore, lower T_ms are observed when odd-carbon diols are coupled with the bicyclo rings. Similarly, this result can be used to explain the difference in T_m of the two polymers **(62)** (x = 6) and **(54)** (x = 4). Two polymer repeating units possess the same number of carbon atoms and similar structural units; the difference is in the arrangement of methylene group- ester group link.



(62) (x= 6)

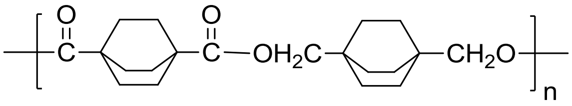
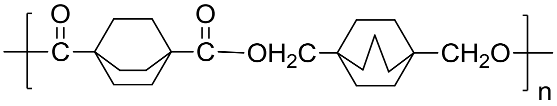
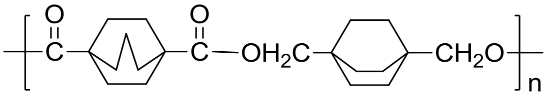
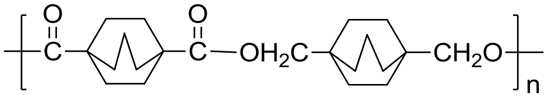
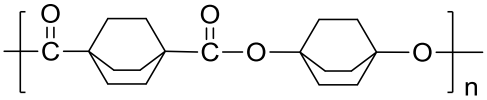


(54) (x = 4)

When the carbonyl group is directly attached to the rigid and symmetrical bicyclo ring in **(62)** (x = 6), the melting point (147 ^{o}C) is higher than that of **(54)** (x = 4) (101 ^{o}C) when the carbonyl group is attached to a flexible methylene group. The dipole-dipole repulsions of the carbonyl groups in **(62)** (x = 6) are sufficiently strong to orient these groups since the intervening unit—bicyclo ring itself is rigid. As far as the polymethylene chain in **(54)** (x = 4) is concerned, the orienting effect is offset by this flexible property of the connecting chain.

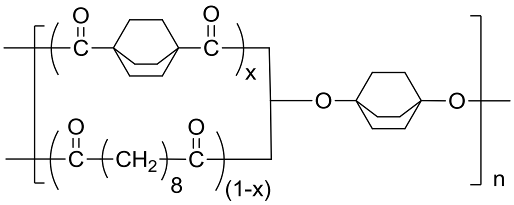
Polymers with a combination of two rigid bridged ring systems in a repeat unit were also synthesized; their melting points are exhibited in **Table 2.17**.

Table 2.17 T_m and inherent viscosity (IV) of bridged polyesters having different bicyclo diol and diacid units[31]

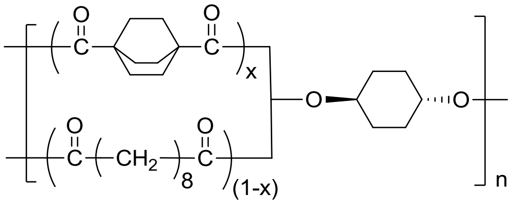
Series #	Polyester structures	T_m (°C)	IV(dl/g)
(64)		390	0.25
(65)		246	0.21
(66)		227	0.24
(67)		177	0.27
(68)		no melting before decomposition	

The first four different repeat units were thought to have the same rigidity, but different symmetry from the diol and/or diacid components. A remarkably high melting point (up to 390 °C) was obtained when two bicyclo[2.2.2]octane rings were combined in a polymer repeat unit **(64)**. The melting point showed a sharp drop when one of two bicyclo[2.2.2]octane rings were replaced by a less symmetrical bicyclo[3.2.2]nonane ring **(65)** and **(66)**. Naturally, a quick drop in melting point was observed when two bicyclo[3.2.2]nonane rings were combined in a polymer repeat unit **(67)**. All of these data emphasize the importance of symmetry. Most of these polyesters containing cyclic units, as studied by Taimr,[31] were not soluble in common organic solvents, so molecular weight data were not available. The inherent viscosities of these polymers (in **Table 2.17**) were determined in a 60/40 (w/w) phenol/tetrachloroethane solvent; they were not affected significantly by the different type of bicyclic units. Possibly the first four polyesters are melt stable and can be melt processed since the combination of two bridged rings could improve the thermal stability and oxidative stability.[31] However, when compared to the polyester **(64)** based on bicyclo[2.2.2]octane-1,4-dimethanol **(48)**, the polyester **(68)** based on bicyclo[2.2.2]octane-1,4-diol **(49)** showed no melting before decomposition due to the more rigid structure of **(49)** than **(48)**.[27]

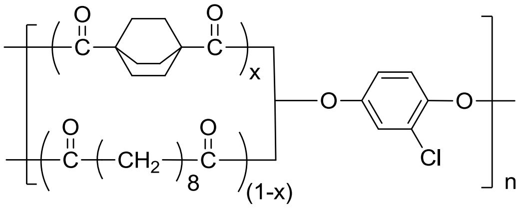
Some copolyesters containing the bicyclo[2.2.2]octane ring might exhibit liquid crystalline behavior. Polk *et al.* prepared a series of random copolyesters [**(69), (70), (71a) and (71b)]** based on bicyclo[2.2.2]octane-1,4-dicarbonyl chloride **(56c)** and sebacoyl chloride, which served as a flexible spacer.[27, 29, 131] The copolyester **(69)** (x= 0.5 or 0.7) decomposed at temperatures below the melting temperature, but the copolyester **(70)** with a ratio of 7:3 of **(56c)** to sebacoyl chloride (that is, x = 0.7) had a melting temperature low enough to observe the liquid crystalline transition.



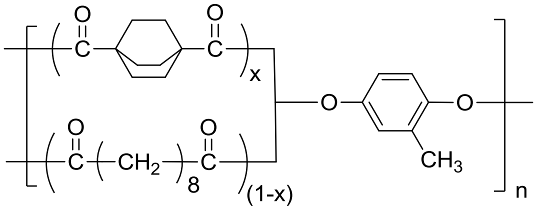
(69)



(70)



(71a)



(71b)

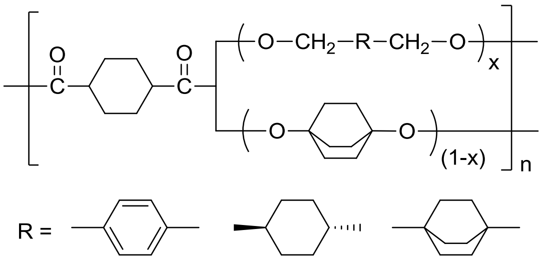
Table 2.18 Thermal properties and inherent viscosities (IV) of copolyesters[29, 131]

Copolyester	IV (dL/g)[a]	DSC transitions, (°C)[b]	Hot-stage polarizing optical microscopy transitions, (°C)
(70)	0.28	288, 317[c]	229,[d] 254[e]
(71a)	0.90	140, 240, 340[c]	150,[d] 199,[e] 317[c]
(71b)	0.60	127, 255	166,[d] 208,[e] 345[c]

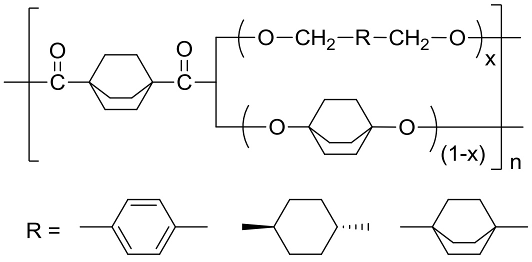
a. inherent viscosities were measured at a concentration of 0.5 g polymer in 100ml *o*-chlorophenol at 30 °C; b. The temperature programming rate was 50 °C/min (20 °C/min for **(70)**); c. the decomposition temperature; d. the softening temperature; e. the transition temperature to a birefringent fluid state.

The inherent viscosities and thermal properties of random copolyesters **(70)**, **(71a)** and **(71b)** are listed in **Table 2.18**. It was found that these copolyesters could form birefringent fluid states in the melt.[29, 131] (Birefringent materials have the ability to refract unpolarized incident light into two separate polarized light rays.) These data also showed that the copolyester **(70)** had the highest transition temperatures among these three copolyesters due to the high symmetry of *trans*-1,4-cyclohexanediol **(16)**, which was used for the preparation of the copolyester **(70)**.

Harruna *et al.*[30] also synthesized a number of main-chain type random copolyesters **(72a)**, **(72b)**, **(72c)**, **(73a)**, **(73b)** and **(73c)**, based on bicyclo[2.2.2]octane-1,4-diol with several semi-flexible spacers: 1,4-benzene dimethanol, *trans*-1,4-CHDM, and 1,4-bicyclo[2.2.2]octane dimethanol (BODM).



(72a) **(72b)** **(72c)**



(73a) **(73b)** **(73c)**

All of these copolyesters were found to possess high T_g values in the range of 145-185 ^{o}C. The copolyesters **(72a)**, **(72b)**, **(73a)** and **(73b)** were found to exhibit thermotropic liquid crystalline behavior. However, copolyesters **(72c)** and **(73c)** with 1,4-bicyclo[2.2.2]octanedimethylene spacers decompose without melting. The liquid crystalline properties of these polymers may be due to the rigidity, linearity, similarity in geometry and polarization of 1,4-disubstituted bicyclo[2.2.2]octane.[132] Due to their liquid crystalline properties, these bicyclo[2.2.2]octane ring-containing transparent polyester films could be useful as polarizing plates for liquid crystal displays.[132]

Main chain thermotropic cycloaliphatic polyesters generally contain mesogenic units consisting of structures with two or more cycloaliphatic rings; these units may or may not be connected by flexible spacers. Flexible spacers in the form of aliphatic groups are used to lower the T_m of rod-like (high axial ratio) polymers below their decomposition temperatures. Flexible spacers having more than ten units are not liquid crystalline, whereas those of shorter length exhibit liquid-crystalline transitions. As mentioned above, a series of liquid-crystalline copolyesters were reported based on bicyclo[2.2.2]octane as a mesogen with the sebacoyl group as a flexible spacer. Both the molecular structure of the components and their self-assembly characteristics can greatly affect the thermal properties of these polymers.[133] In fact, the geometry and the polarizability of the mesogenic units can be altered by changing the type and even the direction of their connecting bonds. Ultimately, the liquid crystal properties would also be altered.

2.4 Some specific properties of cycloaliphatic polyesters

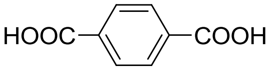
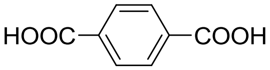
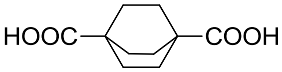
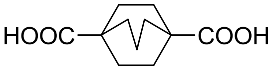
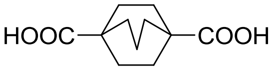
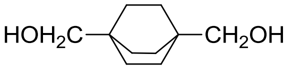
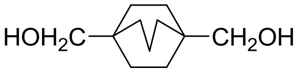
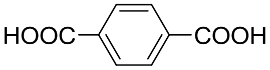
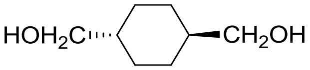
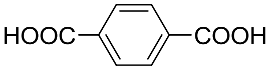
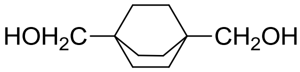
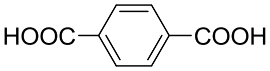
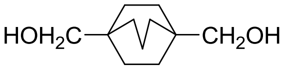
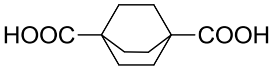
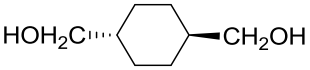
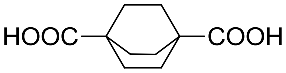
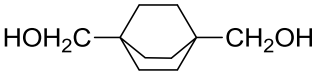
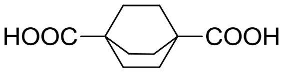
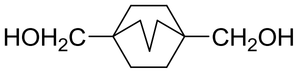
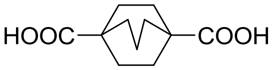
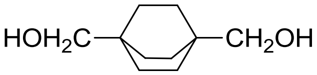
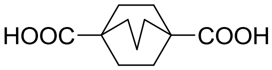
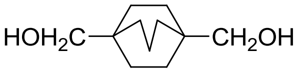
2.4.1 Thermal properties

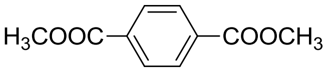
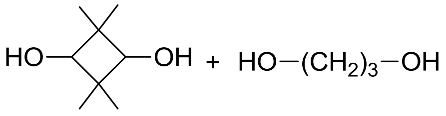
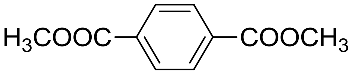
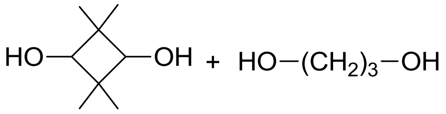
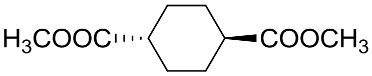
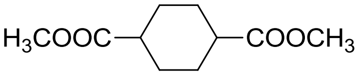
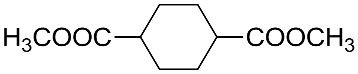
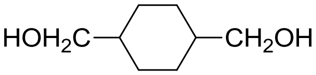
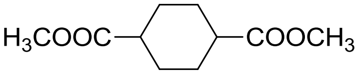
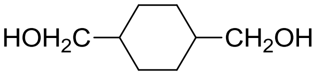
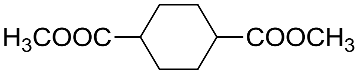
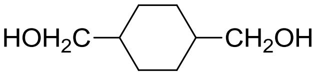
From the previous discussion of different cycloaliphatic polyesters, we can observe that the thermal properties of cycloaliphatic polyesters are typically influenced by (i) the ratio of ring units to linear units in the chain, (ii) the position of the ester groups, (iii) the stereochemistry (*cis* or *trans* forms) of the rings; and (iv) the symmetry changes where the rings are bridged. Aromatic components were once thought to be necessary to obtain high T_m polymers. However, polymers with high T_m can also be synthesized in the presence of cycloaliphatic units. For example, as far as polyesters from *trans*-1,4-CHDM and aliphatic diacids are concerned, it can be concluded that the *trans*-1,4-CHDM has an ability equal to that of 1,4-BDM to provide high melting points to the polyesters.[134] This ability results from the rings' rigidity and symmetry, which are not uniquely characteristic of the aromatic rings. Also, polyesters with *trans*-1,4-CHDM form exceptionally high melting points while the polyesters prepared with *cis*-1,4-CHDM have lower T_ms due to the reduced symmetry of the *cis* units.

As far as T_g of a polyester is concerned, the main parameters influencing T_g are molecular weight, chain flexibility, the nature of intermolecular packing, and the bulkiness of side groups attached to the backbone chain.[135] The effect of the rigid cyclic aliphatic units on T_g is similar to the effect of common aromatic backbone groups. The conformational restriction in the cyclic ring results in polymer chain rigidity. For example, the homopolymer of TMCBD (52 % *trans*) and terephthalic acid (TPA) exhibits a T_g of 174 ^oC (184 ^oC for 60 % *trans* TMCBD),[75] which is about 130-140 ^oC higher than the T_g (40 ^oC) of amorphous poly(trimethylene terephthalate) (PTT).[136] Of course, the heating rate and heating history can also affect the T_g. For instance, semicrystalline PTT has a T_g near 70 ^oC; but the T_g is lower for quenched, amorphous samples.

The thermal stability of cycloaliphatic polyesters has been measured by thermogravimetric analysis (TGA); high thermal stability is necessary for melt processing polymers. Both aromatic and cyclic aliphatic units can enhance the thermal stability of the polymers. Thermal stability of some cyclic polyesters is exhibited in **Table 2.19**. Those polyesters with a single ring in one repeating unit show composition temperatures of 400 ^oC for 10 % weight loss. When two rings appear in one repeating unit, those polyesters exhibit somewhat higher thermal stability. The weight loss about 10 wt% happens at 420-430 ^oC. Polyesters containing 1,4-CHDM have lower thermal stability than those containing bridged analogs. Polyesters containing two bridged rings in the same repeating unit show the greatest thermal stability (> 450 ^oC) (**Table 2.19**). This behavior occurs because the incorporation of bicyclo rings into a polymer backbone makes the structure close to an ideal ladder polymer. When the concentration of rings in the backbone increases, the polyester has a lower probability of thermal decomposition through the breakdown of the appropriate bonds to produce volatile substances. For example, it is not possible to undergo β–hydrogen elimination in these polyesters containing bicyclic rings.[31]

Table 2.19 Thermal stability of the polyesters containing cycloaliphatic units[31]

Diacid unit	Diol unit	T_d at 10 % weight loss (°C)	T_d at 5 % weight loss (°C)
	$HO-(CH_2)_2-OH$	404	---
	$HO-(CH_2)_4-OH$	395	---
	$HO-(CH_2)_6-OH$	398	---
	$HO-(CH_2)_6-OH$	400	---
	$HO-(CH_2)_4-OH$	392	---
$HOOC-(CH_2)_4-COOH$		398	---
$HOOC-(CH_2)_4-COOH$		412	---
	 (trans)	414	---
		438	---
		430	---
	 (trans)	422	---
		452	---
		455	---
		455	---
		457	---

	 (*cis*/*trans* = 48/52) 87/13 TMCBD/PD	---	417
	 (*cis*/*trans* = 48/52) 64/36 TMCBD/PD	---	393
 (*trans*)	$HO-(CH_2)_4-OH$	---	410
 (*cis*/*trans* = 48/52)	$HO-(CH_2)_4-OH$	---	410
 (*cis*/*trans* =19/81)	 (*cis*/*trans* = 34/66)	---	435
 (*cis*/*trans* =34/66)	 (*cis*/*trans* = 34/66)	---	437
 (*cis*/*trans* =76/24)	 (*cis*/*trans* = 34/66)	---	436

The terephthalate copolyesters of TMCBD/PD were thermally stable at processing (injection molding) temperatures.[25] Furthermore, The 87/13 TMCBD/PD terephthalate copolyester showed a higher thermal stability than the 64/36 TMCBD/PD copolyester did, as shown in **Table 2.19**. This finding indicates that the incorporation of TMCBD into polyester backbones can enhance the thermal stability. As far as poly(butylene 1,4-cyclohexanedicarboxylate) (PBCD) based on *trans*-DMCD was concerned, the degradation process of PBCD occurred above 350 °C and PBCD was kind of more thermally stable than PBT.[90] As shown in the above table, the two PBCD polyesters with different *cis*/*trans* ratio of the 1,4-cyclohexylene units had an equal thermal stability, indicating that the thermal stability does not depend on the stereochemistry of the cycloaliphatic rings.[90] Similarly, the PCCD homopolyesters at the bottom of **Table 2.19** exhibited high thermal stability, which was not influenced by the *cis*/*trans* ratio of the 1,4-cyclohexylene units.[95]

2.4.2 Mechanical Properties

Currently low-cost polyester materials are needed in the field of performance plastics. They are expected to be easily molded into various articles and exhibit a superior combination of mechanical properties such as high hardness, high impact strength, and high heat resistance. These properties would be most desirable for melt processing of polyesters used for injection molded plastics and fibers. Currently, many commercially available polyesters do not possess a balance of these three properties. PET and PBT possess poor impact resistance with notched Izod values less than 80 J/m.[137, 138] Low impact resistance of polymers can be observed when the rigidity of their polymer chains is increased. Commercial engineering thermoplastics with T_g's above 100 ^oC often exhibit Izod impacts below 100 J/m. Bisphenol A polycarbonate is one exception and it has a notched Izod of 650-850 J/m and a T_g about 150 ^oC.[137] The high impact resistance of bisphenol-A polycarbonate has been attributed to cooperative chain motions, which are correlated to sub-T_g (low energy) relaxations.[139]

All-aromatic polyesters usually have high hardness levels and high heat resistance due to the rigidity and relatively high T_g of the aromatic components. However, these all-aromatic copolyesters are usually very brittle and have low impact strength. The copolyesters, prepared from TPA, TMCBD and EG,[140] exhibited high impact strength, high hardness and high heat resistance. Of course, these mechanical properties of this copolyester are also dependent on the composition of TMCBD and EG (**Table 2.20** and **Figure 2.9**).

Table 2.20 Properties of copolyesters of TPA (100 mol%), TMCBD (*cis*/*trans* = 50/50) and EG[140]

TMCBD mol %	EG mol %	Izod impact Strength (J/m)	Rockwell L Hardness	Heat deflection temperature (^oC)
0	100	35.2	76	61
13	87	41.1	76	66
34	66	83.8	84	80
50	50	129.8	90	90
56	44	396.2	92	79
64	36	662.2	94	102
69	31	611.4	95	108
84	16	137.8	103	118
100	0	*	*	*

* The polyester molded with extreme difficulty and degraded severely during processing

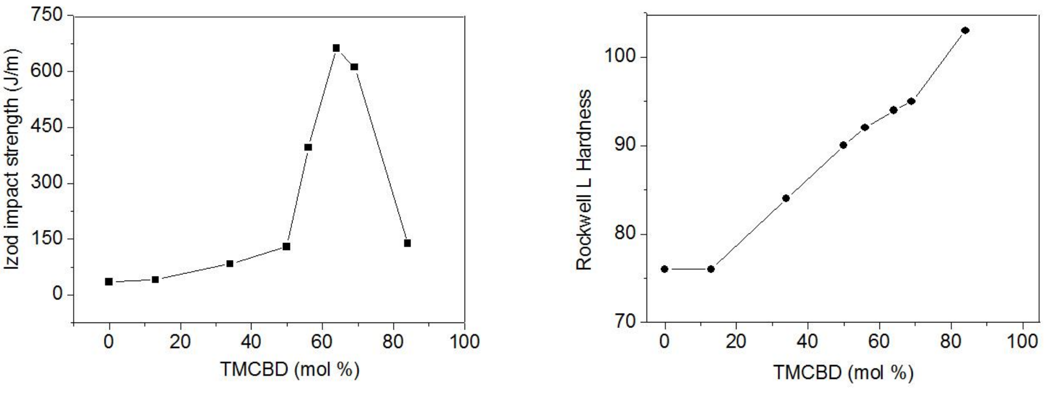


Figure 2.9 Effects of the TMCBD content on properties of copolyesters

Table 2.21 Properties of copolyesters of TPA (100 mol%), 1,4-CHDM (*cis*/*trans* = 30/70) and EG[140]

1,4-CHDM mol %	EG mol %	Izod impact Strength (J/m)	Rockwell L Hardness	Heat deflection temperature (°C)
0	100	44.9	81	62
16	84	55.0	70	60
31	69	48.6	63	64
44	56	90.8	63	61
50	50	921.7	62	66
59	41	1531.5	59	64
77	23	1580.1	56	67
83	17	1170.0	56	65
100	0	1000.7	57	67

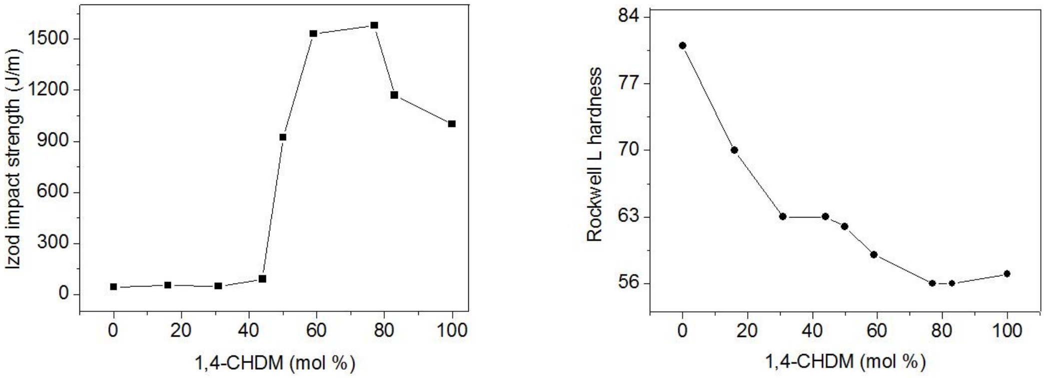


Figure 2.10 Effects of the 1,4-CHDM content on properties of copolyesters

Table 2.21 and **Figure 2.10** show the composition and mechanical properties of PETG copolyesters. Increasing the content of EG in PETG copolyesters generally results in increased hardness and decreased impact strength. As far as TMCBD/EG copolyesters are concerned, increasing EG content significantly lowers both the hardness and impact strength (**Table 2.20** and **Figure 2.9**). TMCBD is a very rigid compound and has a higher T_g than 1,4-CHDM, and its combination with EG would be expected to provide copolyesters with higher rigidity, hardness and brittleness than PETG copolyesters. When comparing the above two graphs, it is evident that the terephathalate copolyesters of TMCBD/EG have an advantageous combination of impact strength, hardness and heat resistance in a particular composition range.

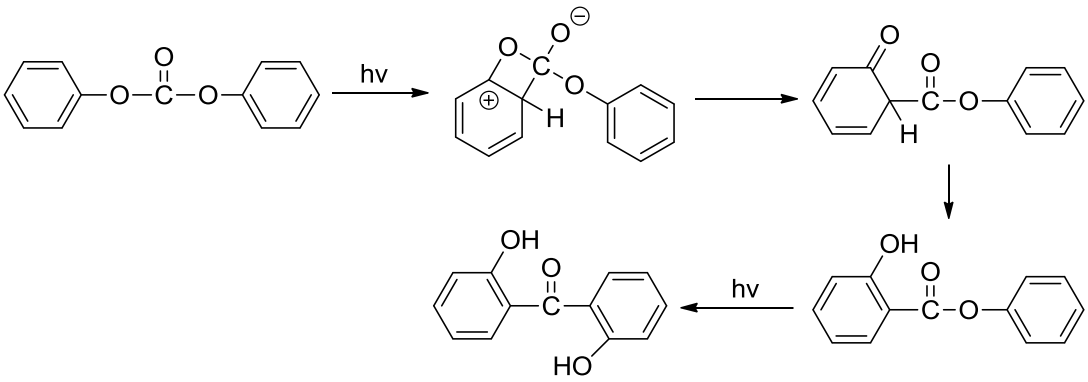
From **Table 2.20**, we can see that TMCBD with 30 to 85 mol % was incorporated into PET polyester backbones with excellent properties. Copolyesters containing less than 25 mol % TMCBD tend to exhibit unacceptable impact strength and have low hardness. However, copolyesters containing above 85 mol % TMCBD possess extremely high inherent viscosities, which make it difficult to process the copolyesters without additional thermal degradation. TPA/TMCBD copolyesters with EG below 15 mol % do not exhibit enough hardness. However, TPA/TMCBD copolyesters with EG above 75 mol % do not have sufficiently high impact strength for engineering plastic applications where high impact strength is required. The amorphous terephthalate copolyesters with TMCBD/aliphatic diol were confirmed as remarkably tough materials with high notched Izod impacts of up to 1070 J/m. The Izod impact decreases with the increase of the TMCBD content of the copolymers, but T_g increases when the TMCBD content is increased. Thus, this appears to be an unusual relationship between toughness and T_g. The properties can be adjusted to meet different requirements by changing the content of TMCBD. For example, high T_g above 100 ^{o}C and excellent toughness were observed for copolyesters with TMCBD in the range of 50-80 mol %. Particularly, when the content of

TMCBD is about 50-60 mol %, the terephthalate copolyesters of TMCBD/aliphatic diol has a Izod impact comparable to that of polycarbonates although these copolyesters have lower T_g's than polycarbonates (notched Izod ~ 650-800 J/m and T_g ~ 150 ^{o}C). However, copolymers with TMCBD levels about 70-80 mol % have Tg's close to those of polycarbonates and still maintain a Izod impact of above 250 J/m. TMCBD/EG terephthalate copolyesters show a maximum of 660 J/m notched Izod impact at a TMCBD/EG ratio of 64/36, compared to the highest notched Izod impact value of 1070 J/m at a TMCBD/PD ratio of 40/60.[140]

Shear yielding under impact can occur for TMCBD terephthalate copolyesters. Shear yielding is defined as one of the primary localized deformation mechanisms for glassy polymers and is a plastic deformation in the form of shear bands, which play a role in crack initiation. Right after yield, the material softening is observed, and then the material hardens upon further deformation because of molecular orientation.[141] Since the tetramethylcyclobutylene unit is conformationally rigid, it is remarkable to observe the very high impact resistance of these TMCBD terephthalate copolyesters. This result is opposite to what generally is observed when adding a T_g enhancing monomer, such as 1,4-CHDM, to a polyester backbone. This effect remains an unanswered question for TMCBD containing polyesters. TMCBD has a considerably different molecular structure compared to bisphenol A or 1,4-CHDM, thus, the high impact resistance of the TMCBD/aliphatic diol terephthalate copolymers cannot be easily explained until we better understand how polymer structure affects impact behavior.

2.4.3 Photooxidative stability

Many aromatic polymers, such as bisphenol A polycarbonate, poly(bisphenol A terephthalate), and PET, can undergo degradation and yellowing under ultraviolet (UV) exposure, especially in presence of heat, moisture, oxygen, or atmospheric pollutants.[142, 143] The photochemistry degradation of bisphenol A polycarbonate involves photo-Fries rearrangements, which produce phenyl salicylate and benzophenones, as shown in **Scheme 2.18**.[144-146]



Scheme 2.18 Photo-Fries rearrangements of bisphenol A polycarbonate[146]

Then the occurrence of photooxidative reactions causes the cleavage of main chains to produce – CHO and –COOH end groups, and radicals, which are responsible for the formation of the three dimensional networks.[147] On the other hand, linear aliphatic polyesters such as poly (butylene succinate) (PBSU), and copolyesters, such as poly(butylene succinate-*co*-adipate) (PBSA), undergo photodegradation by different mechanism---Norrish II type, which leads to the cleavage of main chains, producing CH_2 = CH- , -COOH, and -$COCH_3$ end groups.[147] Typically, the degradation of materials can result in embrittlement, chalking, surface crazing, discoloration, and loss of physical properties such as strength and impact. Therefore, studies of the weatherability of polymers are important since polymer resins have an increasing importance as desirable materials for outdoor use. Aliphatic-aromatic polyester resins often have limited weather resistance, which can be improved for increased outdoor stability by adding stabilizers.[148] For example, stabilization of these materials against weathering damage can be achieved by adding UV-screening agents, absorbers and quenchers.

Cycloaliphatic units such as tetramethylcyclobutylene rings are relatively stable under photooxidative conditions and do not undergo photo-Fries rearrangements. Chain cleavage can be prevented by the cyclic TMCBD units, which has two sterically hindered tertiary hydrogens. Even if one carbon-carbon bond is broken, the cyclic structure can still retain backbone connectivity. In order to determine the relative UV stability of cycloaliphatic polyesters, an accelerated UV weathering test was done on the TMCBD/PD (78/22) terephthalate copolyester **(11)** (m = 3) (49/51 *cis*/*trans* TMCBD) and on a commercially available bisphenol A polycarbonate, which did not contain UV stabilizers.[25] The comparison is shown in **Figure 2.11**.

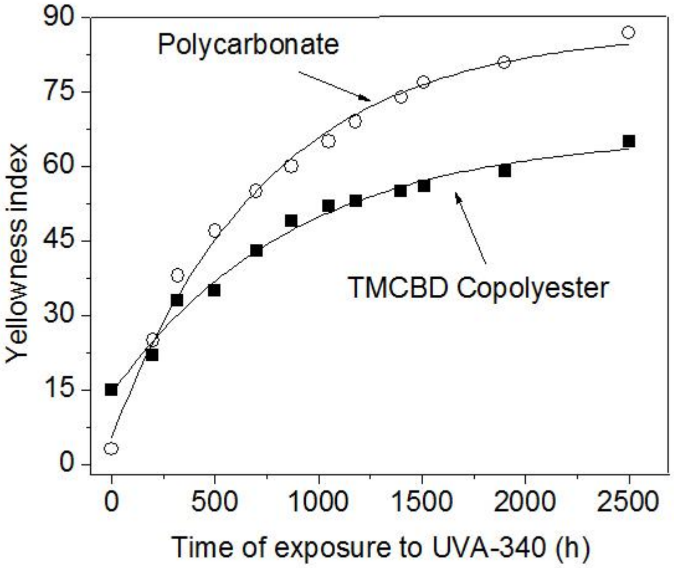


Figure 2.11 Yellowness index (YI) during accelerated UV aging of TMCBD/PD (78/22) copolyester and unstabilized bisphenol A polycarbonate[25]

The plots in **Figure 2.11** indicate that yellowness index (YI) of TMCBD/PD terephthalate copolyester increased at a slower rate than that of the polycarbonate. Furthermore, the former had a lower absolute yellowness index than the latter after exposure to UVA-340 of about 2500 h. Similar changes were observed in haze, gloss, and transmission for the two polymers, as shown in **Table 2.22**.[25]

Table 2.22 Accelerated UV weathering of TMCBD/PD copolyester and bisphenol A polycarbonate for 2500 h[25]

Properties	TMCBD/PD copolyester			Bisphenol A polycarbonate		
	Initial	Final	Change	Initial	Final	Change
yellowness index	17	67	+294 %	3	87	+2800 %
haze (%)	19	29	+53 %	3	17	+470 %
transmission (%)	70	63	-10 %	87	72	-17 %
gloss at 45^o	68	62	-9 %	93	63	-32 %
notched Izod (J/m)	390	110	-72 %	990	70	-93 %

Furthermore, it was found in **Table 2.22** that the TMCBD/PD copolyesters maintained a higher notched Izod impact than bisphenol A polycarbonate after 2500 h of exposure to an accelerated UV weathering condition. These results suggest that the TMCBD copolyesters possess certain inherent photooxidative stability, especially to yellowing. However, in industry, Tritan^{TM} **(12)** are still often protected against degradation when exposed to the UV wavelengths contained in sunlight. It was found that a Tritan^{TM} sheet with a protected cap layer containing UV absorbing additives provided excellent resistance to yellowing when exposed to natural sunlight.[149] Tritan^{TM} also exhibited excellent light transmittance (≥ 90%) and low haze (< 1%), and thus is suited for outdoor sign applications.[150]

2.5 Potential applications of cyloaliphatic copolyesters

2.5.1 Cyloaliphatic copolyesters as weatherable materials

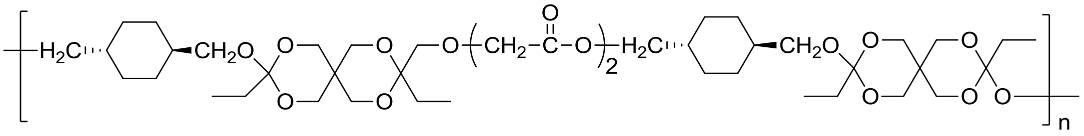
A substantial amount of work has also been reported in patents on weather resistant coating materials.[151-153] Neopentyl glycol, which lacks β-hydrogens, is usually used as the major glycol component in combination with terephthalic acid (TPA) to produce weather resistant aliphatic-aromatic polyester powder coating resins. However, their performance and physical properties can be impacted by adding small amounts of other cycloaliphatic diols and diacids. Johnson and Sade[153] have studied different monomers for polyester powder coating resins. The use of 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) in preparation of polyester resins affords improved flexibility, UV resistance and resistance to yellowing when compared to the use of aromatic diacids such as TPA and isophthalic acid (IPA). This combination of multiple components is effective in producing powder coating resins with T_g's in the range of 50-80 ^oC. The T_g of these resins must exceed the storage temperature of the formulated coatings. If storage temperature reaches or exceeds the T_g, the amorphous resin begins to cold flow and the finely divided particles can agglomerate, which make the powder unsuitable for practical applications. However, the T_g of polyester coating resins decreases when all the TPA is replaced by 1,4-CHDA. Thus, one or more additional monomers need to be added to compensate for the T_g inadequacy. T_g is enhanced when hydrogenated bisphenol A (HBPA) **(36)** [26] is used for the preparation of the coating resins. As discussed in previous section, HBPA has three isomers, all of which are structurally rigid due to steric hindrance from rotational and conformational changes. Therefore, T_g enhancement from incorporating HBPA is not unexpected.

Polyesters, which exhibit good weatherability and meet the basic T_g requirements for powder coatings, are becoming particularly important for outdoor applications. Aliphatic polyesters prepared from 1,4-CHDA and TMCBD have been potential for use as film and adhesives[154] and possess improved weatherability. These polyesters have sufficiently high enough molecular weights for use in molding plastics. All-aliphatic polyester resins based on 1,4-CHDA and cycloaliphatic diols, such as hydrogenated bisphenol A, have properties suitable for use in weatherable powder coating resins.[155]

2.5.2 Certain cyloaliphatic copolyesters as biomaterials

Biodegradable materials for use in biomedical applications have been of particular interest to many material scientists in recent years.[156-158] Synthetic aliphatic polyesters are an important class of biodegradable and hydrolysable polymers among these biodegradable materials.[22, 159] However, almost all biodegradable polyesters are linear aliphatic polyesters.[22, 160] The incorporation of cyclic structures into the backbone is of particular interest for new biodegradable materials, since they are expected to provide improved physical and chemical properties such as higher T_g and better resistance to heat.

In a previous work by Zhang and coworkers,[161] cycloaliphatic poly(ester anhydride)s were prepared from ethylene glycol (EG), 1,3-propanediol (PD), 1,4-butanediol (BD), or 1,6-hexanediol (HD) with 1,4-CHDA in acetic anhydride by melt-polycondensation. Their results revealed that all the poly(ester anhydride)s show excellent drug delivery properties. The delivery of ibuprofen [α-(4-isobutylphenyl)propionic acid, 2 wt%] from poly(ester anhydride)s depends on the ratio of the number of anhydride bonds to the number of ester bonds in the polymer main chain. Wang *et al.* also demonstrated that aliphatic/aromatic copolyesters based on 1,4-CHDA were biodegradable and the degradation rate was dependent on the 1,4-CHDA composition.[162] Ng *et al.* prepared a poly(ortho ester) **(74)** based on *trans*-1,4-CHDM, glycolide, and 3,9-diethylidene-2,4,8,10-tetraoxaspiro[5.5]undecane (DETOSU).[163]


(74)

This poly(ortho ester) **(74)** can be hydrolytically degraded without additional catalysts. Furthermore, the mechanical properties can be controlled by changing the diol monomer ratios. For example, Heller *et al.* showed that the T_g of one biodegradable poly(ortho ester) containing a rigid diol (*trans*-1,4-CHDM) and a flexible diol (HD) could be varied from 20 to 105° by increasing the content of the rigid diol.[164]

In conclusion, polyesters can be readily modified to meet different application requirements by changing their monomer structures or introducing additional functional groups. A better understanding of polymerization mechanisms is also helpful to further define the polymer chemical structures. The Ph.D. research described in this dissertation focuses on new strategies for introducing cyclic groups into polyester/copolyester backbones in order to achieve high performance materials. These new polyester structures have the potential to expand the practical applications of current polyesters.

2.6 Summary

Current research in the field of polyesters containing cycloaliphatic units reveals that a large variety of cycloaliphatic polyesters have been synthesized using various types of monomers and synthetic methods. Compared to aromatic polyesters, cycloaliphatic polyesters such as the ones covered in this review possess certain important properties, such as relatively good UV stability and high transparency. They also possess high T_gs and thermal stability compared to linear aliphatic polyesters. Based on the extensive applications for cycloaliphatic polymers, a broader investigation is extremely important for gain deeper insight into the structure-property relationship of cycloaliphatic polymers.

2.7 References

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Chapter 3: Synthesis and Properties of Cyclic Diester Based Aliphatic Copolyesters

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3.1 Abstract

Melt polycondensation was used to prepare a systematic series of random and amorphous copolyesters using the following cycloaliphatic diesters: dimethyl-1,4-cyclohexane dicarboxylate (DMCD), dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate (DMCD-1), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3), 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M) and the aliphatic diols – ethylene glycol (EG) and 1,4-cyclohexane dimethanol (1,4-CHDM). The polymer compositions were determined by nuclear magnetic resonance (NMR) and the molecular weights were determined using size exclusion chromatography (SEC). The polyesters were characterized by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The copolyester based on DMCD-2 was observed to have a higher glass transition temperature (T_g up to 115 ºC) than the other copolyesters in this chapter. For poly[x(DMCD-2)y(DMCD)30(EG)70(1,4-CHDM)], T_g increases linearly with the increase of DMCD-2 mole content. DMA showed that all of the cycloaliphatic copolyesters have secondary relaxations, resulting from conformational transitions of the cyclohexylene rings.

3.2 Introduction

Aliphatic polyesters were among the first, if not the first, intentionally prepared synthetic polymers in the pioneering work of Carothers.[1] They were abandoned as useful polymers for fibers because of their low T_gs and melting points. The inclusion of aromatic terephthaloyl groups from dimethyl terephthalate by Winfield and Dickson led to acceptable T_gs and melting points for fiber applications and resulted in the huge commercial success of poly(ethylene terephthalate) (PET).[2] However, aromatic group containing polyesters have some drawbacks. Because of the UV light absorption of the aromatic groups, these polyesters do not exhibit good stability in outdoor applications. In addition, biomedical applications of aromatic groups-containing polyesters are limited because of toxicity concerns about the aromatic degradation products of these polymers. Therefore there has been a significant effort in recent years to study the polymerization chemistry and properties of all-aliphatic polyesters.[3] All-aliphatic polyesters have been shown to possess excellent UV stability since they do not contain any functional groups that absorb UV light, which enhances their photostability and renders them much more readily stabilizable for outdoor applications.[4-6] However, they often have low T_gs that limit their applications. In fact, many of these polymers have T_gs below room temperature. The introduction of alicyclic units to the main chain of the polymer can improve solubility and impart enhanced glass transition temperatures due to the rigidity of the alicyclic structure.[7] Moreover, polymers having different isomers of alicyclic structures in a main chain have difficulty crystallizing and are, therefore, amorphous and transparent. Thus, such materials have potential applications in many fields due to their environmental resistance and potential low toxicity.

Cyclohexyl groups have been incorporated into a wide variety of polyesters to impart desirable physical properties.[8-10] For example, 1,4-cyclohexane dicarboxylic acid (1,4-CHDA) is an important monomer for raising the T_g in all-aliphatic polyesters and has found wide applications as a monomer in coating resins. The all cycloaliphatic polyester poly(cyclohexylene dimethylene cyclohexane dicarboxylate) (PCCD) based on 1,4-CHDA and 1,4-CHDM has a T_g of only around 65-70 °C and has some apparent applications in situations where UV stability is required.[8, 11] Also, higher T_g all-aliphatic polyesters could have important applications in UV protective cap layers for extruded sheet products, as stable substrates for flexible displays and solar cells, and as substrates for microfluidic devices where the optical properties of the substrate are important.

Although there are numerous reports about the properties of various cyclic diol containing polyesters,[12] there are few reports of all-aliphatic copolyesters based on a systematic variation of the cyclic diacids. To the best of our knowledge there are no suitable all-aliphatic diacid or diester monomers that can, when incorporated into a polyester backbone, achieve the T_g necessary to meet the needs of applications described above. The research described in this report is directed at a systematic incorporation of several alicyclic diesters into an all-aliphatic polyester backbone with the goal to synthesize high T_g all-aliphatic polyesters to provide a useful combination of optical transparency, thermal stability, weatherability, and surface chemistry attributes.

The alicyclic monomers studied include bridgehead-bridgehead bicyclo[2.2.l]heptyl (DMCD-1), bicyclo[2.2.2]octyl (DMCD-2), bicyclo[3.2.2]nonyl (DMCD-3) diesters, as well as the non-bridged model 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M). In this study we synthesized a variety of copolyesters containing these bicycloalkanes groups in the backbone and investigated the effect of bicycloalkanes groups on the properties of these copolyesters. The polyesters based on DMCD-2 stood out in terms of enhanced T_g compared to the other bicyclic structures. Colorless and transparent films were readily obtained by compression molding or by solvent casting, and their properties were studied and compared to the other bicyclic diester based polyesters.

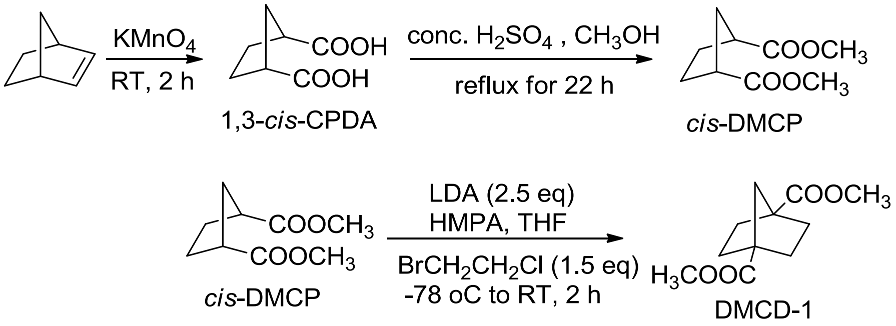
3.3 Experimental

3.3.1 Materials

All reagents were used without further purification. EG (≥ 99 %), 1,4-CHDM with a 70/30 *trans*/*cis* isomer mixture (99 %), 1-bromo-2-chloroethane (98%), hexamethyl phosphoramide (HMPA) (99 %), butyllithium (2.5M solution in hexane), iodomethane (99 %), norbornylene (99 %), and potassium permanganate (ACS reagent) were purchased from the Aldrich Chemical Co. N,N-diisopropylamine (99 %) was purchased from Sigma Chemical Co. Titanium(IV) butoxide (98 %) was purchased from Alfa Aesar Chemical Co. DMCD (*cis* /*trans* = 3/1) was donated by Eastman Chemical Co.

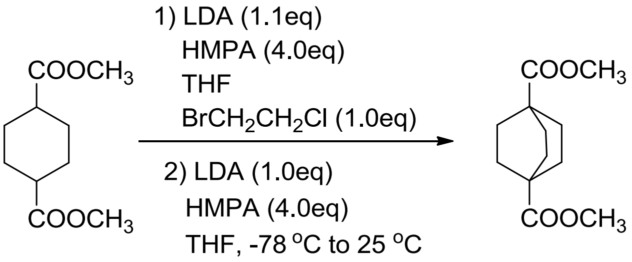
3.3.2 Synthesis of cycloaliphatic diesters

Synthesis of dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate (DMCD-1) (Scheme 3.1). A modification of the improved synthesis (**Scheme 3.1**) of Della[13] was used. Acetone, instead of water, was used as the solvent for the synthesis of *cis*-1,3-cyclopentane dicarboxylic acid. Yield: 83.3%, mp: 116.2-117 °C. The diacid and a large excess of methanol containing concentrated sulfuric acid were reacted under reflux for 22 h to produce the corresponding dimethylesters. Vacuum distillation (73-76 ^{o}C / 0.4 – 0.5 mmHg) gave the pure *cis*-dimethyl cyclopentane-1,3-dicarboxylate (*cis*-DMCP); yield: 74 %. The bisenolate of the cyclopentane diester in the presence of lithium diisopropylamide (LDA) solution was treated with a solution of 1-bromo-2-chloroethane in THF. The workup involved the same procedure as above and afforded a yellow solid, which upon sublimation (60-65 °C / 0.2 mmHg) gave the bicyclic diester DMCD-1 (56 %) as colorless crystals. M.p.: 57.2-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.66 (s, 6H, COOC*H*$_3$), 2.01 (d, 4H, *J* = 6.4 Hz, C*H*$_2$CH$_2$), 1.89 (s, 2H, CC*H*$_2$C), 1.66 (d, 4H, *J* = 7.2 Hz, CH$_2$C*H*$_2$); ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 175.35 (*C*OOCH$_3$), 52.54 (*C*COOCH$_3$), 51.64 (COO*C*H$_3$), 44.92(C*C*H$_2$C), 32.92 (*C*H$_2$*C*H$_2$).



Scheme 3.1 Synthesis of DMCD-1

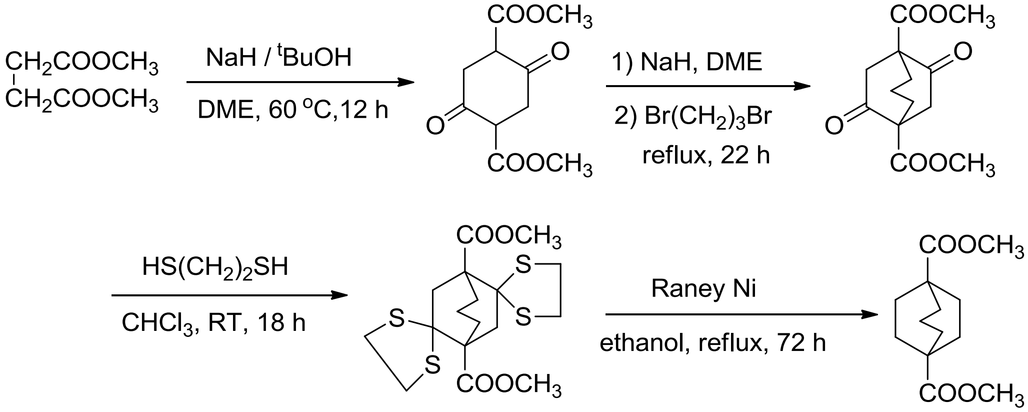
Synthesis of dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2). DMCD-2 was prepared by a published literature procedure (**Scheme 3.2**).[14] A solution of N,N-diisopropylamine (33.8 mL, 240 mmol) in THF (280 mL) was stirred and cooled to -70 ºC under N_2, n-BuLi (88 mL, 2.5 M in hexane, 220 mmol) was added by a syringe. The mixture was stirred for 30 min at -78 ºC. HMPA (144 mL, 800 mmol) was added, and a solution of DMCD (40 g, 200 mmol) in THF (40 mL) was charged subsequently over a period of 20 min. The mixture was stirred further for 40 min, and then 1-bromo-2-chloroethane (16.6 mL, 199.6 mmol) was added dropwise. After the mixture was stirred at -78 ºC for 1 h, a solution of HMPA (144 mL, 800 mmol) in THF (240 mL) was added slowly. At the same time, preparing LDA again: 80 mL of n-BuLi (2.5 M in hexane, 200 mmol) was added to N,N-diisopropylamine (31.2 mL, 222.4 mmol) in THF (280 mL) at -78 ºC. By cannula, the freshly prepared LDA was transferred to the reaction mixture at -78 ºC over a period of 40 min. The resultant mixture was stirred at -78ºC for 1.5 h. The cold bath was removed and the mixture was stirred further for 4–6 h at RT. The clear brown solution was then quenched with saturated aqueous NH_4Cl (160 mL). The salt solid was precipitated and was filtered. After that, the solution was concentrated in vacuo to remove THF. The residue was diluted with 320 mL of water and extracted with hexane (3×240 mL). The combined extracts were washed with saturated NaCl aqueous solution (280 mL), dried with Na_2SO_4, and concentrated in vacuo to give a yellow sticky solid. The workup method was modified to improve the purity of the product. This modification involved vacuum distillation (130 ºC/ 0.1-0.2 mmHg) and recrystallization from hexanes. Finally a white crystalline solid was obtained, yield: 38.5 %, mp: 98.8-99.1 ºC (literature 92.8 ºC). The structure was confirmed by NMR measurement. NMR data were as follows: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.61 (s, 3H, OC*H*$_3$), 1.75(s, 6H, C*H*$_2$); ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 177.77 (*C*OOCH$_3$), 51.66 (COO*C*H$_3$), 38.57 (*C*COOCH$_3$), 27.69 (*C*H$_2$).



Scheme 3.2 Synthesis of DMCD-2

Synthesis of dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3). DMCD-3 was synthesized following a literature procedure (**Scheme 3.3**).[15] The

Dieckmann condensation of dimethyl malonate obtained white solid product dimethyl succinylsuccinate in 72 % yield.[16] M.p.126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 12.12 (s, 2H, CO*H*), 3.79 (s, 6H, $COOCH_3$), 3.18 (s, 4H, $CH_2CCOOCH_3$); ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 171.93 ($COOCH_3$), 168.82 (*C*OH), 93.42 ($CCOOCH_3$), 52.10 ($COOCH_3$), 28.77 (CH_2).



Scheme 3.3 Synthesis of DMCD-3

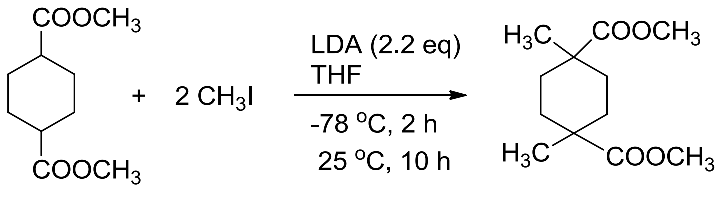
Dimethyl succinylsuccinate was treated with sodium hydride in dry DME and then reacted with 1,3-dibromopropane to obtain a white product 1,5-biscarbomethoxybicyclo[3.2.2]nonane-6,8-dione. Yield: 26 % m.p. 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.77 (s, 6H, $COOCH_3$), 3.39 (s, 1H, CH_2CO), 3.35 (s, 1H, CH_2CO), 2.78 (s, 1H, CH_2CO), 2.73 (s, 1H, CH_2CO), 2.45-2.52 (m, 2H, $CH_2CH_2CH_2$), 1.92-1.99 (m, 2H, $CH_2CH_2CH_2$), 1.75-1.82 (m, 2H, $CH_2CH_2CH_2$).

The bisdithiane was prepared from the diketone using the literature procedure[16] in 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.64 (s, 6H, $COOCH_3$), 3.57 (s, 1H, CH_2CS), 3.54 (s, 1H, CH_2CS), 3.40-3.36 (m, 4H, SCH_2CH_2S), 3.26-3.21 (m, 4H, SCH_2CH_2S), 2.96 (s, 1H, CH_2CS), 2.93 (s, 1H, CH_2CS), 2.56-2.53 (m, 2H, $CH_2CH_2CH_2$), 1.89-1.86 (m, 4H, $CH_2CH_2CH_2$); ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 174.05

($COOCH_3$), 70.20 ($CSCH_2$), 55.97($COOCH_3$), 55.07 ($CCOOCH_3$), 52.24 (CH_2CS), 40.89 (SCH_2CH_2S), 40.75 (SCH_2CH_2S), 37.19($CH_2CH_2CH_2$), 22.01 ($CH_2CH_2CH_2$).

Desulfurization of the dithioketal by Raney nickel slurry occurred in ethanol, which was refluxed for 3 days. The product was purified by distillation under high vacuum (110 ^{o}C / 0.08 mmHg) to give colorless solid DMCD-3. Yield: 70 %, m.p. 34-35 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.63 (s, 6H, $COOCH_3$), 1.94-1.67(m, 14H, CH_2CH_2). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 178.81 ($COOCH_3$), 51.87 ($COOCH_3$), 42.68 ($CCOOCH_3$), 37.38 ($CH_2CH_2CH_2$), 27.95 (CH_2CH_2), 21.36 ($CH_2CH_2CH_2$).

Synthesis of 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M). DMCD-M was prepared from the DMCD by following a procedure described by Weagley et al.[17] for the dialkylation of 1,3-di(methoxycarbonyl)cyclopentane (**Scheme 3.4**). Vacuum distillation (90-100 °C /0.2 mmHg) gave the product as a colorless oil (liquid and solid mixture, *cis*- and *trans*- product), yield, 88 %. Recrystallization from hexane gave a white crystalline solid (*trans*- product), yield, 51 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.63 (s, 6H, $COOCH_3$), 2.07 (d, 4H, J = 10 Hz, CH_2CH_2), 1.20 (d, 4H, J = 10 Hz, CH_2CH_2), 1.13 (s, 6H, CCH_3); ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 177.87 ($COOCH_3$), 51.89 ($COOCH_3$), 42.92 (CCH_3), 33.05 (CH_2CH_2), 27.51 (CCH_3). mp: 94.5-95.3 °C, MS (*m/z*): calcd for $C_{12}H_{20}O_4$, 228.14; found, 229.6 $[M+H]^+$.



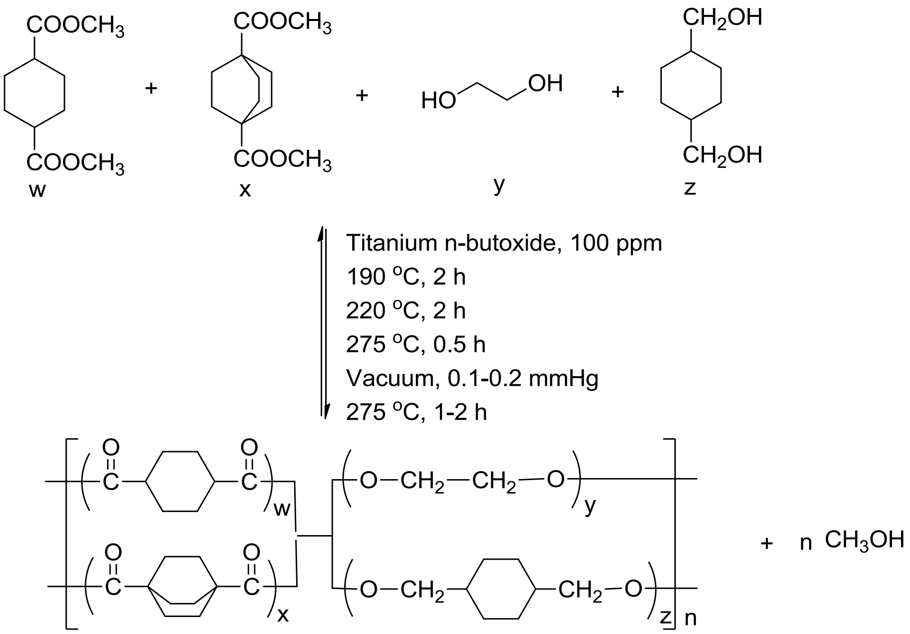
Scheme 3.4 Synthesis of DMCD-M

Preparation of a catalyst solution. The Ti catalyst solution was obtained by mixing titanium n-butoxide with n-BuOH in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

3.3.3 Polymerization

Abbreviation of polyesters. The polymer nomenclature used in this manuscript is based on a polyester containing 100 mol% of diester and 100 mol% of diol. For example, the polymer designated by poly[50(DMCD-2)50(DMCD)30(EG)70(1,4-CHDM)] describes this targeted polymer containing 50 mol% DMCD-2 and 50 mol% DMCD as its diester units and 30 mol% EG and 70 mol% 1,4-CHDM as its diol units. The letters stand for specific monomers′ abbreviations and the numbers indicate targeted mol % of monomers, respectively.

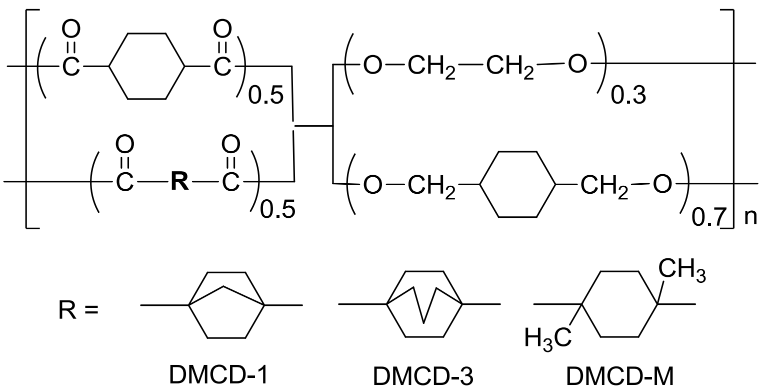
Preparation of poly[100(DMCD-2)30(EG)70(1,4-CHDM)]. It was prepared from DMCD-2, EG and 1,4-CHDM and the detailed procedure is as follows: 3.62 g (16 mmol) DMCD-2, 1.10 g (17.6 mmol) of EG (120 % excess), 1.15 g (8 mmol) 1,4-CHDM, and 0.05 mL (100 ppm) of a titanium n-butoxide solution (0.06 g/mL in butanol) were added to a 100 mL two-necked, round-bottom glass flask. This reaction flask was immersed into a molten Belmont metal bath that was pre-heated to 190 °C. A multi-step temperature procedure was used for the reaction, i.e. the reaction mixture was stirred at 190 °C for 2 h, then 220 °C for 2 h. After that the temperature was increased to 275 °C and held for 30 min. The pressure was then gradually reduced and the temperature was raised to 275 °C. The final stage involved applying a high vacuum (up to 0.08 mmHg) for an additional 2 h at 280 °C and a highly viscous copolyester was obtained. Some copolyesters started to take on yellow color due to the titanium catalyst and the long reaction time. The vacuum was stopped and nitrogen was bled into the flask. The polymer was cooled to room temperature, dissolved in chloroform, then precipitated into methanol. The solid precipitate was obtained by vacuum filtration and was dried under vacuum at 30-60 °C overnight before characterization. The same procedure was employed to prepare poly[w(DMCD)x(DMCD-2)y(EG)z(1,4-CHDM)] (where w and x, y and z add up to 100, respectively) (**Scheme 3.5**).



Scheme 3.5 Synthesis of poly[w(DMCD)x(DMCD-2)y(EG)z(1,4-CHDM)]

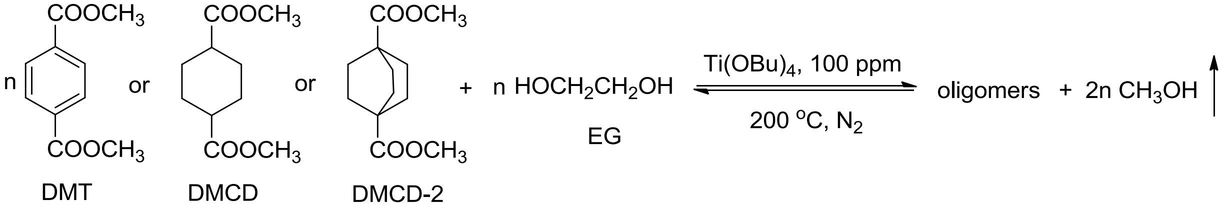
Synthesis of all-aliphatic poly[50(DMCD-1 or DMCD-3 or DMCD-M) 50(DMCD)30(EG)70(1,4-CHDM)] copolyesters

These copolyesters were prepared by the same procedure as the above copolymer except that DMCD-1, DMCD-3 or DMCD-M was used in place of DMCD-2. Their structures with targeted compositions were shown in **Scheme 3.6**.



Scheme 3.6 Structures of targeted poly[50(DMCD-1 or DMCD-3 or DMCD-M) 50(DMCD)30(EG)70(1,4-CHDM)] copolyesters

Kinetics studies of ester exchange reaction of DMT, DMCD, DMCD-2 with EG. A certain amount of diester DMT, ethylene glycol (EG, 20 mol% in excess) and the catalyst titanium n-butoxide (100 ppm based on Ti) were added to a one-necked glass flask equipped with a stirrer, nitrogen input and a receiving flask, which was located in an ice bath. The reaction flask was then immersed into a metal bath that was preheated to 200 °C. The side product methanol evaporated at 200 °C and reached the receiving flask along with nitrogen (the flow rate of nitrogen was kept constant) and then became a liquid again in the ice bath. The amount of methanol produced over time was measured and compared to the theoretical amount of methanol, thus the conversion of the reaction over time can be calculated. The same procedure was applied to DMCD or DMCD-2 with EG. The reaction was described in **Scheme 3.7**.



Scheme 3.7 Kinetics studies of the reaction of DMT, DMCD, DMCD-2 with EG

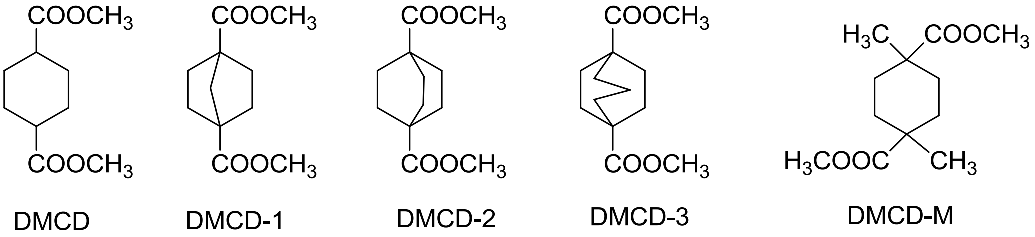
3.3.4 Characterization

^{1}H and ^{13}C NMR spectra were obtained using a Varian Inova 400 (400 MHz) spectrometer at room temperature; measurements were internally referenced to tetramethylsilane (TMS). ^{1}H NMR spectra were used to determine the final polyester compositions. SEC was run in chloroform at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set. Monodispersed polystyrene standards were used to construct a universal molecular weight calibration curve. A Viscotek refractive index detector and a viscometer were used for the molecular weight determination. DSC data were obtained from a Perkin Elmer Pyris1. Samples were run from -20 to 200 °C at a heating/cooling rate of 20 °C/min under nitrogen. The glass transition temperature (T_g) was taken from the midpoint in the second heating cycle DSC traces. TGA was run at a heating rate 10 ^{o}C/min from room temperature to 600 $^\circ$C under nitrogen on a TA Instrument TGA 2950. Tensile tests were performed on an Instron Model 4400 Universal Testing System with Series IX software. Samples were run at a constant cross-head speed of 15 mm/min using an initial grip-to-grip separation of 10 mm. All reported tensile data represented an average of at least three independent measurements. A TA Instrument Q1000 DMA was used to acquire storage modulus, loss modulus and tan delta for films, which were deformed (10 micrometer amplitude) in the tension mode at a frequency of 1 Hz using a temperature ramp rate of 3 °C /min under nitrogen. For compression molding, the sample was sandwiched between two pieces of 3 mm thick aluminum plate and was centered in a mold of the desired thickness. The samples were heated 40 °C above their T_g and a pressure of about 500 PSI was applied. The pressure was released after 15 min and these films were then used for various thermal and mechanical analyses.

For hydrolytic degradation tests, the polyester films, which were obtained by casting from $CHCl_3$ solution (10 % w/v), were placed into a 20 mL phosphate buffer saline (PBS) solution (pH 7.40) in a shaking air bath at 37 °C. The films were removed from the buffer solution after selected time intervals, washed with distilled water three times, and then dried under vacuum at room temperature to constant weight. The extent of hydrolytic degradation was characterized by the weight loss percent, which was calculated from the mass difference between before and after hydrolytic degradation, divided by the initial sample weight.

3.4 Results and discussion

Selection and synthesis of diester monomers. The structures and abbreviations of all cycloaliphatic diesters in this paper are listed in **Scheme 3.8**.



Scheme 3.8 Structures and abbreviations of cyclic diesters

Functionally bridgehead-substituted bicycloalkanes, such as DMCD-2, have been known for many years and polymers containing DMCD-2 possess interesting physical properties. Although liquid crystal copolyesters (rod-like) containing the bicyclo[2.2.2]octane ring were reported several decades ago,[18] prior literature did not describe its use in amorphous copolyesters.[18-20] Amorphous DMCD-2-containing copolyesters with high T_g were initially synthesized in this study. A convenient one-pot preparation method of DMCD-2 was followed[14] and pure product was obtained by modifying the work up procedure as detailed in the experimental section. It is well known that structural factors, such as the rigidity and symmetry of units, can greatly affect the properties of polymers. Therefore, we have also examined the effect of other cyclic compounds whose structures are similar to that of DMCD-2. The bicyclo[2.2.1]heptane ring derivative (DMCD-1) and bicyclo[3.2.2]nonane ring one (DMCD-3) are suited for this purpose. DMCD-1 has a rigid symmetrical structure with a similar steric size to that of DMCD-2. A one-pot procedure, which includes alkylation and cyclization of the bisenolates of DMCP with 1,2-dihaloethane, was successfully applied to the synthesis of DMCD-1. DMCD-3 has a reduced symmetric structure due to the extra carbon on the bridge. This bicyclo derivative was synthesized by well-documented procedures.[15, 16] Synthesis of DMCD-M involves dialkylation of readily available diester DMCD using two equivalents of base; followed by two equivalents of methyl iodide in one step.

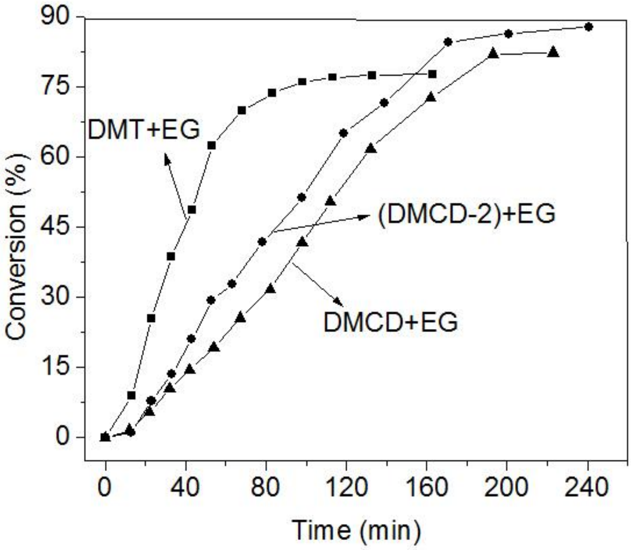


Figure 3.1 Kinetics of transesterification for different diesters--DMT, DMCD-2 or DMCD

The cyclic diesters of this study were found to readily participate in melt-phase polycondensation with little, if any, effect of the bulky cyclic units. For example, DMCD-2 was found to readily undergo polycondensation with EG, as shown in **Figure 3.1**. The rate of the transesterification and elimination of methanol was observed to be faster than the rate when using DMCD but somewhat slower than when using DMT.

Synthesis of copolyesters and their composition by ^{1}H NMR spectra. Melt transesterification is a preferred route to prepare polyesters and it requires high reaction temperatures, a high vacuum, and proper catalysts.[7] All the polyesters examined in this study were prepared by melt-phase polymerization with the use of titanium n-butoxide as catalyst. The polymerization time was about 6 h and the temperature 190-275 ^{o}C. However, an attempt to synthesize a high molecular weight polyester from DMCD-2 and 1,4-CHDM by melt polymerization was unsuccessful because of the low volatility of 1,4-CHDM and the high melt viscosity of oligomers. As EG has higher volatility and can be removed easily under vacuum, it was used in excess to improve the molecular weights of polyesters in our study. Therefore, for this study we chose polymers containing both EG and 1,4-CHDM diols to compare the properties of polyesters with various cyclic diesters. The copolyester samples were soluble in common chlorinated solvents at room temperature, such as dichloromethane and chloroform.

Figure 3.2 shows the ^{1}H NMR spectrum of representative copolyester based on DMCD-2, EG and 1,4-CHDM with a targeted molar ratio 30/70 of EG/1,4-CHDM. The correlations between the various structural components and the observed NMR peaks are shown.

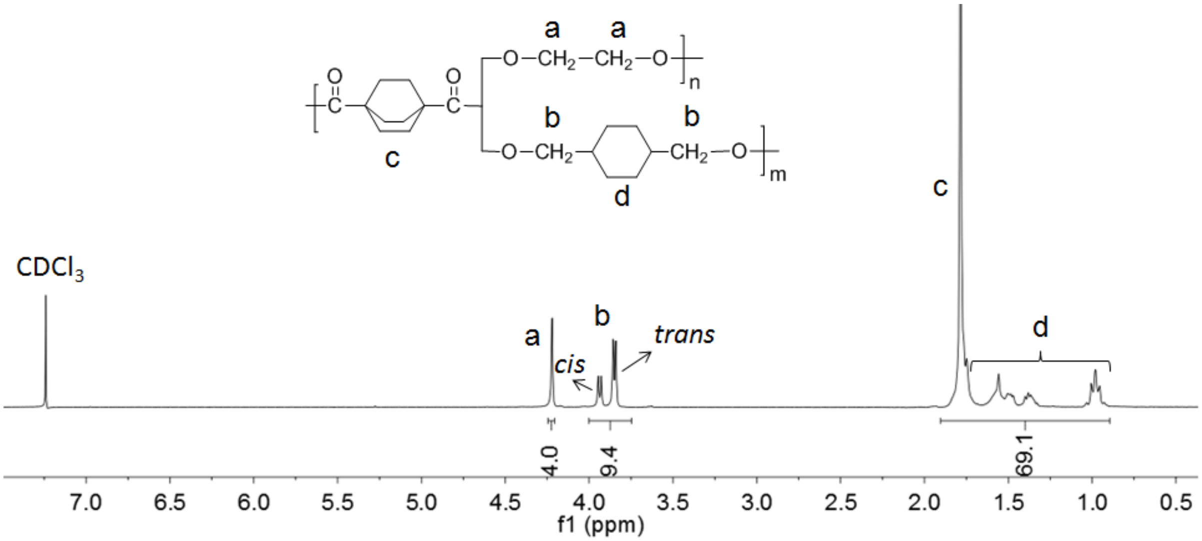


Figure 3.2 ^{1}H NMR spectrum of poly[100(DMCD-2)29(EG)71(1,4-CHDM)]

Peak "a" is assigned to the methylene group adjacent to the oxygen at ethylene glycol unit (single peak), and peak "b" is the methylene group adjacent to the oxygen at 1,4-CHDM unit (*cis*/*trans* = 30/70). The *cis*/*trans* ratios of 1,4-CHDM were determined by comparing the α-hydrogens on the *cis* and *trans* isomers; they did not change during polymerization. The broad peaks "c" and "d" come from the protons on the cycloaliphatic rings. The polymer composition calculated from this ^{1}H NMR spectrum based on the peak area ratio of "a" to "b" gave 29 % EG and 71 % 1,4-CHDM (calculated copolyester composition values from peak areas are reported in **Table 3.1**). The ^{1}H NMR spectrum of each of these polymers showed that its actual composition was in good agreement with the targeted polymer composition.

Molecular weights and thermal properties of different copolyesters. The molecular weights and thermal properties of the soluble polyesters poly[w(DMCD)x(DMCD-2)y(EG)z(1,4-CHDM)] are summarized in **Table 3.1**.

Table 3.1 Properties of poly[w(DMCD)x(DMCD-2)y(EG)z(1,4-CHDM)]

polyester composition DMCD/(DMCD-2)/EG/1,4-CHDM w/x/y/z (^{1}H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (g/mol)	T_g (°C)
0/100/100/0	363	47,000	65,000	75
0/100/75/25	382	37,000	55,000	92
0/100/50/50	378	29,000	45,000	102
0/100/31/69	372	26,000	43,000	115
0/100/0/100	N/A	N/A	N/A	N/A
100/0/0/100	380	16,200	30,700	45
90/10/0/100	381	9,700	23,000	49
75/25/0/100	377	16,500	29,000	58
50/50/0/100	372	9,200	18,000	71
31/69/31/69	370	30,000	46,000	83
50/50/29/71	367	31,000	52,000	70
77/23/28/72	360	30,000	51,000	52
100/0/29/71	355	28,000	48,000	40

Initially, we synthesized copolyesters based on 100 % DMCD-2 and different EG and 1,4-CHDM contents. These results in **Table 3.1** show that high molecular weight polyesters can be readily achieved with DMCD-2. These samples displayed PDIs close to 2 with a main peak followed by several small peaks, suggesting the presence of some oligomers during polymerizations. The copolyesters were all amorphous as no melting transitions were observed by DSC. The SEC trace of one sample is shown in **Figure 3.3** as a representative of these samples.

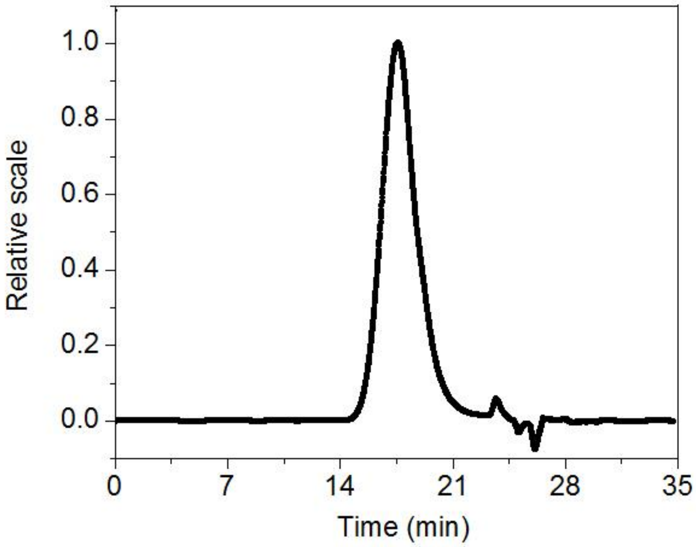


Figure 3.3 SEC trace of poly[100(DMCD-2)29(EG)71(1,4-CHDM)]

Polyesters with 100 % DMCD-2 were brittle, but the incorporation of DMCD was shown in **Table 3.1**, as expected, to lower T_g and render the sample more flexible. Therefore, a second series of copolyesters was prepared by varying the diester content by adding DMCD and holding the 1,4-CHDM/EG ratio constant at 70/30. The characterization results of poly[x(DMCD-2)w(DMCD)31(EG)69(1,4-CHDM)] are also shown in the bottom of **Table 3.1**. An inspection of the data shows that DMCD-2 is a very effective monomer for raising the T_g, when compared to DMT. For example, the copolyester based on 100 % DMT and a 30 % EG and 70 % 1,4-CHDM diol has a T_g of 85 ^{o}C, which is lower than the T_g of 115 ^{o}C for poly[100(DMCD-2)31(EG)69(1,4-CHDM)], indicating the rigid structure of bicyclo[2.2.2]octane group in the polyester main chain. A sharp decrease in T_g was observed when DMCD was added. The actual T_g

data and calculated T_g data from Fox equation were plotted in **Figure 3.4**. It exhibited a good linear relationship between T_g and DMCD-2 mole percent and thus the Fox equation was not fitted for those compositions. The molecular weights of polyesters in our study are high, up to 30,000 g/mol, and have little effect on T_g.

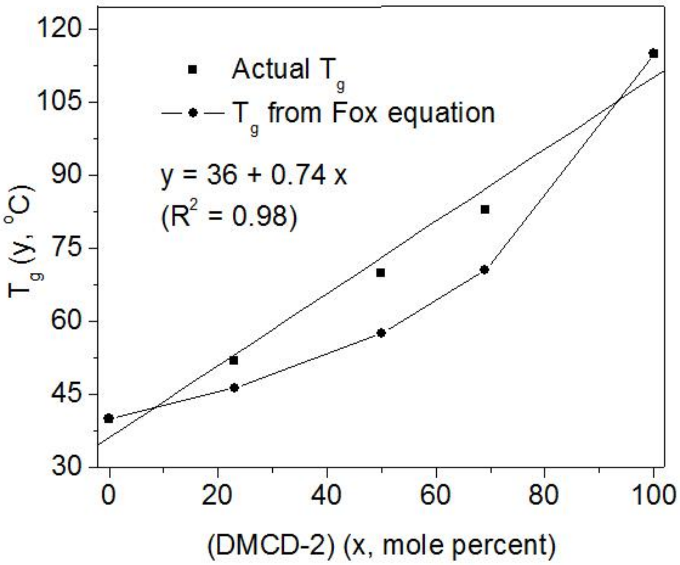


Figure 3.4 T_g versus DMCD-2 content for poly[w(DMCD)x(DMCD-2)30(EG)70(1,4-CHDM)]

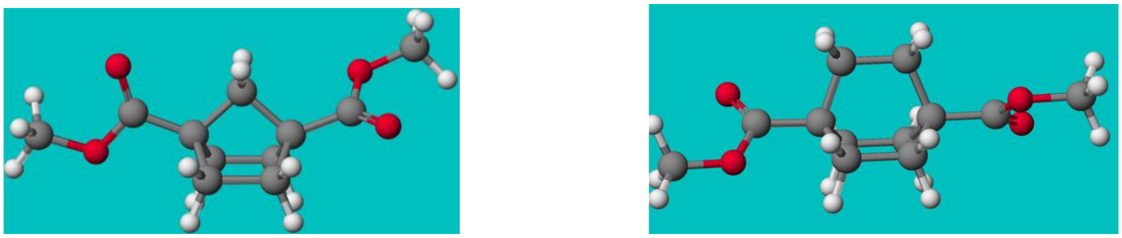
Using the same type of diols, we also synthesized other cycloaliphatic copolyesters based on DMCD-1, DMCD-3, DMCD-M and DMT for comparative purposes. The corresponding properties were shown in **Table 3.2**.

From table **Table 3.2**, we see the high molecular weights obtained for all soluble copolyesters. When bicyclo[2.2.2]octane units are incorporated into the polyester at 50 mol%, the molecular weight of the copolyester is the highest among those five copolyesters with similar compositions of EG/1,4-CHDM. We also found that the copolyester based on 50 % DMCD-2 has a higher T_g than one based on 50 % DMT, although these two copolyesters have similar molecular weights.

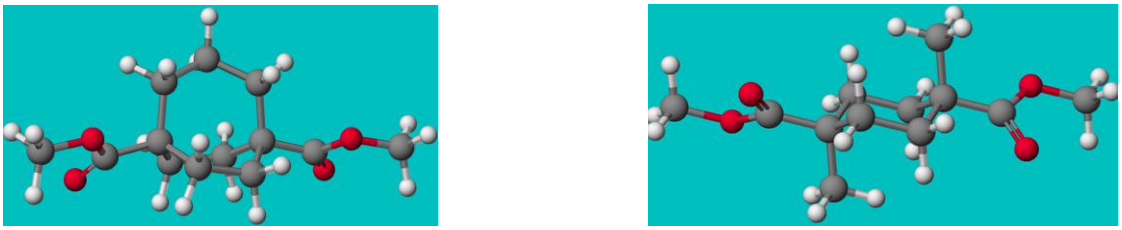
Table 3.2 Properties of various copolyesters based on different cyclic diesters

Polyester composition **R**/DMCD/EG/1,4-CHDM (from ^{1}H NMR)	SEC M_n (g/mol)	SEC M_w (g/mol)	T_g (°C)	Tensile stress at break (MPa)	Tensile strain at break (%)	Modulus (MPa)
R = (DMCD-1) 48/52/29/71	27,000	58,000	35	44±3	361±9	1330±40
R = (DMCD-2) 50/50/29/71	31,000	52,000	70	25±8	114 ± 30	1815±154
R = (DMCD-3) 48/52/31/69	28,000	53,000	46	19±2	392 ± 30	673±30
R = (DMCD-3) 100/0/27/73	18,100	33,900	72	N/A	N/A	N/A
R = (DMCD-M) 49/51/29/71	24,000	36,000	36	52±3	660±37	1473±36
R = (DMCD-M) 100/0/29/71	14,300	22,200	22	N/A	N/A	N/A
R = DMT 50/50/29/71	30,700	47,900	62	34±3	86±5	588±18
R = DMT 100/0/29/71	N/A	N/A	85	N/A	N/A	N/A

The copolyester based on 50 % DMCD-2 also has a higher T_g than other cycloaliphatic polyesters. As DMCD-1 is supposed to have a rigid structure, it was surprising that the T_g of the copolyester based on 50 % DMCD-1 was only 35 ^{o}C, similar to the T_g value of the copolyester based on DMCD. This is probably due to the inefficient chain packing of DMCD-1 structure. The related copolyester based on 50 % DMCD-3 had a T_g of 46 ^{o}C, which was lower than that of the polyester based on 50 % DMCD-2. This is most likely due to asymmetric structure of bicyclo[3.2.2]nonane due to the extra carbon on the bridge. The three dimensional models of these cyclic diesters are shown in **Figure 3.5**.



DMCD-1 DMCD-2



DMCD-3 DMCD-M

Figure 3.5 3-D models of DMCD-1, DMCD-2, DMCD-3 and DMCD-M

These 3-D structures were obtained from geometry optimization in the augmented MM3 force field contained in a Scigress Explorer Ultra version 7.7.0.47. Models show that diester groups attached to the bridgehead carbons of the bicyclo[2.2.2]octane ring are linear to one another; however, these same groups form an angle of approximately 150 ^{o} and 120 ^{o}, respectively, in the bicyclo[3.2.2]nonane ring and the bicyclo[2.2.1]heptane ring. This result indicates the importance of symmetry in improving T_g values.

The tensile mechanical properties of copolyesters. Tensile tests were conducted on compression molded films, which are optically clear. The results are summarized in **Table 3.2** and the stress-stain curves are plotted in **Figure 3.6**. Poly[50(DMCD-2)50(DMCD)29(EG)71(1,4-CHDM)] has the highest modulus (1815 MPa) and yield stress (96 MPa) among these six copolyesters due to the rigid structure of DMCD-2. It is interesting to note that even though the polyester based on 50 % DMCD-2 has the lowest average strain to failure, 114 %, it still exhibits high ductility. The high level of 1,4-CHDM is the likely basis of the ductility.

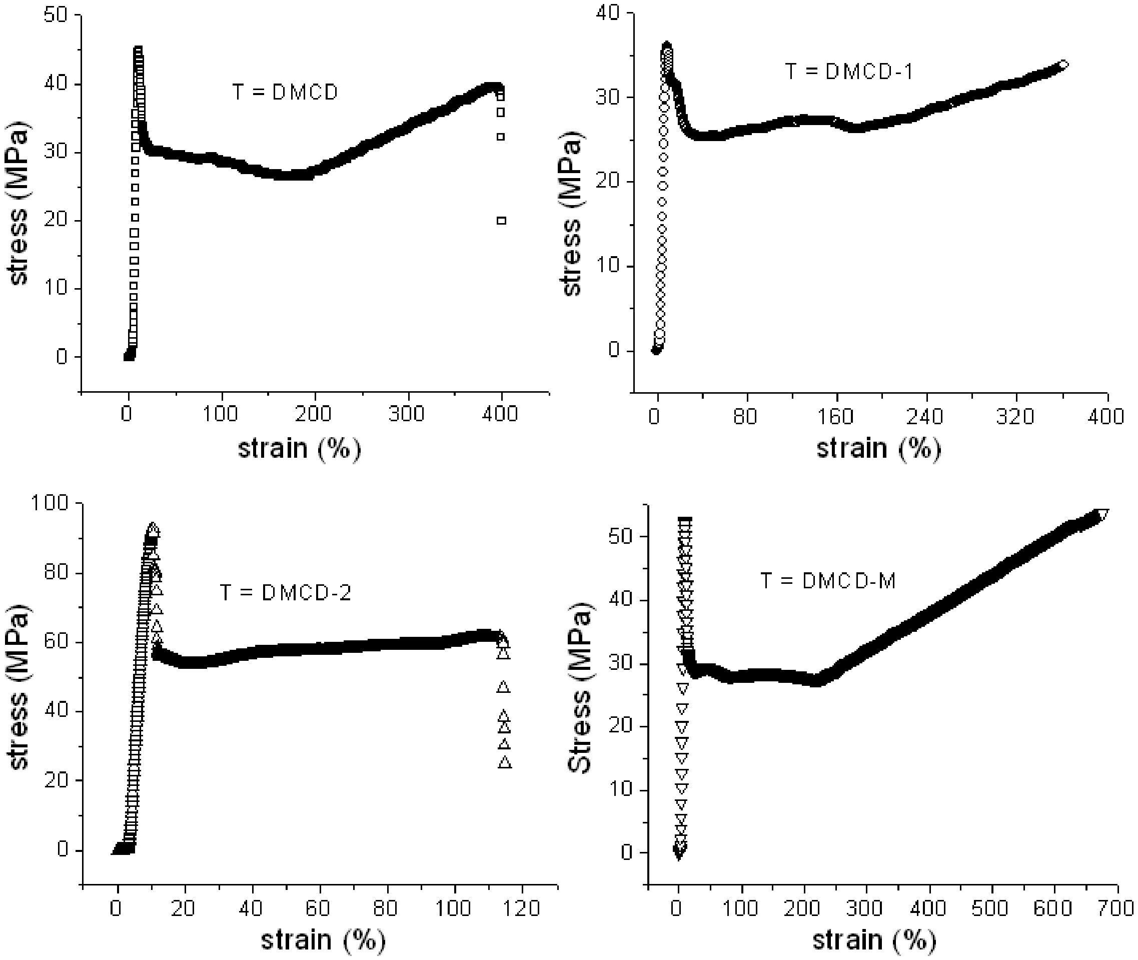


Figure 3.6 Tensile properties of poly[50(T)50(DMCD)29(EG)71(1,4-CHDM)] at RT

The secondary relaxation of copolyesters. Figure 3.7 showed the secondary relaxation of these copolyesters. The β relaxation peaks appeared at about -60 ^{o}C. This plot of tan δ versus temperature demonstrates that the magnitude of these secondary relaxation peaks is similar due to the existence of the cyclohexyl units in the backbones of all these copolyesters. The β relaxation with small intensity, results from the chair-boat-chair conformational transition of the cyclohexylene ring. The presence of 50 mol % rigid diesters, such as DMCD-2 and DMCD-1, failed to depress the β relaxation intensity.

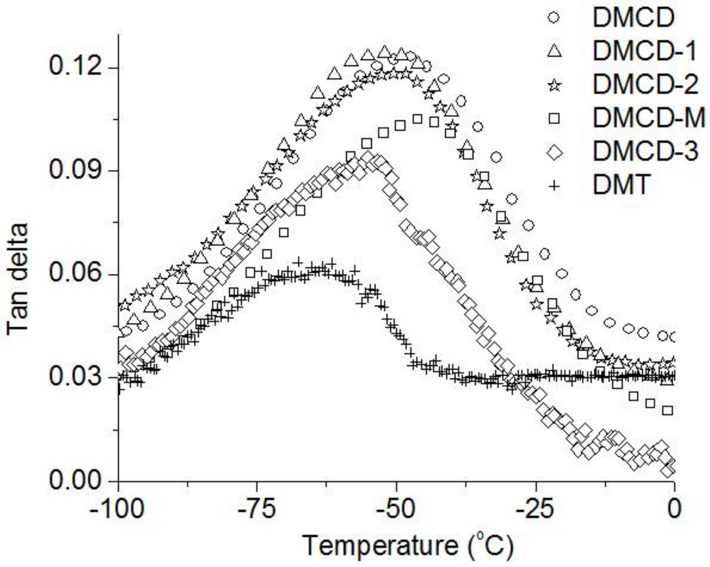


Figure 3.7 Tan delta versus temperature of poly[50(T)50(DMCD)29(EG)71(1,4-CHDM)]

Hydrolytic degradation of the polyesters. Hydrolytic degradation of the polyesters in PBS solution was studied on solvent cast polyester films. The degradation was followed by mass loss during the experiments. The weight loss of the polyester based on DMCD-3 in the hydrolytic tests is the highest among these samples (**Figure 3.8**).

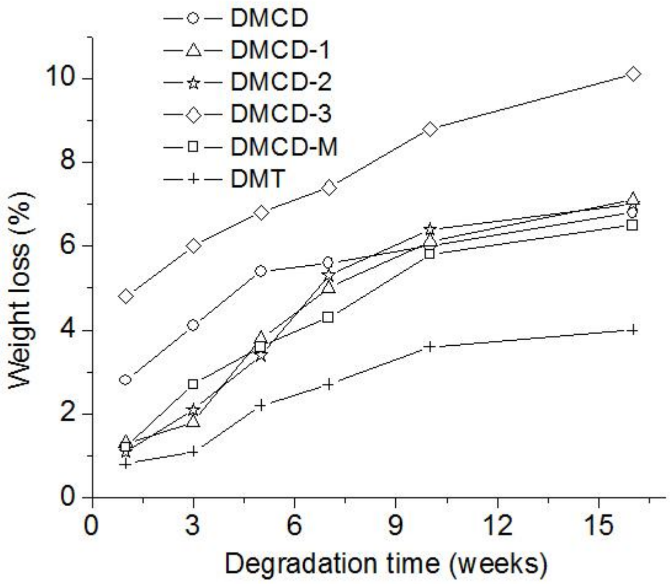


Figure 3.8 Weight loss of polyesters versus hydrolysis time in PBS (pH 7.4, 37 ^{o}C)

The incorporation of the bulky and somewhat bent monomer DMCD-3 may open up the structure and increase free volume, which could facilitate the diffusion of water molecules and attack the ester bond and hence accelerate hydrolytic degradation. Aromatic polyesters are well known to undergo very slow hydrolytic degradation; this finding was confirmed since the polyesters based on DMCD, DMCD-1, DMCD-2 or DMCD-M have faster hydrolytic degradation rates than the DMT containing polyester in this study.

3.5 Conclusions

In summary, we have described the synthesis of various all-aliphatic polyesters from cyclic diesters with different compositions by melt polycondensation and characterized some of their properties. Copolyester compositions confirmed by NMR analysis are close to targeted ones. Amorphous DMCD-2-containing copolyesters were found to exhibit significantly higher T_gs (up to 115 ^{o}C) than any of the other alicyclic polyesters, and higher than the T_g of the terephthalate analog in this study. For copolyesters based on linear and symmetrical diester DMCD-2, T_g increases linearly with the increase of DMCD-2 mole percent. Poly[50(DMCD-2)50(DMCD)29(EG)71(1,4-CHDM)] was also found to possess the highest T_g and the highest modulus among these six copolyesters containing DMCD due to the rigid units of DMCD-2 in the backbone. DMA showed that these cycloaliphatic copolyesters have similar secondary relaxations, which result from the conformational transition of cyclohexylene rings in the backbone. Among these samples, the polyester based on DMCD-3 in the hydrolytic tests undergoes the fastest hydrolytic degradation in PBS solution at 37 ^{o}C.

3.6 Acknowledgements

The authors are grateful to Eastman Chemical Company for donating DMCD. We acknowledge the Department of Chemistry and Macromolecules and Interfaces Institute (MII) for financial support. We would also like to thank Dr. McGrath's group for allowing us to use TGA and DSC equipment, and Dr. Long's group for allowing us to use INSTRON tensile and hydrolysis equipment.

3.7 References

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3.8 Supporting information:

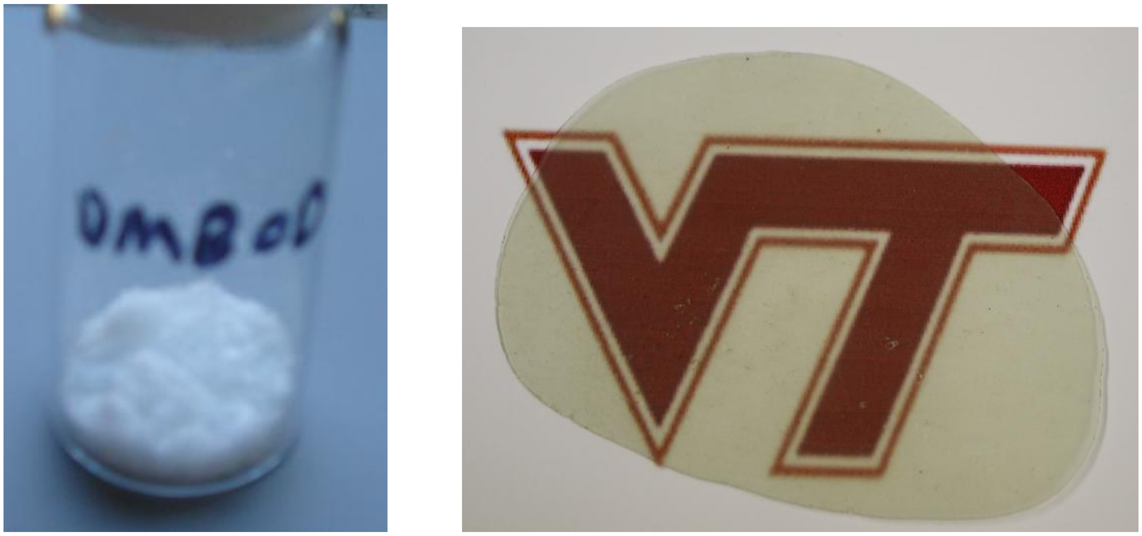


Figure 3.9. White DMCD-2 monomer (left) and the transparent film of poly[50(DMCD-2)50(DMCD)30(EG)70(1,4-CHDM)] (right) prepared by a melt press

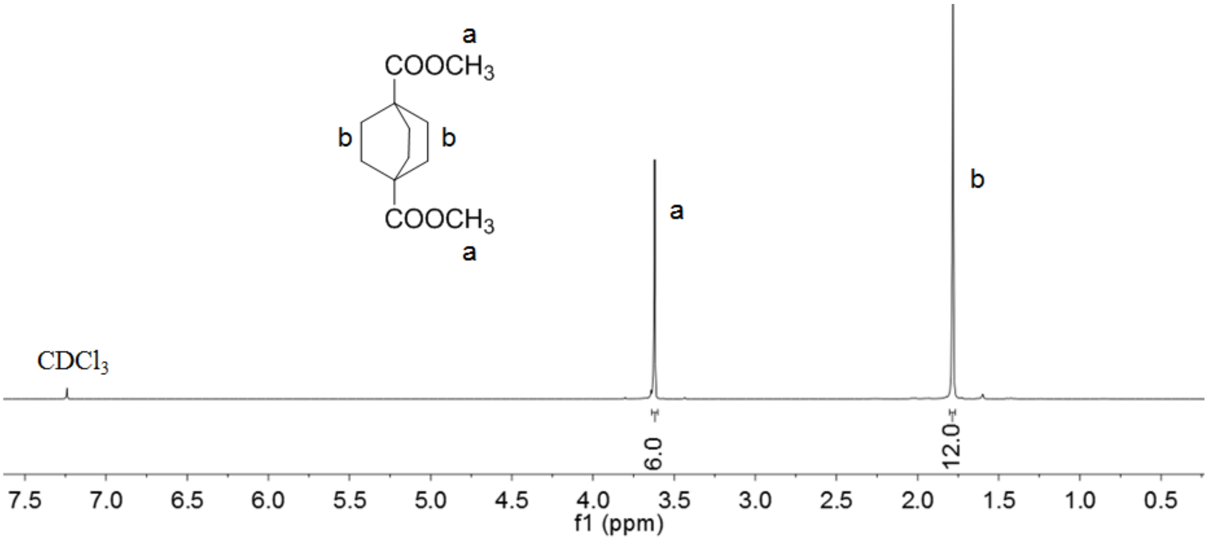


Figure 3.10 ^{1}H NMR of DMCD-2

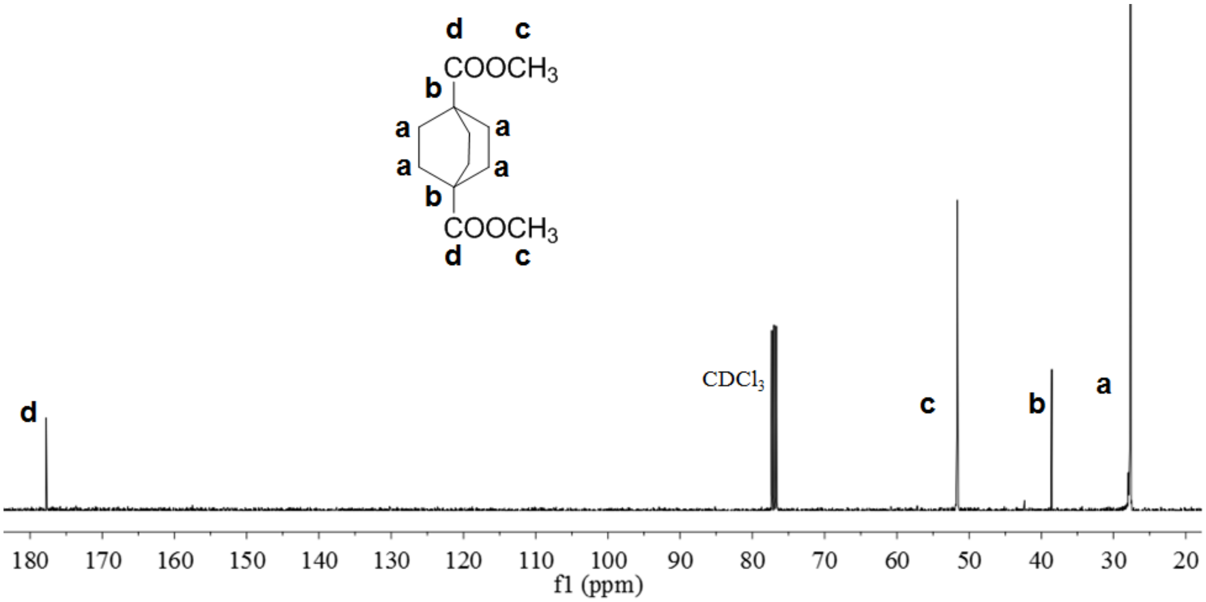


Figure 3.11 ^{13}C NMR of DMCD-2

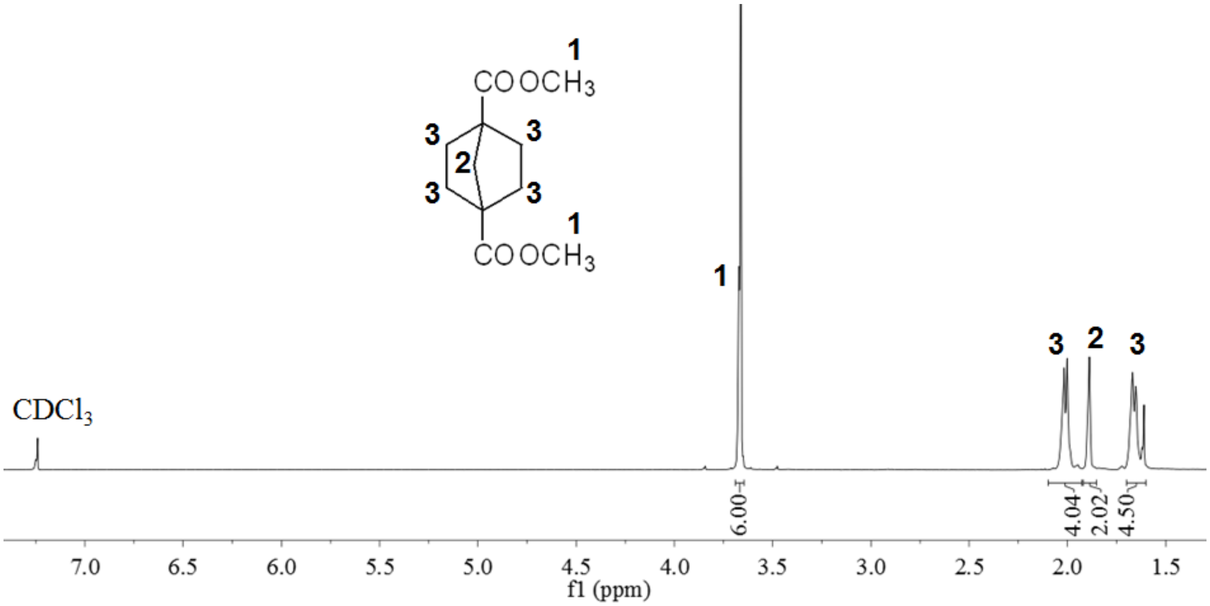


Figure 3.12 ^{1}H NMR of DMCD-1

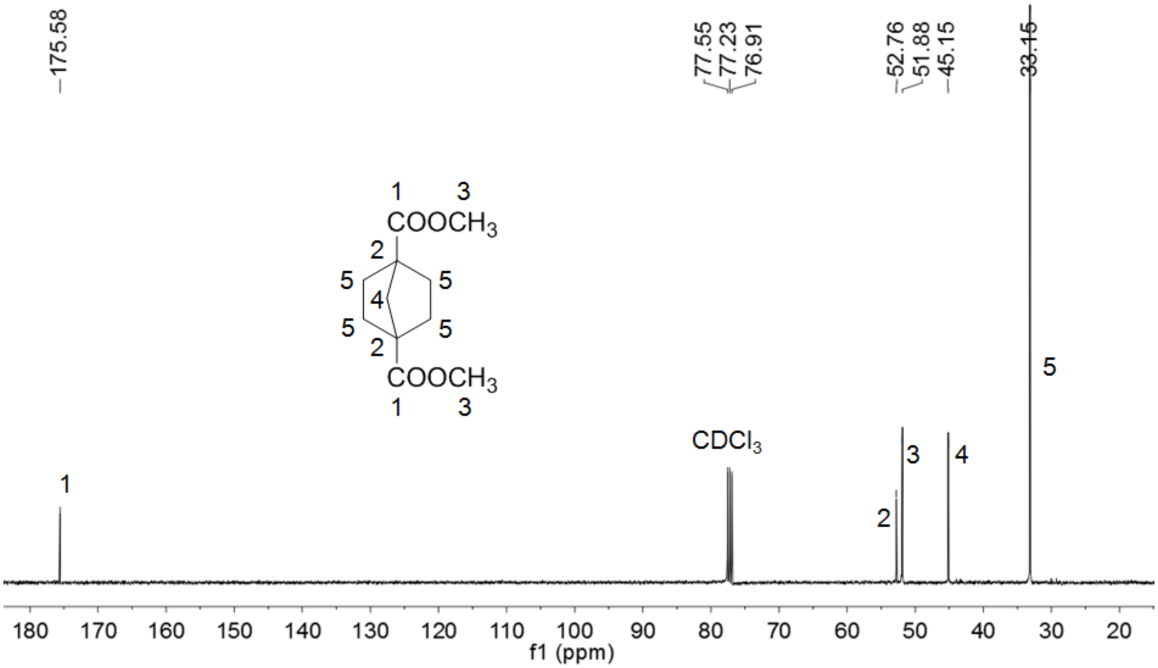


Figure 3.13 ^{13}C NMR of DMCD-1

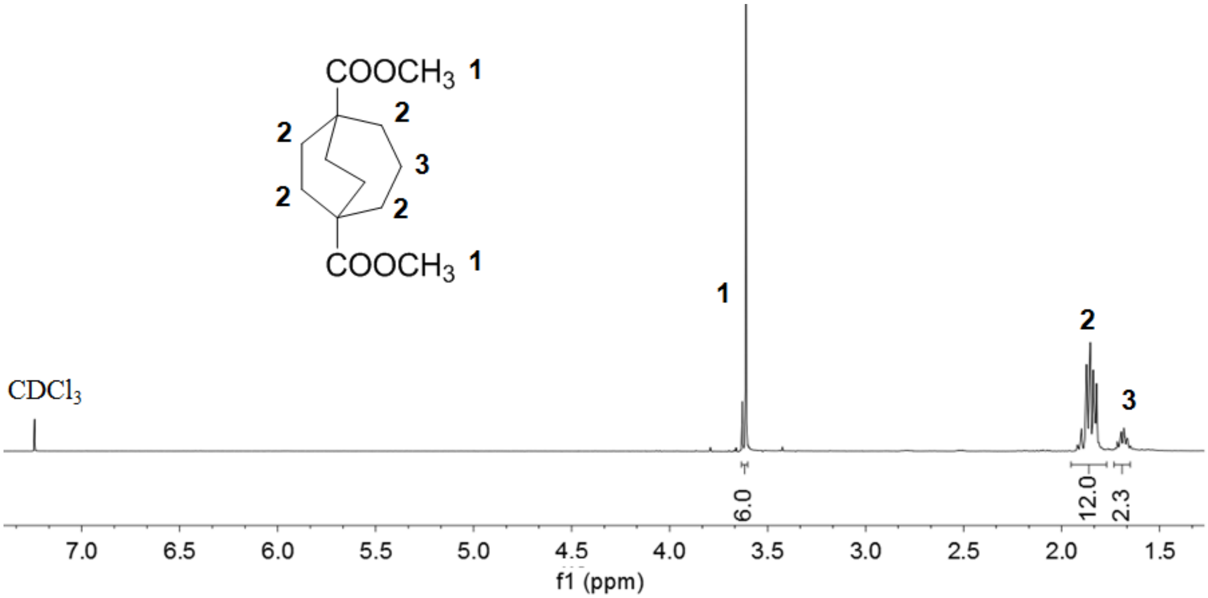


Figure 3.14 ^{1}H NMR of DMCD-3

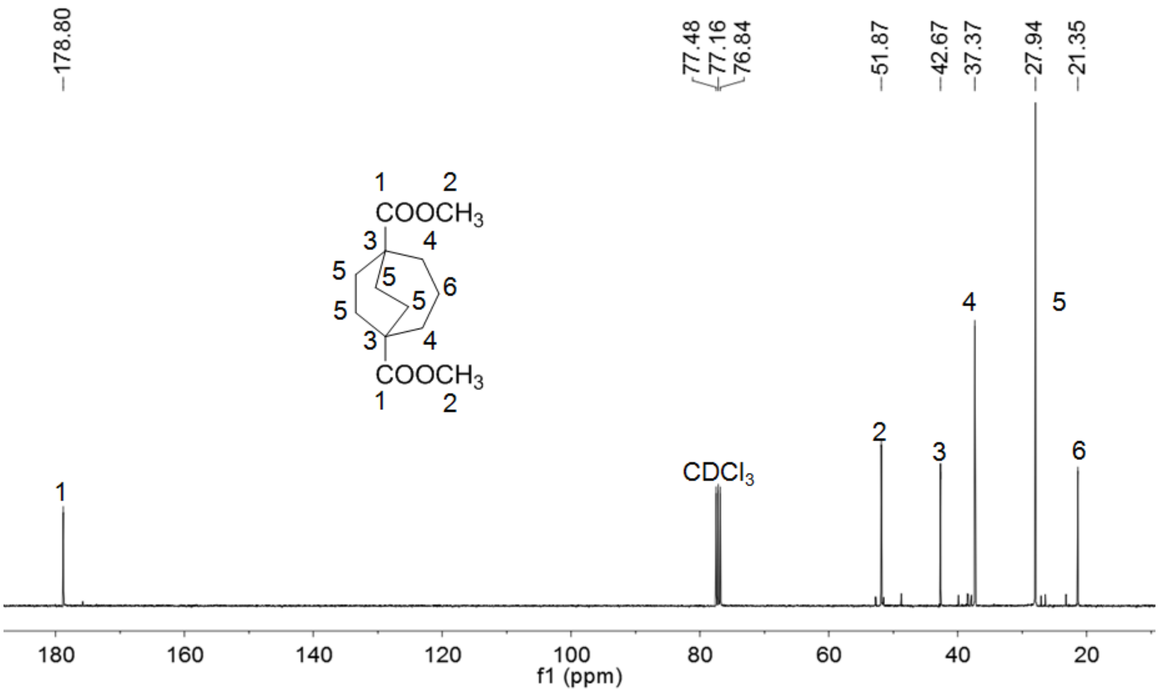


Figure 3.15 ^{13}C NMR of DMCD-3

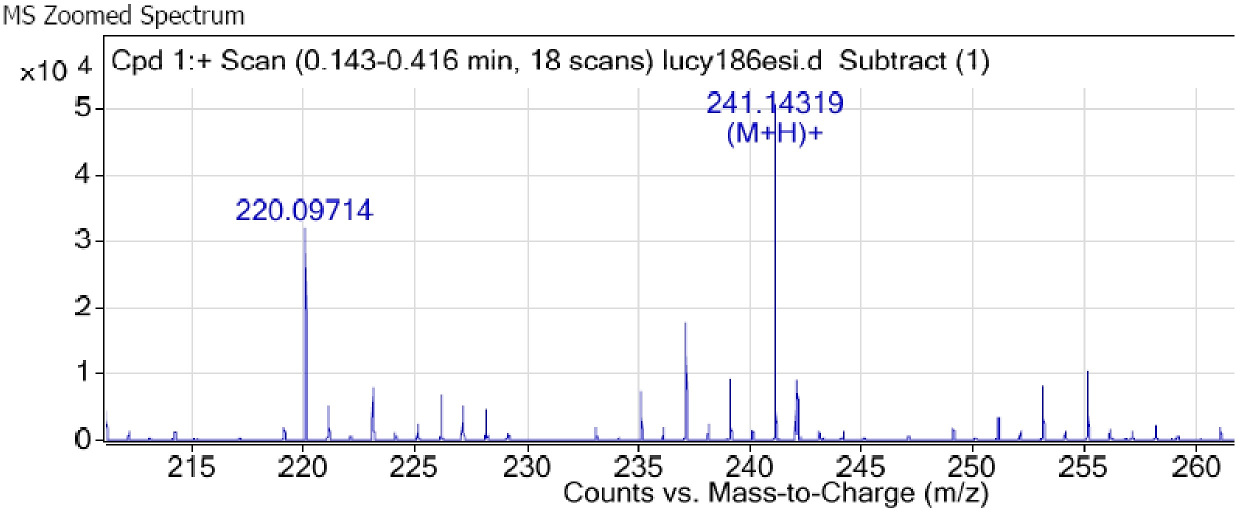


Figure 3.16 Mass spectrum of DMCD-3

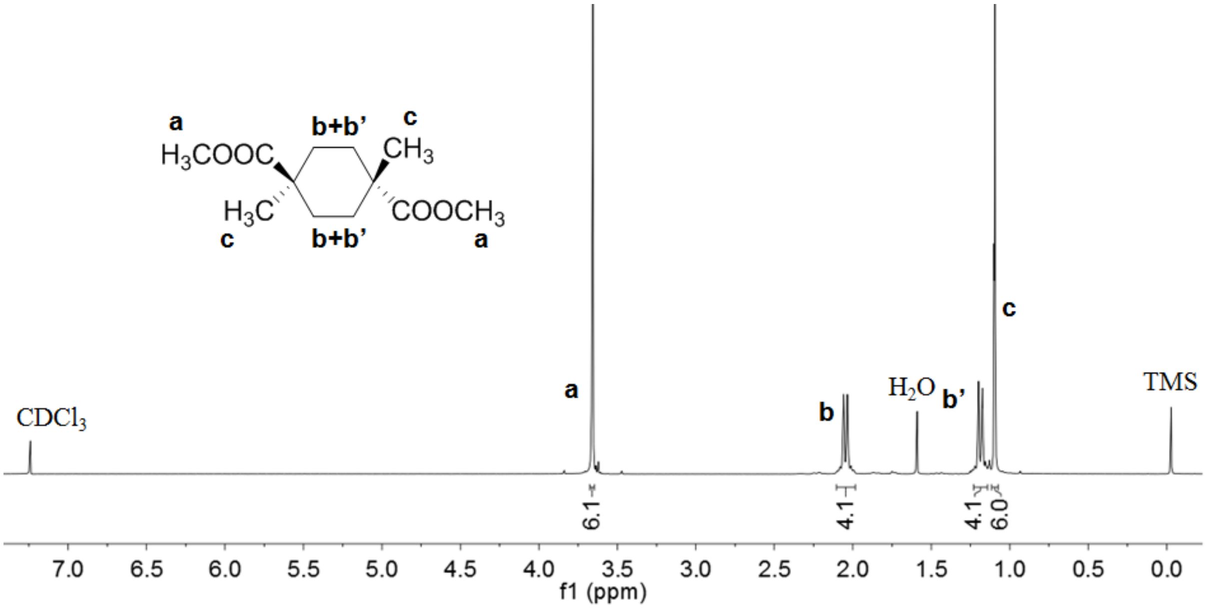


Figure 3.17 ^{1}H NMR of *trans*-DMCD-M

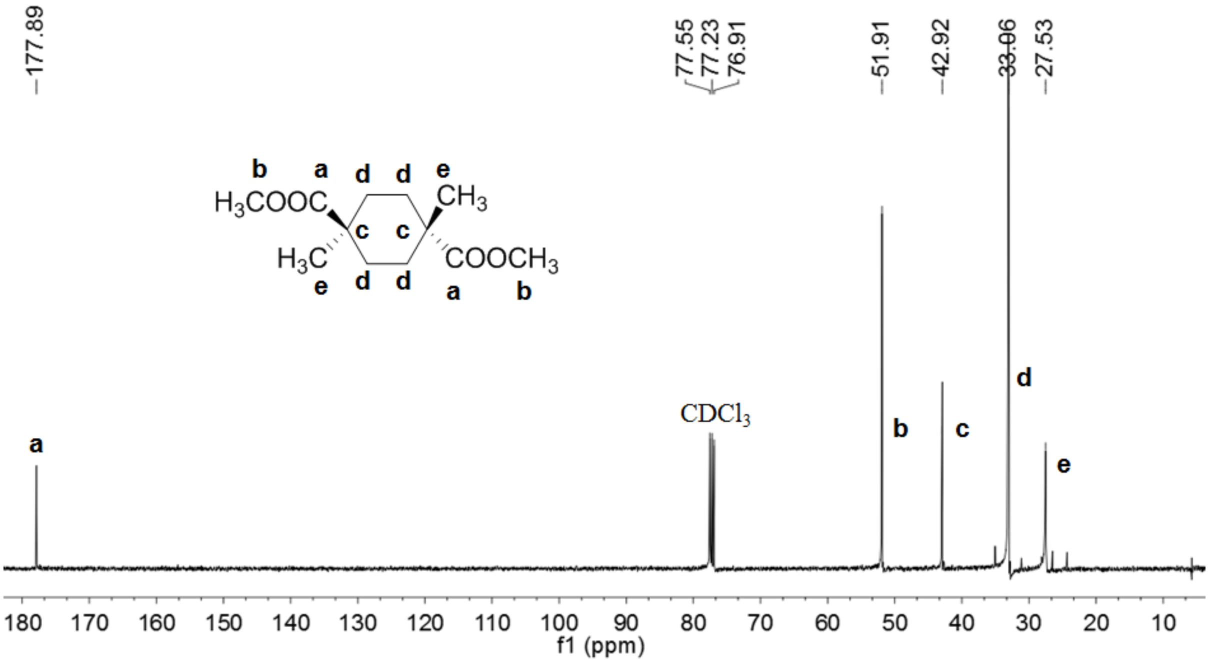


Figure 3.18 ^{13}C NMR of *trans*-DMCD-M

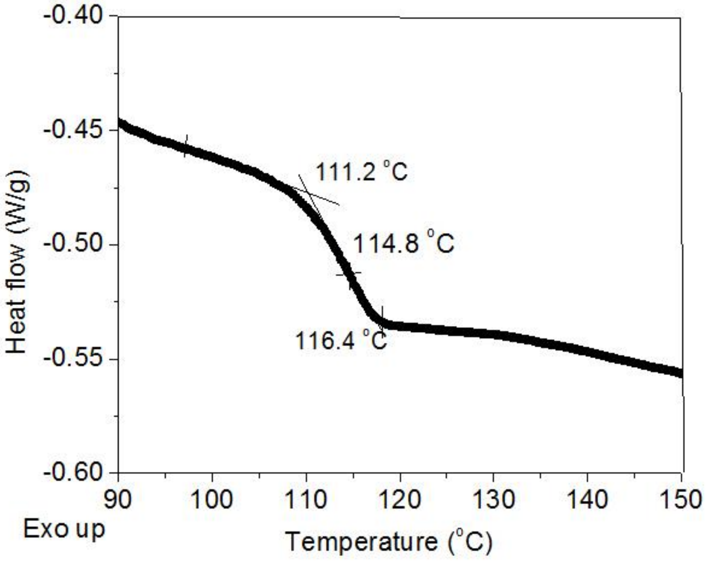


Figure 3.19 DSC trace of poly[100(DMCD-2)29(EG)71(1,4-CHDM)]

with a T_g of 115 °C

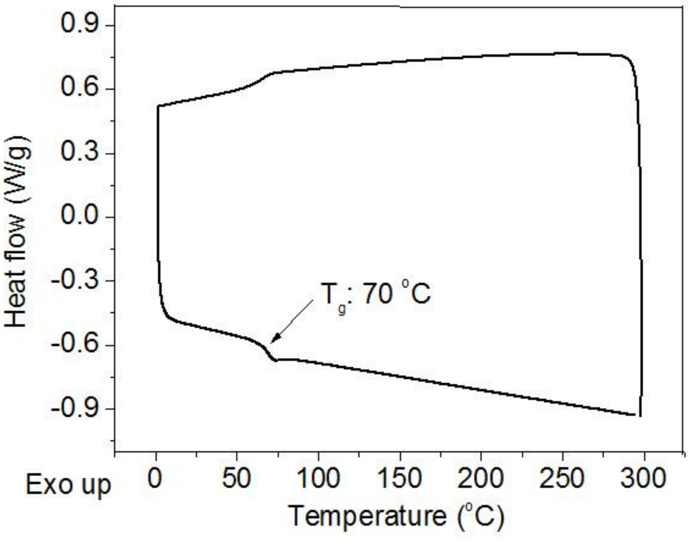


Figure 3.20 Full DSC trace of poly[50(DMCD-2)50(DMCD)29(EG)71(1,4-CHDM)]

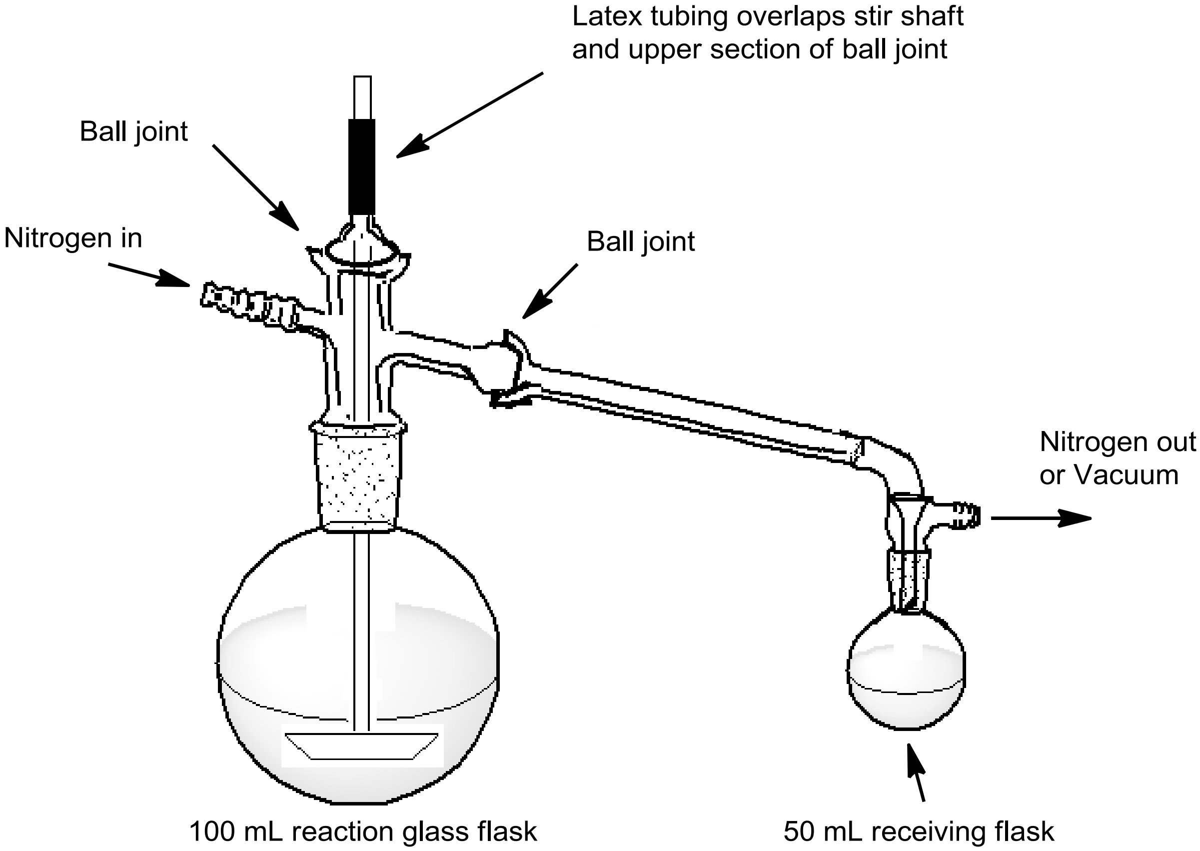


Figure 3.21 Melt-phase polymerization reactor

Chapter 4: Synthesis and Properties of Various Cycloaliphatic Polyesters (unpublished)

4.1 Abstract

In this chapter, melt polycondensation was used to prepare a series of random and amorphous copolyesters containing the following cycloaliphatic monomers: dimethyl-1,4-cyclohexane dicarboxylate (DMCD), dimethyl spiro[3.3]heptane-2,6-dicarboxylate (DMSHD), *cis*-dimethyl cyclopentane-1,3-dicarboxylate (*cis*-DMCP), bicyclo[2.2.2]octane-1,4-dimethanol (BODM), 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD), 1,1-cyclohexanedimethanol (1,1-CHDM) or 1,4-cyclohexanedimethanol (1,4-CHDM), and ethylene glycol (EG). Polymer composition was determined by nuclear magnetic resonance (NMR) spectroscopy and molecular weight was determined via SEC. The polyesters were characterized by DMA, DSC and TGA. The copolyesters containing DMCD-2 and BODM units were observed to have a higher glass transition temperature (up to 115 ºC) compared to the other copolyesters described in this chapter. DMA confirmed that the cycloaliphatic copolyesters displayed secondary relaxations, resulting from conformational transitions of the cyclohexylene rings.

4.2 Introduction

As discussed earlier, all aliphatic polyesters possess relatively good UV stability, making them appropriate, for example, for use in outdoor applications.[1-3] The introduction of alicyclic units to the main chain of the polymer can improve glass transition temperatures due to the rigidity of the alicyclic structure.[4] Moreover, polymers containing different isomeric alicyclic structures in their main chain have difficulty crystallizing; therefore, they are amorphous and transparent. Thus, such materials are appropriate for a number of industrial applications, such as for use in signs and other transparent outdoor areas.[5] Cyclohexyl groups have been incorporated into a wide variety of polyesters to achieve desirable thermal and mechanical properties.[6-9] Since there are few reports on aliphatic copolyesters based on a systematic variation of their cyclic diols or diesters, this chapter will summarize our findings regarding the incorporation of several additional cycloaliphatic monomers into polyester backbones. For example, linear spiro condensation polyesters have not been reported except in this chapter. Our goals are to elucidate the structure-property relationships of different cycloaliphatic polyesters, as well as suggest potential applications for these materials.

The cycloaliphatic monomers reported herein include spiro unit DMSHD, cyclopentyl ring-containing *cis*-DMCP, bicyclic structure BODM, cyclobutane unit TMCBD, as well as 1,1-CHDM with a pendant cyclohexyl ring. We synthesized random copolyesters containing these cyclic groups and then studied the effects of different cycloaliphatic rings on the properties of these copolyesters.

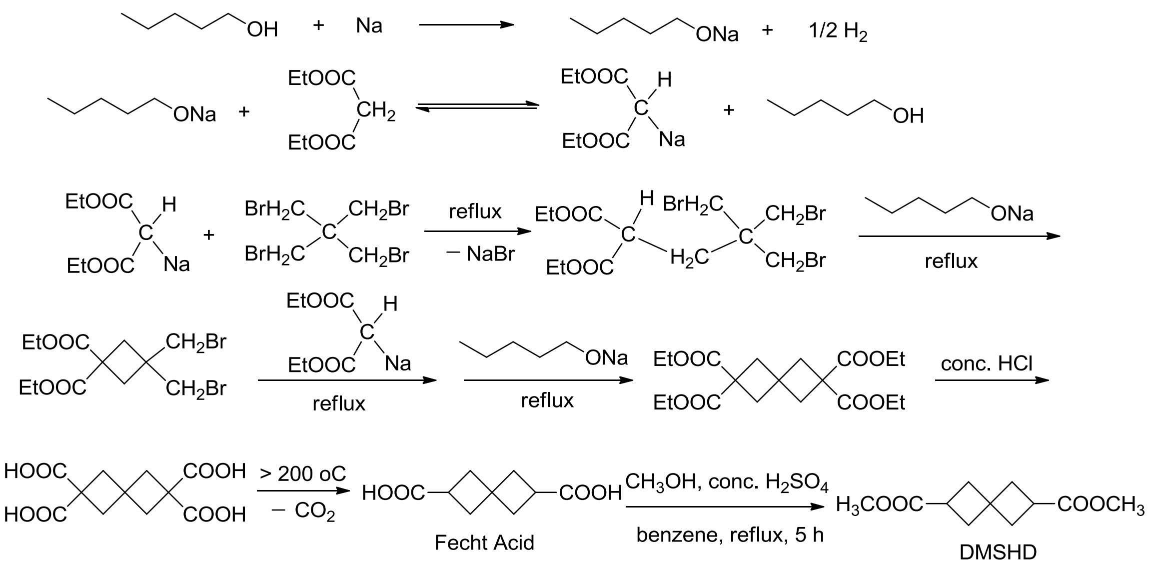
4.3 Experimental

4.3.1 Materials

All reagents were used without further purification. EG (≥ 99 %), 1,4-CHDM (99 %, *cis*/*trans*= 70/30), sodium (in kerosene, 99 %), 1-pentanol (≥ 99 %), diethyl malonate (99 %), pentaerythritol tetrabromide (96 %), sodium ethoxide (95 %), 1,5-dibromopentane (97 %), and lithium aluminum hydride ($LiAlH_4$, 95 %) were purchased from the Aldrich Chemical Co. Titanium(IV) butoxide (98 %) was purchased from Alfa Aesar Chemical Co. DMCD (*cis* /*trans* = 3/1) was donated by Eastman Chemical Co. *cis*-DMCP was synthesized in Chapter 3.

4.3.2 Synthesis

Synthesis of dl-Spiro[3.3]heptane-2,6-dicarboxylic acid (Fecht Acid)[10-12] **(Scheme 4.1).** Sodium of 12 g (0.5 mol) was dissolved in 500 mL of absolute 1-pentanol, followed by the addition of 80 g (0.5 mol) of diethyl malonate. The mixture was stirred and warmed until the sodium pentoxide was completely dissolved. Then, 38.8 g. (0.1 mol) of pentaerythritol tetrabromide was added and the mixture was distilled until the vapor temperature reached the boiling point of 1-pentanol (130 ^oC). Most of the ethanol was contained in the distillate. A reflux condenser was used and 1-pentanol, with a volume equal to the amount of distillate, was added. The mixture was subsequently refluxed for 40-50 h. Most of the 1-pentanol was then removed by distillation. Some water was added and the remainder of the 1-pentanol was removed by distillation. Deionized water of 400 mL was added and the mixture was extracted several times with diethyl ether. The combined ether extract was then washed for 3 times with 250 mL of water and the ether was removed by evaporation using the rotovapor. The yellow residue (the ester salt) was saponified by adding a solution of 84 g of potassium hydroxide in 750 mL of ethanol. The mixture was maintained at room temperature for 48 h. The potassium salt was filtered, dissolved in water (200 mL), and acidified with concentrated hydrochloric acid (80 mL). Water was evaporated and the residue was pyrolyzed at 190-200 ^oC for 1 h under reduced pressure (2 mmHg) to obtain a yellow and brown solid mixture. The reaction product was extracted in a soxhlet apparatus with ethyl acetate for 24 h. The solvent was evaporated and 12.8 g (yield: 70 %) of the yellow product spiro[3.3]heptane-2,6-dicarboxylic acid (Fecht Acid) was obtained.



Scheme 4.1 Synthesis of DMSHD

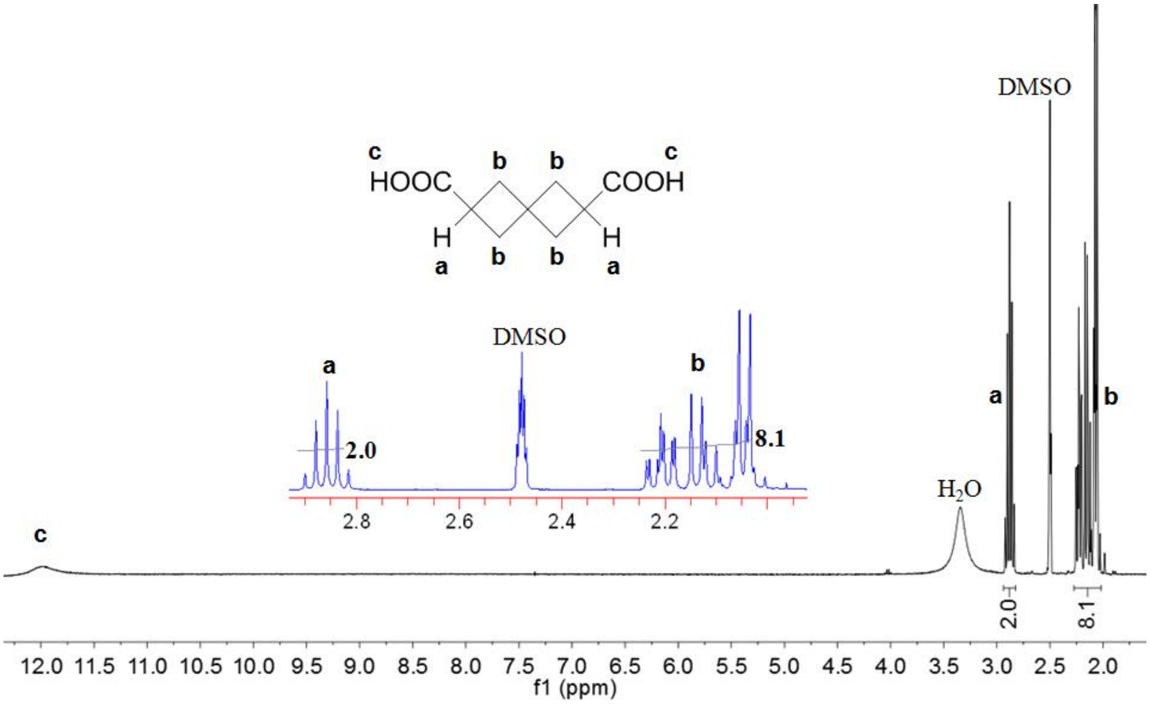


Figure 4.1 ^{1}H NMR of Fecht acid

Synthesis of dimethyl spiro[3.3]heptane-2,6-dicarboxylate (DMSHD) (**Scheme 4.1**).[10] A mixture of 12.8 g Fecht acid (0.07 mol), 166 mL of benzene, 69 mL of methanol, and 15 mL of concentrated sulfuric acid was added to a 500 mL one-necked round-bottom glass flask and was refluxed over a period of 5 h. The mixture was allowed to cool and poured onto melting ice. The solution was extracted with diethyl ether several times. The ether layer was washed with water and the solvent was removed under reduced pressure to obtain a brown liquid. After vacuum distillation (80 ^{o}C/0.2 mmHg), 13.5 g of colorless liquid diester DMSHD was obtained, yield: 81 %. ^{1}H NMR ($CDCl_3$): 3.63 (s, 6H), 3.92-3.01 (q, 2H), 2.13-2.33 (m, 8H).

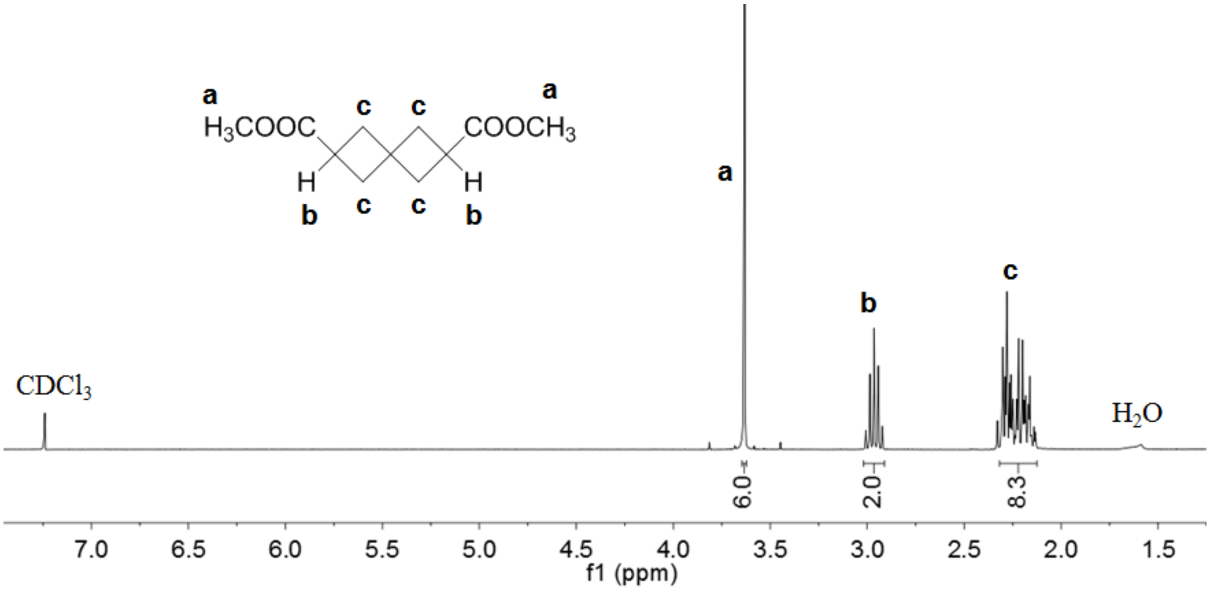
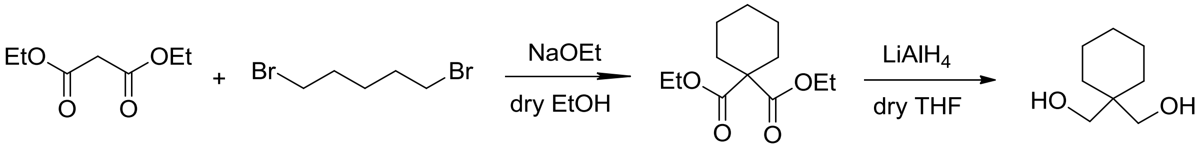


Figure 4.2 ^{1}H NMR of DMSHD

Synthesis of diethyl 1,1-cyclohexanedicarboxylate (Scheme 4.2).[13] Diethyl malonate (32 g, 200 mmol) was added dropwise to a solution of sodium ethoxide (28.6 g, 420 mmol) and dry ethanol (200 mL). The sodium ethoxide was freshly prepared from sodium and dry ethanol. The mixture was refluxed for 30 min and then diluted with 160 mL dry ethanol. After 1,5-dibromopentane (41.8 g, 181.8 mmol) was added dropwise, the mixture was boiled for 3 h and was then stirred at room temperature for 18 h. After the solvent was evaporated, the residue was dissolved in 240 mL of water and extracted with Et_2O (5 ×160 mL). The individual organic layers that had separated were combined and washed with saturated brine (2×160 mL). After drying over Na_2SO_4, the solution was filtered. Following the evaporation of the solvent, the crude product was distilled by vacuum to obtain a colorless liquid with a yield of: 23 g (50 %). ^1H NMR ($CDCl_3$): δ 4.15-4.20 (q, 4H, $COOCH_2CH_3$), 1.98-1.83 (m, 4H, $C(CH_2CH_2)_2CH_2$), 1.56-1.38 (m, 6H, $C(CH_2CH_2)_2CH_2$), 1.24 (t, 6H, $COOCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 171.75 ($COOCH_2$-CH_3), 60.85 ($COOCH_2CH_3$), 54.74 ($C(CH_2CH_2)_2CH_2$), 31.17 ($C(CH_2CH_2)_2CH_2$), 25.06 ($C(CH_2CH_2)_2CH_2$), 22.56 ($C(CH_2CH_2)_2$-CH_2),13.88($COOCH_2CH_3$). Bp: 73-74°C/0.2 mmHg.



Scheme 4.2 Synthesis of 1,1-CHDM

Synthesis of 1,1-cyclohexanedimethanol (1,1-CHDM) (Scheme 4.2).[13] 1,1-Cyclohexanedicarboxylic acid diethyl ester (18.24 g, 80 mmol) was dissolved in dry THF (70 mL) and the solution was added dropwise over a period of 1 h to a suspension of $LiAlH_4$ (6.8 g, 176 mmol) in dry THF (180 mL) at 5 °C. The reaction mixture was stirred at room temperature for 90 min, then cooled to 5 °C, followed by the addition of EtOAc (88 mL). The resulting solution was poured into 2 M HCl (228 mL) and two layers were formed. The water layer was separated and extracted with EtOAc (5 × 140 mL). The combined organic layer was washed with saturated brine (3 × 140 mL), dried over Na_2SO_4, and filtered. After the solvent was removed, the crude solid was recrystallized from a mixture of EtOAc and petroleum ether. Finally, 8.7 g of colorless crystals were obtained. (Yield: 76 %). ^1H NMR (**Figure 4.3**) ($CDCl_3$): δ3.68 (d, 4H, CH_2OH), 2.53 (t, 2H, OH), 1.52-1.39 (m, 10H, $C(CH_2CH_2)_2CH_2$). ^{13}C NMR (**Figure 4.4**) ($CDCl_3$): δ 70.27

($\mathit{C}\mathrm{H_2OH}$), 38.41 ($\mathit{C}\mathrm{(CH_2CH_2)_2CH_2}$), 29.81 ($\mathrm{C(}\mathit{C}\mathrm{H_2CH_2)_2CH_2}$), 26.63 ($\mathrm{C(CH_2CH_2)_2}\mathit{C}\mathrm{H_2}$), 21.57 ($\mathrm{C(CH_2}\mathit{C}\mathrm{H_2)_2CH_2}$). Mp: 96-97 °C.

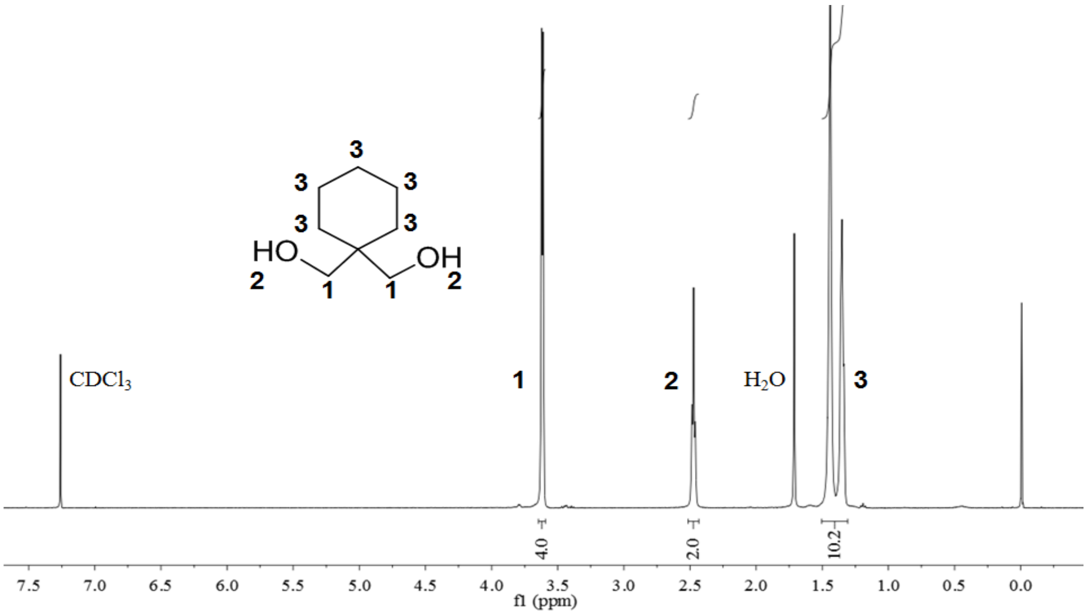


Figure 4.3 ^{1}H NMR of 1,1-CHDM

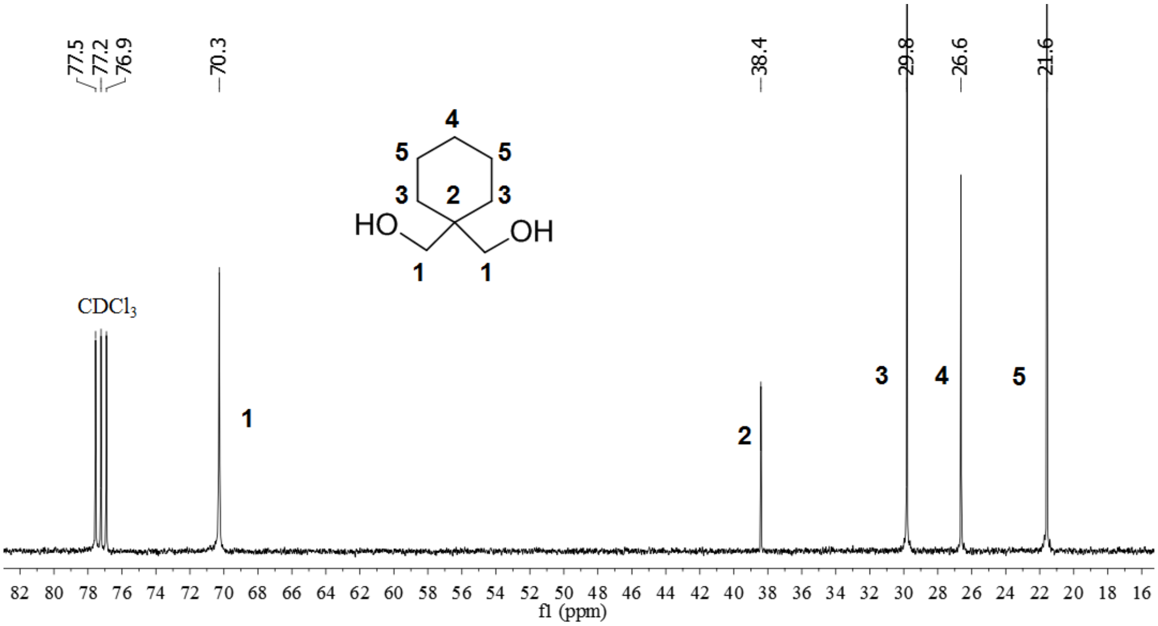
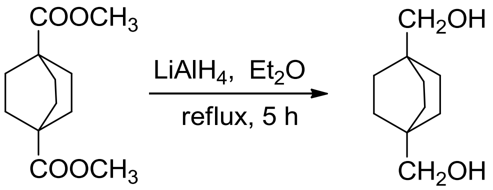


Figure 4.4 ^{13}C NMR of 1,1-CHDM

Synthesis of bicyclo[2.2.2]octane-1,4-dimethanol (BODM) (Scheme 4.3). The diester was reduced to the diol following established procedures.[14]



Scheme 4.3 Synthesis of BODM

50 mL of dry diethyl ether and $LiAlH_4$ (4.3 g, 113 mmol**)** were added to a three-necked flask. Bicyclic diester DMCD-2 (9.5 g, 42 mmol) in 75 mL of dry ether in a pressure-equalized addition funnel was added dropwise to the reaction flask with stirring over 50 min. Spontaneous reflux was allowed to occur and after that the mixture was allowed to reflux for an additional 5 h. The reaction was quenched via the slow addition of 4.3 mL of water, 1.25 mL of 15 % NaOH solution, and an additional 12.75 mL of water. The reaction mixture was filtered and the solids were washed with ether. The combined ether layers were dried over anhydrous Na_2SO_4. After removal of the solvent, white solid diol was obtained (6.65 g, 93 % yield). Mp: 106-108 ^oC (lit.107-108 ^oC). ^1H NMR ($CDCl_3$): 1.42 (s, 12H), 3.28 (s, 4H), 1.24 (t, 2H) (**Figure 4.5**).

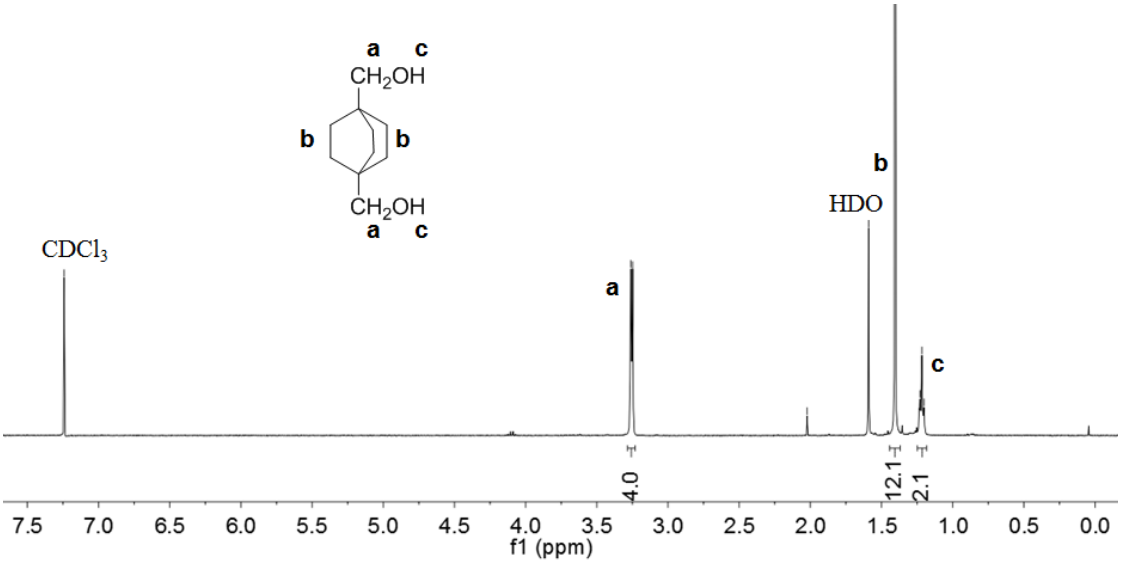
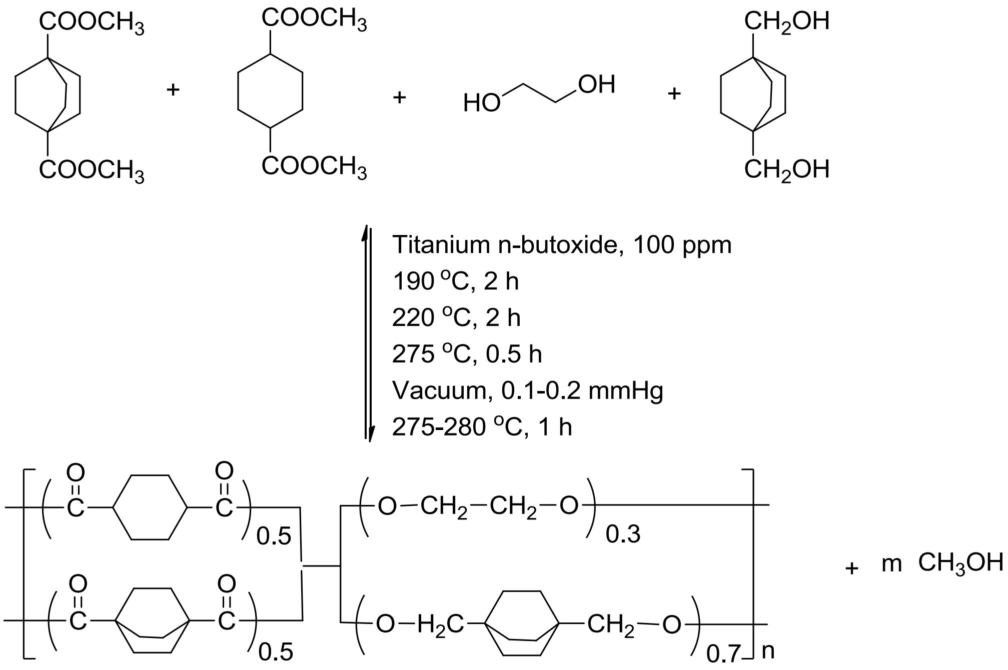


Figure 4.5 ^1H NMR of BODM

Preparation of the catalyst solution. A Ti catalyst solution was obtained by dissolving titanium n-butoxide in n-BuOH in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

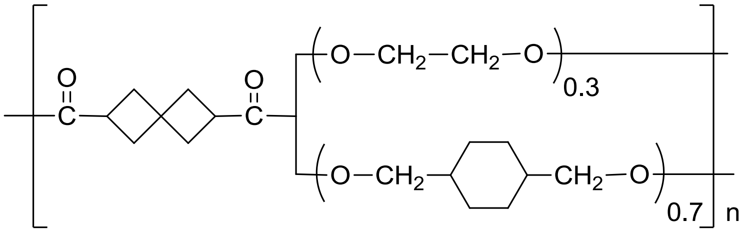
Polymer nomenclature. The polyester nomenclature used in this manuscript is based on a polyester containing 100 mol% of diester and 100 mol% of diol. For example, the polymer designated by poly[50(DMCD-2)50(DMCD)30(EG)70(BODM)] means this targeted polymer contains 50 mol% DMCD-2 and 50 mol% DMCD as their diester units and 30 mol% EG and 70 mol% BODM as their diol units. The letters represent the monomer, and the numbers indicate the targeted mol% of that particular monomer.

Polymerization. Poly[50(DMCD)50(DMCD-2)30(EG)70(BODM)] was prepared from DMCD, DMCD-2, EG and BODM. The detailed procedure (**Scheme 4.4**) is as follows: 2.26 g (10 mmol) DMCD-2, 2.0 g (10 mmol) DMCD, 0.82 g (13.2 mmol) of EG (120 % excess), 2.38 g (14 mmol) BODM, and 0.10 mL (100 ppm) of a titanium n-butoxide solution (0.06 g/mL in butanol) were added to a 100 mL two-necked, round-bottom glass flask. The reaction flask was immersed into a molten Belmont metal bath that was pre-heated to 190 °C. The reaction mixture was initially stirred at 190 °C for 2 h, then at 220 °C for an additional 2 h. The temperature was then increased to 275 °C and held for 30 min. The pressure was then slowly reduced while the temperature was kept at 275 °C. The final stage involved applying a high vacuum (0.1 mmHg) for an additional 2 h at 280 °C, after which a highly viscous copolyester was obtained. It should be noted that some copolyesters began to turn yellow due to the titanium catalyst and the long reaction time. The vacuum was stopped and nitrogen was bled into the flask. The polymer was cooled to room temperature, dissolved in chloroform, and precipitated into methanol. The solid precipitate was separated by filtration and was dried at 30-60 °C under vacuum overnight before characterization.



Scheme 4.4 Synthesis of poly[50(DMCD)50(DMCD-2)30(EG)70(BODM)]

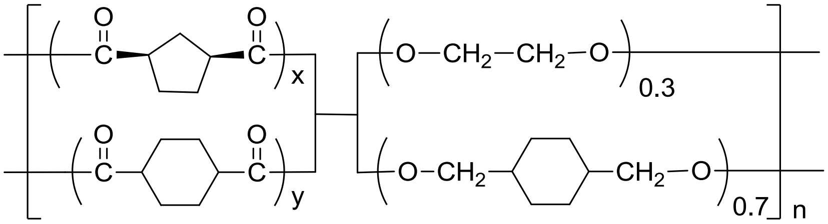
Synthesis of all-aliphatic poly[100(DMSHD)30(EG)70(1,4-CHDM)] polyester. This copolyester was prepared following the same procedure used for the copolymer described above. 1,4-CHDM was used as the diol and DMSHD was used as the diester in place of DMCD and DMCD-2. The polyester structure is shown as **Scheme 4.5**.



Scheme 4.5 Structure of poly[100(DMSHD)30(EG)70(1,4-CHDM)]

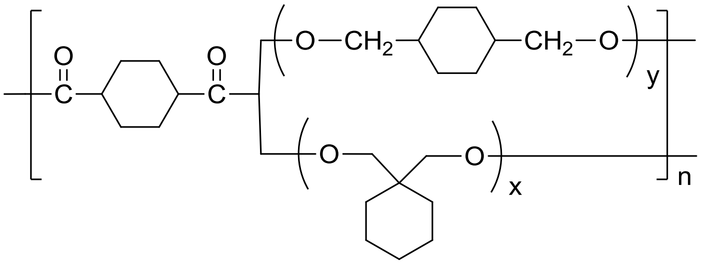
Synthesis of all aliphatic polyester poly[x(DMCP)y(DMCD)30(EG)70(1,4-CHDM)]. Copolyesters were synthesized according to the procedures described earlier;

the resulting copolyester structure is shown in **Scheme 4.6**.



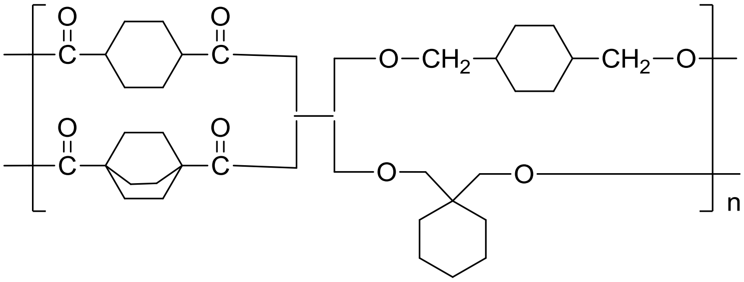
Scheme 4.6 Structure of poly[x(DMCP)y(DMCD)30(EG)70(1,4-CHDM)]

Synthesis of all-aliphatic polyesters poly[100(DMCD)x(1,1-CHDM)y(1,4-CHDM)]. Copolyesters were synthesized according to the procedures described earlier; the resulting copolyester structure is shown in **Scheme 4.7**.



Scheme 4.7 Structures of poly[100(DMCD)x(1,1-CHDM)y(1,4-CHDM)]

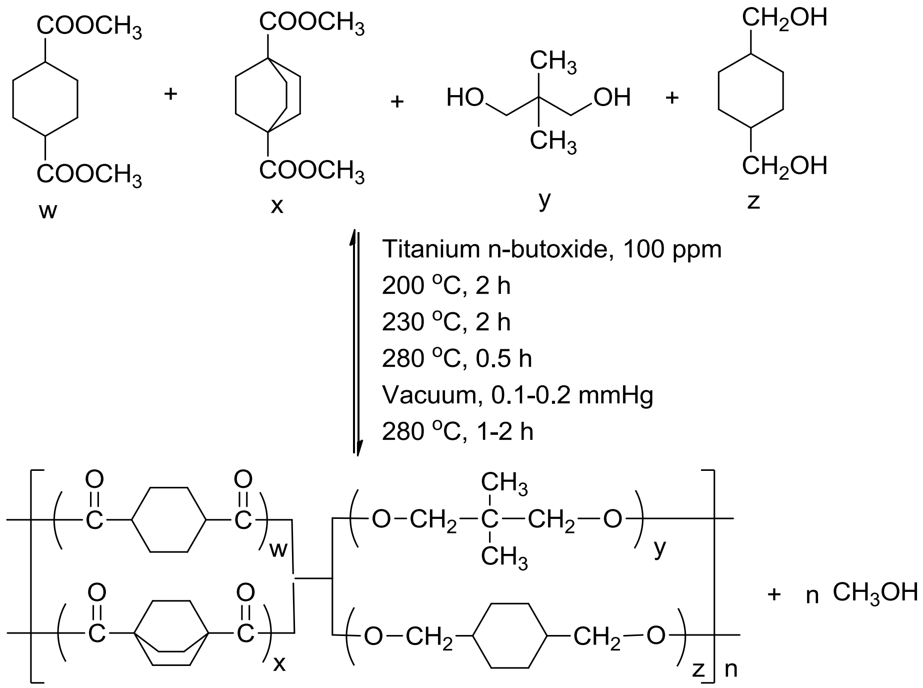
Synthesis of all-aliphatic poly[50(DMCD)50(DMCD-2)50(1,1-CHDM)50(1,4-CHDM)] polyesters. Similar procedures were used to prepare these copolyesters, whose structures are shown in **Scheme 4.8**.



Scheme 4.8 Structures of poly[50(DMCD)50(DMCD-2)50(1,1-CHDM)50(1,4-CHDM)]

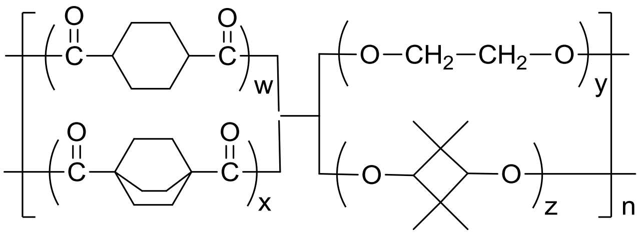
Synthesis of all-aliphatic polyesters containing NPG ----

poly[w(DMCD)x(DMCD-2)y(NPG)z(1,4-CHDM)]. These copolyesters were synthesized according to the procedures described above, which are further detailed in **Scheme 4.9**.



Scheme 4.9 Preparation of poly[w(DMCD)x(DMCD-2)y(NPG)z(1,4-CHDM)]

Synthesis of all-aliphatic poly[x(DMCD-2)w(DMCD)y(EG)z(TMCBD)] polyesters. These copolyesters were prepared via standard melt-phase polymerization and their structures are shown in **Scheme 4.10**.



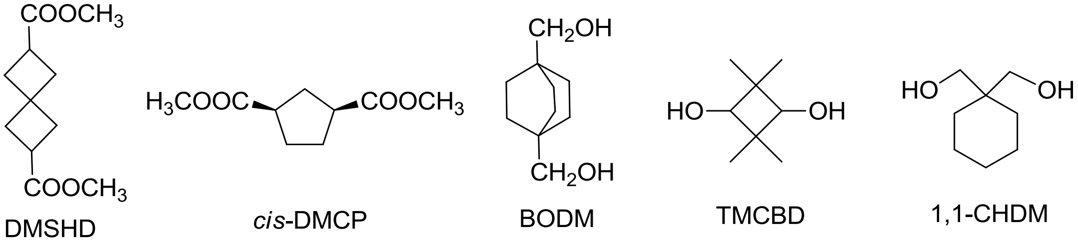
Scheme 4.10 Structures of poly[w(DMCD)x(DMCD-2)y(EG)z(TMCBD)]

4.3.3 Characterization

^1H and ^{13}C NMR spectra were obtained using a Varian Inova 400 (400 MHz) spectrometer at room temperature, internally referenced to tetramethylsilane (TMS). ^{1}H NMR spectra were used to determine the final polyester compositions. SEC was run in chloroform at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set. Monodispersed polystyrene standards were utilized to construct a universal molecular weight calibration curve. A Viscotek refractive index detector and a viscometer were used for molecular weight determination. DSC data were obtained from a Perkin Elmer Pyris I. Samples were run from -20 to 200 °C at a heating/cooling rate of 20 °C/min under nitrogen. The T_g was obtained from the midpoint of the second order transition of the DSC traces during the second heating cycle. TGA results were obtained on a TA Instruments TGA 2950 at a heating rate of 10 °C/min from RT to 600 °C under nitrogen. For compression molding, the sample was sandwiched between two pieces of 3 mm thick aluminum plate and was centered in a mold of desired thickness. The samples were heated 50 °C above their T_g and a pressure of about 500 PSI was applied. The pressure was released after 15 min and these films were then used for various thermal and mechanical analyses. Tensile testing was performed on an Instron Model 4400 Universal Testing System with Series IX software. Samples were run at a constant cross-head speed of 15 mm/min using an initial grip-to-grip separation of 10 mm. All reported tensile data represented an average of at least three independent measurements. A TA Instrument Q1000 DMA was used to acquire storage modulus, loss modulus and tan delta for films, which were deformed (10 micrometer amplitude) in the tension mode at a frequency of 1 Hz using a temperature ramp rate of 3 °C /min under nitrogen.

4.4 Results and Discussion

Selection and synthesis of cyclic monomers. The structures and abbreviations of some difunctionally cycloaliphatic monomers in this chapter are listed in **Scheme 4.11**.



Scheme 4.11 Structures and abbreviations of cyclic monomers

The spiral diester, DMSHD, has two four-membered rings that are vertical to each other. Linear spiro condensation polyamides have been synthesized and are reported to be valuable as fibers and oriented films.[11] There have also been studies on optically active polyamides prepared from a diamine and (R)-spiro[3.3]heptane-2,6-dicarboxylic acid chloride [(R)-SHDAC)], which was synthesized by the reaction of (R)-spiro[3.3]heptane-2,6-dicarboxylic acid [(R)-SHDA] with excess thionyl chloride.[15, 16] Optically active [(R)-SHDA] could be obtained by the optical resolution of its complex with brucine.[16] It was believed that polymers prepared from an optically active spiral derivative would show a large optical rotation and would experience a 90^o unit by unit twist, resulting in an ordered conformation---although this is dependent on the structure of the other polymer components.[16] However, there has been little study on polyesters containing spiral structure. Therefore, we are interested in incorporating the spiral diester into the polyester backbone to investigate the resulting properties. *Cis*-DMCP was discussed in the literature review and was synthesized in the previous chapter. It is well known that *cis*-DMCP can provide flexibility to polymers due to its non planar structure, so *cis*-DMCP is used to synthesize all-aliphatic random polyesters for comparative purpose in this chapter. Bridgehead-substituted bicyclic diesters, such as DMCD-2, have been synthesized, as discussed in Chapter 3. As described, they were found to readily participate in melt-phase polycondensation reactions. The bicyclic diol BODM has also a rigid and symmetrical structure and its incorporation into the polyester backbone is also expected to increase the glass transition temperatures of these polymers. Additionally, as discussed in Chapter 2, TMCBD has been widely incorporated into semi-aromatic polyester backbones and the corresponding copolyesters exhibited excellent properties. However, since there are few studies on all-aliphatic copolyesters containing TMCBD units, an investigation of the thermal and mechanical properties of these materials is warranted. While the bulky pendant cyclohexyl ring group of 1,1-CHDM imparts these polyesters with good solubility in common organic solvents, it also makes them more flexible when compared to polyesters based on 1,4-CHDM. Cycloaliphatic polyesters based on *trans*-DMCD and 1,1-CHDM have also been described.[17] These polyesters tend to be highly crystalline with a melting point of 192 ^{o}C. For this chapter, several all-aliphatic copolyesters based on 1,1-CHDM were synthesized and their mechanical properties were compared to those of other cycloaliphatic polyesters containing rigid rings in their backbones in order to clarify important structure-property relationships.

Synthesis of copolyesters and their characterization by ^{1}H NMR spectrametry. The melt transesterification method was again used to prepare all the polyesters evaluated in this chapter, which also employed other well established conditions, such as high reaction temperatures, high vacuum, and proper catalyst amount.[4] The polymerization time was about 6 h and the temperature was in the range of 190-275 ^{o}C. However, an attempt to synthesize high molecular weight polyesters from

DMCD-2 and BODM via melt polymerization was unsuccessful due to the non-volatility of BODM and the high melt viscosity of the oligomers. An excess of EG was used as a co-diol to improve the molecular weights of the polyesters since it can be removed easily under vacuum due to its high volatility. Based on these results, we chose polymers containing both EG and cyclic diols to compare their properties. The copolyester samples were amorphous and soluble in chlorinated solvents such as chloroform. **Figure 4.6** shows the ^{1}H NMR spectrum of representative copolyesters based on DMCD, DMCD-2, EG and BODM with targeted percentages of 50/50/30/70.

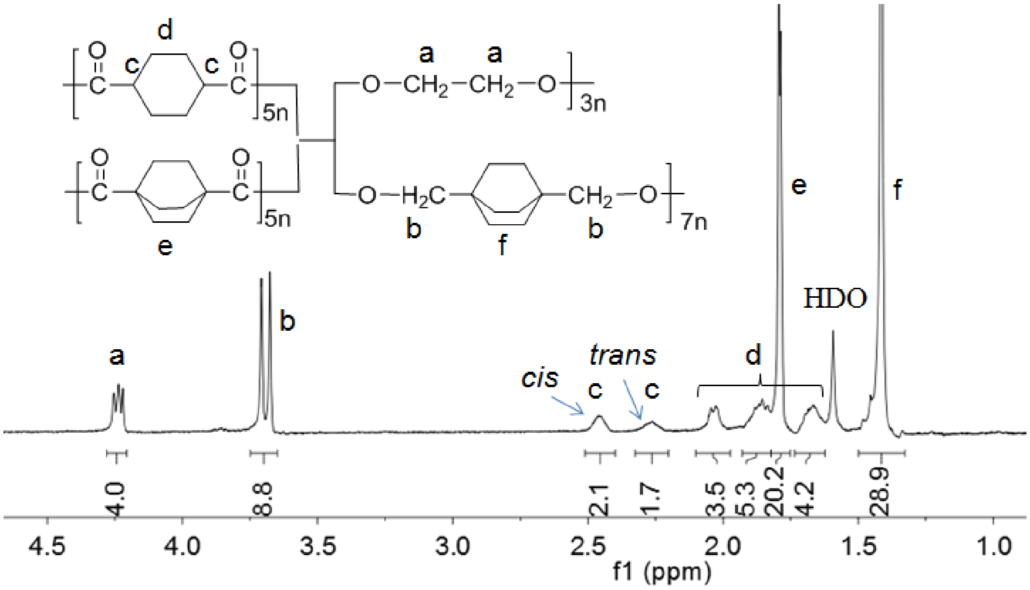


Figure 4.6 ^{1}H NMR spectrum of poly[50(DMCD)50(DMCD-2)31(EG)69(BODM)]

Peak "a" in **Figure 4.6** is assigned to the methylene group adjacent to the oxygen at the ethylene glycol unit (triplet peaks), and peak "b" represents the methylene group adjacent to the oxygen at the BODM unit. These broad peaks "c" and "d" arise from the protons on the cycloaliphatic rings of DMCD. The *cis*/*trans* ratios of DMCD were determined by comparing the α-hydrogens on the *cis* (2.5 ppm) and *trans* (2.3 ppm) isomers. The polymer composition calculated from this ^{1}H NMR spectra based on the peak area ratio of “a” to “b” was 31 % EG and 71 % BODM.

Molecular weights and thermal properties of different copolyesters. The copolyester composition, the molecular weights and thermal properties of the copolyesters based on DMCD-2, DMSHD or BODM are summarized in **Table 4.1**. When EG was used as one of diols, for example, each copolyester was amorphous and no T_m was observed. However, if BD was used as one of diols, as was the case with the poly[100**(**DMCD-2)50(BD)50(1,4-CHDM)], the result was a semi-crystalline polymer with a high M_n (35,400 g/mol), a T_g of 73 ^oC, a T_m of 218 ^oC, and a T_c of 176 ^oC. Therefore, EG was selected as the co-diol in order to obtain amorphous copolyesters.

Table 4.1 Properties of various cycloaliphatic copolyesters

Polyester composition (^1H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (g/mol)	T_g (°C)
(DMCD-2)/DMCD/EG/1,4-CHDM 50/50/29/71	367	31,000	52,700	70
(DMCD-2)/DMCD/EG/BODM 50/50/31/69	374	32,000	54,200	115
(DMCD-2)/EG/1,4-CHDM 100/31/69	372	26,000	43,800	115
DMSHD/EG/1,4-CHDM 100/31/69	350	25,000	42,000	16
DMCP/EG/1,4-CHDM 100/31/69	342	30,700	59,200	2
DMCP/DMCD/EG/1,4-CHDM 51/49/29/71	348	29,500	57,600	20
(DMCD-2)/DMT/EG/1,4-CHDM 50/50/50/50	386	38,000	53,900	85
(DMCD-2)/DMT/EG/1,4-CHDM 50/50/30/70	390	25,000	40,700	90
(DMCD-2)/DMT/EG/1,4-CHDM 50/50/0/100	387	18,100	27,700	94

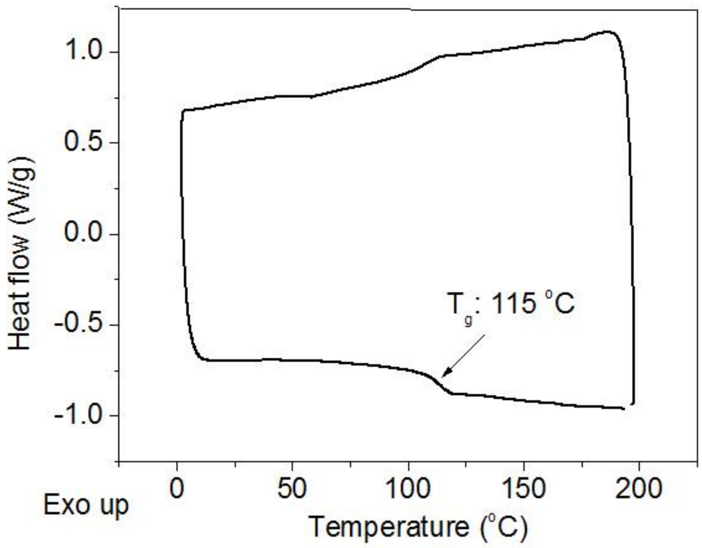


Figure 4.7 DSC trace of poly[50(DMCD)50(DMCD-2)30(EG)70(BODM)]

Table 4.1 also shows that the copolyester poly[50**(**DMCD-2) 50(DMCD)31(EG)69(BODM)] based on BODM has a much higher T$_g$ than the corresponding copolyester poly[50**(**DMCD-2)50(DMCD)29(EG)71(1,4-CHDM)], which is based on 1,4-CHDM. This difference corresponds to the more structural rigidity of BODM compared to 1,4-CHDM. In addition, the DSC trace shown in **Figure 4.7** exhibits the amorphous characteristics of poly[50**(**DMCD-2)50(DMCD)29EG71(1,4-CHDM)].

Conversely, the copolyester based on 100 mol% DMSHD has a T$_g$ of only 16 ^{o}C, which is almost 100 ^{o}C lower than that of the copolyester containing 100 mol% DMCD-2. This discrepancy is probably due to the spiral structure of DMSHD, as shown in **Figure 4.8**, which facilitates the unit-by-unit twisting of the polymer backbone. Tensile tests on the poly[100(DMSHD)31(EG)69(1,4-CHDM)] at RT also confirm its excellent elasticity, with an average elongation-to-break of up to 1700 %, as shown in **Figure 4.9**. However, it has a low modulus of only 1.4 MPa and a low tensile stress at break of only 0.7 MPa.

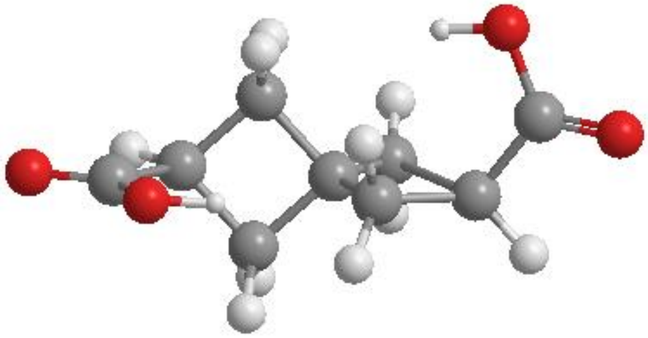


Figure 4.8 3-D structure of DMSHD

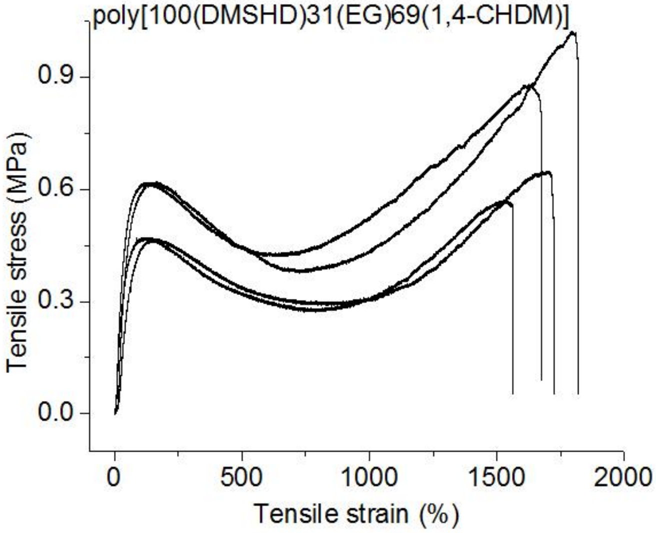
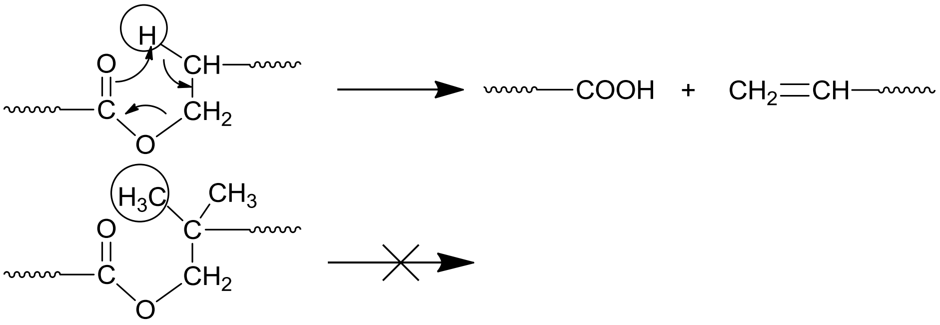


Figure 4.9 Tensile properties of poly[100(DMSHD)31(EG)69(1,4-CHDM)] at RT

Poly[100(DMCP)31(EG)69(1,4-CHDM)] based on *cis*-DMCP possesses a T_g of only 2 ^oC, as shown in **Table 4.1**, indicative of the flexibility of *cis*-DMCP. This flexibility characteristic is consistent with the report in the literature.[18] A series of semi-aromatic poly[(DMCD-2)/DMT/EG/(1,4-CHDM)] copolyesters with varying 1,4-CHDM content was prepared, and their properties are shown at the bottom of **Table 4.1**. These semi-aromatic copolyesters exhibited higher thermal stability and their T_g's increased with increasing 1,4-CHDM content as expected, but the average molecular weights of these copolyesters decreased upon increase in 1,4-CHDM content. Thus, we concluded that it is difficult to obtain high molecular weight polyesters when only 1,4-CHDM is used as one diol. This is due to the fact that 1,4-CHDM has low volatility and cannot be used in large excess over the diester component.

Thermal properties of poly[w(DMCD)/x(DMCD-2)/y(NPG)/z(1,4-CHDM)] copolyesters. For this investigation, neopentyl glycol (NPG) is used as one of glycol components instead of ethylene glycol (EG) since NPG-containing polyesters have been found to be more thermally stable than other linear aliphatic polyesters.[19, 20] As it is well known, the intramolecular hydrogen transfer process is the main thermal degradation pathway of polyesters depending on the nature of the diol units.[19-21] In fact, the β-scission is the most important mechanism in the decomposition of the diol unit and is favored by a six-membered ring transition state, as shown in **Scheme 4.12.**



Scheme 4.12 Thermal fragmentation mechanisms of polyesters via the intramolecular hydrogen transfer process

The introduction of two methyl groups, which replace two β hydrogens in the polyester backbones, can prevent the above reaction and render these polyesters significantly more thermally stable than other aliphatic polyesters. Therefore, NPG is selected as one of diols described in this chapter. The molecular weights and the properties of the prepared copolyesters based on NPG are summarized in **Table 4.2**.

Table 4.2 Characterization results of amorphous aliphatic copolyesters containing NPG

Polyester composition DMCD/(DMCD-2)/NPG/1,4-CHDM w/x/y/z (^{1}H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (k/mol)	T_g (°C)
100/0/50/50	380	25,500	69,000	35
50/50/50/50	378	12,000	28,000	71
0/100/75/25	370	4,800	10,000	105
0/100/100/0	335	2,200	4,000	50
75/25/100/0	385	23,500	66,600	33

As indicated, the NPG-containing polyester poly[75(DMCD)25(DMCD-2)100(NPG)] possess excellent thermal stability with a 5 % weight loss temperature of 385 ^{o}C. The T_g of these all-aliphatic copolyester increases with increasing DMCD-2 content, indicating the rigid structure of the bicyclo[2.2.2] ring group. Low molecular weights were obtained when the content of both NPG and DMCD-2 was ≥ 50 mol%. For example, poly[50(DMCD)50(DMCD-2)50(NPG)50(1,4-CHDM)] has a average molecular weight (M_n) of 12,000 g/mol, while the poly[100(DMCD-2)100(NPG)] oligoester has a M_n of only 2,200 g/mol. This low molecular weight is due to the low volatility of NPG and the low reactivity with DMCD-2, which is also a rigid molecule. The steric hindrance of methyl groups in NPG leads to its low reactivity. When the partial DMCD-2 was replaced by DMCD, the poly[75(DMCD)25(DMCD-2)100(NPG)] copolyester achieved a higher molecular weight compared to the poly[100(DMCD-2)/100(NPG)]; however, its T_g was lower, as shown in **Table 4.2**. We then performed DMA and tensile testing on the amorphous aliphatic copolyesters containing NPG. Due to the brittle nature of the 100 mol% DMCD-2 copolyesters, we were unable to obtain tensile data for these polymers since they could not be fabricated into dogbone samples for testing. However, the tensile strength and DMA mechanical properties of the poly[w(DMCD)x(DMCD-2)y(NPG)z(1,4-CHDM)] will be discussed later.

Thermal properties of copolyesters based on TMCBD. TMCBD is a rigid, cycloaliphatic secondary diol, which was discussed in detail in Chapter 2. For this portion of the study, we incorporated TMCBD (*cis*/*trans* 50/50) into our all-aliphatic polyester system of different compositions, and then compared the molecular weights and thermal properties of the copolyesters. Our results are summarized in **Table 4.3**.

Table 4.3 Properties of aliphatic copolyesters based on TMCBD

Polyester composition DMCD/(DMCD-2)/EG/TMCBD w/x/y/z (^{1}H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (k/mol)	T_g (°C)
100/0/20/80	348	11,600	25,100	62
80/20/20/80	343	13,800	26,800	64
50/50/50/50	373	27,200	53,400	66

As shown by the data, the incorporation of 80 mol% TMCBD into the main chain of the copolyester resulted in low average molecular weights, i.e., below 14,000 g/mol. This finding is consistent with the work of Kelsey *et al.*,[22] and is probably due to the existence of a large amount (80 mol%) of TMCBD, which is a secondary diol with high steric hindrance and has lower reactivity towards diesters, compared to primary diols. With respect to the glass transition temperature, the increase in DMCD-2 from 0-20 % did not yield a significant increase. We attributed this outcome to the presence of a large amount of rigid TMCBD. Molecular weight was improved significantly for the poly[w50DMCD)/50(DMCD-2)/50(EG)/50(TMCBD)] polyester when 50 mol % EG was used as a co-diol, which resulted from the high volatility of EG. Similar to the aliphatic copolyesters containing NPG, we were unable to generate tensile data for the TMCBD-containing copolyesters due to their brittle properties. As before, the samples failed during preparation of dogbone specimens.

Properties of copolyesters based on 1,1-CHDM. When 1,1-CHDM is incorporated into polyester chains, the cyclohexylene ring is a pendant side group relative to the polyester backbone. Several patents reported that 1,1-CHDM could be polymerized with DMT or dimethyl naphthalate (DMN) to obtain polyesters with high T_g values (83 ^oC and 108 ^oC, respectively).[23, 24] It is interesting to compare the properties of polyesters with pendant cycloaliphatic rings as side groups to those of polyesters with cycloaliphatic groups on the backbones. The molecular weights and thermal properties of some copolyesters containing 1,1-CHDM are summarized in **Table 4.4**.

Table 4.4 Properties of copolyesters based on 1,1-CHDM

Polyester composition (^1H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (k/mol)	T_g (°C)
DMCD/EG/(1,1-CHDM) 100/51/49	352	5,700	8,100	32
DMCD/EG/(1,4-CHDM) 100/51/49	372	22,400	48,900	45
DMT/EG/(1,1-CHDM) 100/51/49	347	N/A	N/A	83
DMCD/(1,1-CHDM) 100/100	336	4,400	12,000	35
DMCD/(1,4-CHDM)/(1,1-CHDM) 100/50/50	349	11,200	33,400	40
DMCD/(1,4-CHDM) 100/100	368	16,100	30,800	52
DMCD/(DMCD-2)/(1,4-CHDM)/(1,1-CHDM) 50/50/50/50	347	6,000	13,200	58

When 1,1-CHDM is used as a co-diol or as the only diol during melt polymerization, the resulting copolyesters have low molecular weights (below 12, 000 g/mol), as shown in **Table 4.4**. This is due to the low volatility and bulky structure of 1,1-CHDM. At the end of the polycondensation reaction, the copolyesters based on 1,1-CHDM were not very viscous and displayed a deep yellow color. Semi-aromatic copolyester poly[100(DMT)51(EG)49(1,1-CHDM)] was not soluble in chloroform, so molecular weight data for these polyesters were not available. However, poly[100(DMT)51(EG)49(1,1-CHDM)] exhibited a much higher T_g than poly[100(DMCD)51(EG)49(1,1-CHDM)] as expected, indicating the more rigid structure of DMT in the former polyester than that of DMCD in the latter polyester. **Table 4.4** shows that the poly[100(DMCD)51(EG)49(1,4-CHDM)] displayed higher thermal stability and higher T_g than poly[100(DMCD)51(EG)49(1,1-CHDM)]; moreover, the poly[100(DMCD)100(1,4-CHDM)] polyester displayed higher thermal stability and higher T_g than either the poly[100(DMCD)50(1,4-CHDM)50(1,1-CHDM)] or the poly[100(DMCD)100(1,1-CHDM)]. These results indicate that copolyesters with cyclohexyl ring segments in their main chains are more rigid than those with pendant cyclohexyl units. Tensile testing was not performed for the 1,1-CHDM-containing copolyesters since the samples failed during preparation of dogbone specimens due to low molecular weights and brittle characteristics.

Tensile properties of poly[100(DMCD)/50(NPG)/50(1,4-CHDM)] copolyesters. Tensile testing was conducted on transparent, compression-molded films. Tensile data are not available for copolyesters containing TMCBD or 1,1-CHDM due to their brittle properties, thus only the tensile data for the poly[w(DMCD)/x(DMCD-

2)/y(NPG)/z(1,4-CHDM)] copolyesters are included in this chapter. The stress-stain curves associated with the poly[100(DMCD)50(NPG)50(1,4-CHDM)] copolyester are plotted in **Figure 4.10**. This copolyester is fairly elastic, as evidenced by its high ductility with an average strain to break of close to 400 %. It also exhibits an average modulus of 157 MPa and an average tensile stress at break of 8.5 MPa.

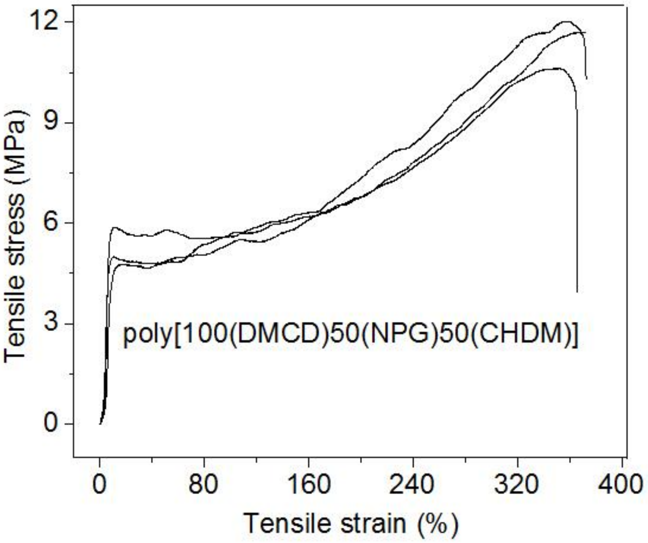


Figure 4.10 Tensile properties of poly[100(DMCD)50(NPG)50(1,4-CHDM)]

Thermo-mechanical properties and secondary relaxation of poly[w(DMCD)/x(DMCD-2)/y(NPG)/z(1,4-CHDM)] copolyesters. The thermo-mechanical properties of several all-aliphatic copolyesters based on NPG were measured by DMA (**Figure 4.11-4.13**). These copolyesters based on DMCD-2 and NPG have an α transition, which is related to T_g, and a β transition, which is related to the molecular relaxation. The DMA traces depicted in **Figure 4.11** and **Figure 4.12** show that the poly[50(DMCD-2)50(DMCD)50(NPG)50(1,4-CHDM)] copolyester has a wider storage modulus plateau and exhibits a higher glass transition temperature than poly[100(DMCD)50(NPG)50(1,4-CHDM)]. This trend is consistent with DSC data.

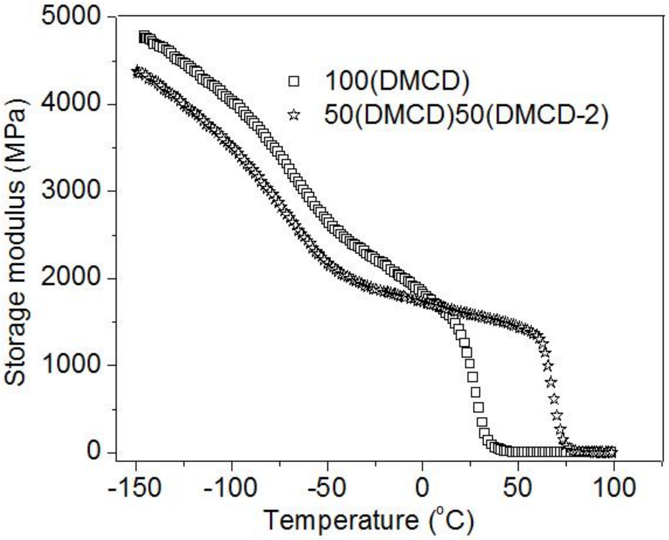


Figure 4.11 Storage modulus vs temperature for poly[100(DMCD)50(NPG)50(1,4-CHDM)] and poly[50(DMCD)50(DMCD-2)50(NPG)50(1,4-CHDM)]

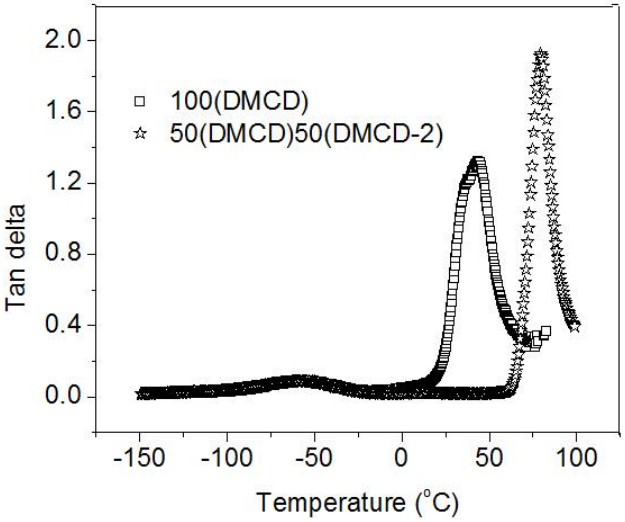


Figure 4.12 Tan delta vs temperature for poly[100(DMCD)50(NPG)50(1,4-CHDM)] and poly[50(DMCD)50(DMCD-2)50(NPG)50(1,4-CHDM)]

The tan δ versus temperature plots depicted in **Figure 4.11** and **Figure 4.12** show the secondary relaxation of all of these NPG-containing aliphatic copolyesters. Secondary relaxation tan δ peaks appear from -57 °C to -50 °C with similar, although small, intensity. These peaks result from the conformational changes of the cyclohexyl units on the backbones of these copolyesters. DMA traces associated with poly[25(DMCD-2)75(DMCD)100(NPG)] are shown in **Figure 4.13**. It has a similar tanδ T_g as the poly[100(DMCD)50(NPG)50(1,4-CHDM)] copolyester. This similarity is also confirmed by the DSC data shown in **Table 4.3**.

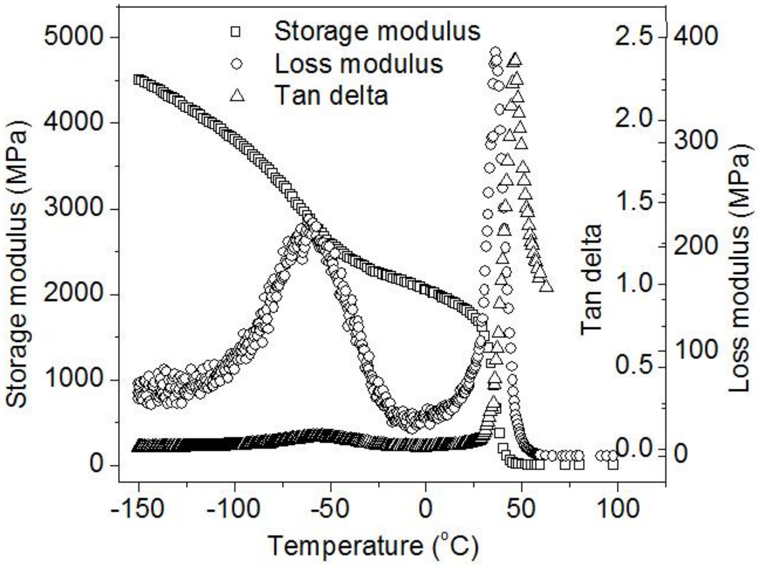


Figure 4.13 DMA traces of poly[25(DMCD-2)75(DMCD)100(NPG)]

4.5 Conclusions

In summary, we have described the synthesis of various all-aliphatic polyesters containing cyclic units via melt polycondensation, and then characterized some of their important properties. The copolyester composition of these materials was confirmed by ^{1}H NMR analysis being close to targeted expectations. Amorphous copolyesters based on DMCD-2 and BODM exhibited significantly higher T_g's (up to 115 °C) than did other alicyclic polyesters described in this chapter, which we attributed to the rigid and symmetrical structure of the bicyclo[2.2.2]octane rings. The cyclopentyl ring-containing polyesters showed the lowest T_g among them due to the nonplanar and flexible structure of cis-DMCP. The NPG-containing polyesters had higher thermal stability than did other polyesters due to the absence of β hydrogens. DMA results confirmed that these cycloaliphatic copolyesters containing DMCD and/or DMCD-2, NPG, and/or 1.4-CHDM displayed similar secondary relaxations due to the conformational transition of the cyclohexylene rings on their backbones.

4.6 Acknowledgements

We are grateful to the Eastman Chemical Co. for donating DMCD (*cis*/*trans* mixture). We acknowledge the Department of Chemistry and the Macromolecules and Interfaces Institute (MII) for financial support. We would also like to thank Dr. Long’s group for TGA, DSC and tensile tests, and Dr. Riffle’s group for SEC measurements.

4.7 Suggested Future Work

As mentioned in the literature review, the cycloaliphatic ring-containing polyesters are expected to possess relatively good photo-oxidative stablility and UV stability compared to aromatic polyesters. In order to confirm this hypothesis, an accelerated UV weathering tests on the cycloaliphatic polyesters synthesized earlier and described in Chapter 3 and Chapter 4 would need to be conducted. This would require the analogous testing of certain aromatic polyesters as controls. The weathering of polyesters could be studied by an accelerated weathering test. Color could be measured on compression-molded films according to ASTM-1925. The polyester films could be studied in a Q-U-V accelerated weathering tester and exposed continuously to UVA-340 lamps at ambient temperature. The panels would need to be rotated regularly and the lamp positions should be altered every one to two weeks. Once a week, the yellowness index, gloss, haze and transmission would need to be measured for each sample. Additionally, mechanical testing, such as notched Izod tests and tensile tests would need to be conducted to monitor any possible changes in mechanical properties.

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Chapter 5: Melt-phase Synthesis and Properties of Triptycene-Containing Copolyesters

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5.1 Abstract

A new triptycene diol (TD) --- triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) ether was synthesized and used to prepare a series of copolyesters with dimethyl 1,4-cyclohexanedicarboxylate (DMCD) by melt condensation polymerization. Straight chain aliphatic spacers, including ethylene glycol (EG), 1,4-butanediol (BD) and 1,6-hexanediol (HD), were all used as co-diols with TD to explore the effects of straight chain flexible spacers on copolyester properties. A concomitant series of non-triptycene copolyesters based on hydroquinone bis(2-hydroxyethyl) ether (HBE), bis[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS), 1,1-bis[4-(2-hydroxyethoxy)-phenyl]cyclohexane (BHPC) or 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) were also prepared for comparison. The results demonstrated that triptycene-containing polyesters in this study have higher thermal stability and higher glass transition temperatures (T_g's) than the corresponding non-triptycene analogs. For triptycene-containing copolyesters, the mechanical properties were found to be dependent on the types and compositions of comonomer diols. A 1,4-butanediol based triptycene copolyester was observed to have a significant increase in its T_g and modulus while maintaining high elongation at ambient temperature. However, all

the studied 1,4-butanediol based copolyesters were brittle and had comparable modulus values at low temperatures (-25 °C or -40 °C).

5.2 Introduction

Material scientists have been pursuing the enhancement of mechanical properties to produce high performance polymers for a wide range of applications. Incorporation of rigid structures within the polymer backbone with the purpose of enhancing mechanical properties, has been studied extensively.[1-3] Polymers containing such rigid building blocks usually show not only increased T_g's but also decreased ductility. For example, adamantyl building blocks usually raise the T_g, but also lower the ductility of a polymer by reducing the flexibility of the polymer backbone and intermolecular chain entanglements.[4-7] A variety of bisphenol derivatives are also well known to produce high T_g polymers.[8-10] However, a recent report from Swager and Thomas, *et al.*[11] shows that incorporation of triptycene, a rigid aromatic cyclic structure, gives an increase in both stiffness and ductility even at a low temperature of -30 °C when incorporated into certain polyester backbones. The authors hypothesized that neighboring chains can lie in a V-shaped cleft of the triptycene units and that this provides a mechanism for molecular interlocking and is the origin of these normally divergent mechanical properties.[11] Unlike common intermolecular interactions, such as hydrogen bonding and ionic interactions, this “mechanical interlocking” is a novel concept and it is not known if this interaction is operative in other polymer structures.

Previous work on triptycene containing polyesters in the late 1960’s from Eastman Kodak resulted in polymers with significantly enhanced glass transition temperatures and increased brittleness as evidenced by the reported brittle nature of cast films.[12, 13] Both of these early reports were based on incorporation of a triptycene monomer with a 9,10-functionality for polymerization into the various polymer backbones studied. In contrast the Swager and Thomas work is based on the use of 1,4-hydroquinono triptycene structure which significantly changes the monomer structure and polymer backbone structure. Also in the recent work, a long aliphatic spacer was found to be necessary to bring this *proposed* mechanical interlocking mechanism into operation. The combination of decanediol and the 1,4-hydroquinone triptycene units in the polyester chain led to these unusual properties.

Our goal is to explore the properties of a series of copolyesters that incorporate the 1,4-hydroquinone triptycene group via a new primary diol triptycene derivative which permits the facile melt phase preparation of copolyesters. We are interested in raising the glass transition temperatures of aliphatic based copolyesters based on 1,4-cyclohexane dicarboxylic acid (via DMCD) without negatively impacting the mechanical properties of these materials. In this research the number of methylene groups in the aliphatic co-diol was varied from two to six (ethylene diol to hexane diol) and selected thermal and mechanical properties of the resulting copolyesters were studied. Furthermore, the incorporation of other bulky hydroxyethoxylated bisphenol derivatives into identical polyester backbones was investigated and the mechanical properties, without the triptycene architecture, of these polyesters were compared to those of corresponding triptycene polyesters.

5.3 Experimental

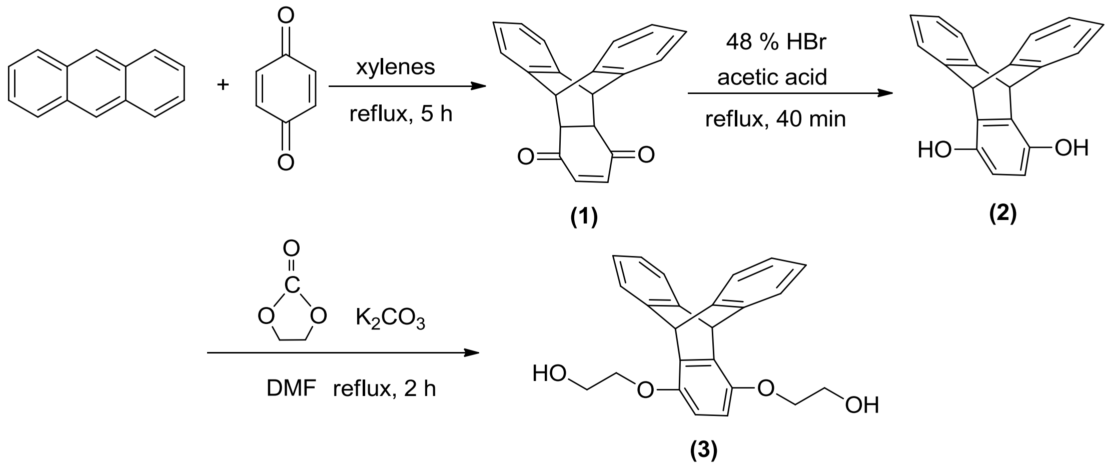
5.3.1 Materials

Anthracene (97 %) was purchased from Aldrich and recrystallized from xylene.

Ethylene glycol ($\geq$ 99 %), 1,4-butanediol (99 %), 1,6-hexanediol (99 %), *p*-benzoquinone, hydroquinone bis(2-hydroxyethyl) ether (98 %) and 4,4'-cyclohexylidenebisphenol (98 %) were purchased from Aldrich and used as received. Dimethyl 1,4-cyclohexanedicarboxylate (DMCD) (*cis*/*trans* = 3/1) and 1,1-bis-(hydroxyphenyl)-3,3,5-trimethylcyclohexane were donated by Eastman Chemical Company and Hi-Bis GmbH respectively. Titanium(IV) *n*-butoxide (>98 %) was purchased from Alfa Aesar.

5.3.2 Synthesis

Synthesis of triptycene-1,4-quinone (1) (Scheme 5.1). Triptycene 1,4-quinone was prepared according to the published procedure.[14, 15] Anthracene (88.26 g, 0.496 mol) and 64.3 g (0.595 mol) of *p*-benzoquinone were heated under reflux in 572 mL of xylene for 5 h. After that, the hot solution was poured into a 1000 mL beaker and cooled overnight at 0 ºC. The solid was obtained by filtration and thoroughly washed with hot water (6 × 200 mL) to remove quinone and quinhydrone. The crude product was recrystallized from xylene, washed with cold xylene and petroleum ether (40-60), and dried in a vacuum oven at 60 ºC overnight to give 116 g of pale yellow solid with a yield of 81 %, mp 231-233 ºC (reported: 227-232 ºC[16]), ^{1}H NMR (400 MHz; $CDCl_3$) δppm : 3.14 (s, 2H, COC*H*), 4.87 (s, 2H, Ar-C*H*), 6.31 (s, 2H, C=C*H*), 7.07–7.10 (m, 2H, Ar-*H*), 7.18–7.20 (m, 4H, Ar-*H*), and 7.35–7.41 (m, 2H, Ar-*H*).

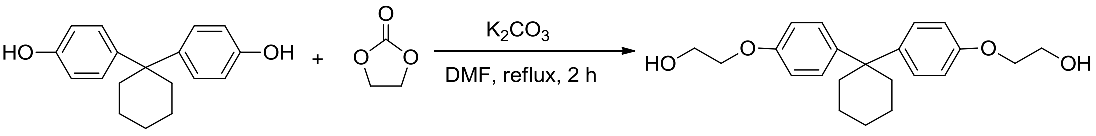


Scheme 5.1 Synthesis of triptycene-1,4-hydroquinone-bis (2-hydroxyethyl) ether **(3)**

Synthesis of triptycene-1,4-hydroquinone (2).[14] A 1000 mL round bottom glass flask was equipped with a reflux condenser. Six drops of 48 % hydrobromic acid were added to a solution of 46 g of triptycene 1,4-quinone in 600 mL of glacial acetic acid at refluxed temperature. Heat released vigorously and the solution took on an orange color, which gradually faded as a fine white solid precipitated out. After another 30 min at the boiling point, the reaction mixture cooled and was filtered. Washed with hexane twice and the mixture was then dried under vacuum oven at 80 ºC overnight. Yield: 90 %, mp 340-342 ºC (lit., 338-340 ^{o}C[14]**)**, ^{1}H NMR (400 MHz; DMSO-d_6) δppm: 5.80 (s, 2H, Ar-C*H*), 6.31 (s, 2H, Ar-*H*), 6.96–6.98 (m, 4H, Ar-*H*), 7.38–7.40 (m, 4H, Ar-*H*), and 8.83 (s, 2H, Ar-O*H*).

Synthesis of triptycene-1,4-hydroquinone-bis (2-hydroxyethyl) ether (3). Synthesis of **(3)** is shown in **Scheme 5.1**. A 500 mL two-necked flask charged with 30 g (0.105 mol) triptycene-1,4-hydroquinone, 1.45 g K_2CO_3 (0.0105 mol) in 250 mL N,N-dimethylformamide (DMF) was heated to reflux temperature (165 ºC) under argon, 18.46 g (0.210 mol) ethylene carbonate in 100 mL DMF was added into the flask drop by drop (about 1 h). After that, the reaction mixture was stirred at reflux temperature for another 2 h and then cooled to room temperature. A fine precipitate was obtained by pouring the reaction mixture into 800 mL of deionized water. The solid was filtered and washed completely with deionized water. After recrystallization from methanol and drying under vacuum oven overnight, a fine white solid (31.4 g) was obtained. Yield: 89 %, mp 238-239.3 ºC. ^{1}H NMR (400 MHz; DMSO-d_6) δppm: 3.74-3.77 (m, 4H, CH_2OH), 3.92-3.96 (m, 4H, ArO-CH_2), 4.94-4.97 (t, 2H, O-*H*), 5.95 (s, 2H, Ar-C*H*), 6.64 (s, 2H, Ar-*H*), 6.97–6.70 (m, 4H, Ar-*H*), 7.15–7.17 (d, 4H, Ar-*H*). ^{13}C NMR (DMSO-d_6, 100 MHz) δppm: 46.81, 60.21, 72.11, 112.09, 124.13, 125.25, 135.71, 145.93, 148.64. Elemental analysis calculated C, 76.99; H, 5.92. Found: C, 77.03; H, 5.89.

Synthesis of 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane (BHPC) (4) (**Scheme 5.2**). A 500 mL two-necked flask was charged with 20 g (74.5 mmol) 4,4'-cyclohexylidenebisphenol, 1 g K_2CO_3 (7.45 mmol) in 180 mL DMF and was heated to reflux temperature (165 ºC) under argon. 13.12 g (149 mmol) ethylene carbonate in 70 mL DMF was added into the flask drop by drop (about 1 h). After that, the reaction mixture was stirred at reflux temperature for another 2 h and then cooled to room temperature. A fine precipitate was obtained by pouring the reaction mixture into 600 mL deionized water. The solid was filtered and washed completely with deionized water. A fine white solid (24 g) was obtained after drying under vacuum oven overnight. Yield: 90 %, mp 101-102 ºC. ^{1}H NMR (400 MHz; DMSO-d_6) δppm: 1.47-1.54 (m, 6H, $CH_2CH_2CH_2CH_2CH_2$), 2.07-2.10 (t, 2H, O-*H*), 2.20-2.22 (m, 4H, CH_2CCH_2), 3.90-3.94 (m, 4H, CH_2OH), 4.03-4.05 (m, 4H, ArO-CH_2), 6.80–6.83 (m, 4H, Ar-*H*), 7.15–7.17 (m, 4H, Ar-*H*).



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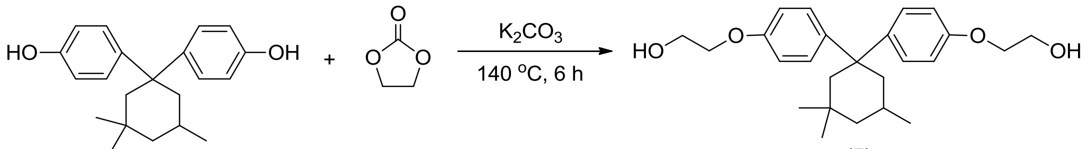
Scheme 5.2 Synthesis of 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane **(4)**

Synthesis of 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) (5) (**Scheme 5.3**). BHPT **(5)** was synthesized according to the literature procedure.[9] 1,1-Bis-(hydroxyphenyl)-3,3,5-trimethylcyclohexane 50 g, ethylene carbonate 31 g, and 0.5 g of potassium carbonate were added to a 500 mL two-necked glass flask which was placed nitrogen gas. The reaction was heated to 140 °C for 6 h, cooled to 100 °C and 100 mL of 4 % NaOH was added. The mixture was kept reflux for 15 min, and 100 mL of water was added, then the mixture was refluxed for 1 h. On cooling, a sticky white solid formed. The water was decanted and 150 mL of fresh water was added, and the mixture was allowed to sit overnight. The water was decanted off and the product was dried under vacuum at 70 °C for 24 h. 62 g of a white glassy solid was obtained with a yield of 97 %. No melting endothermic peak is observed in the DSC curves, the T_g of this monomer is 40 ^{o}C. ^{1}H NMR ($CDCl_3$, 400MHz) δ_H 7.23(d, 2H, J=4.4Hz), 7.10(d, 2H, J=4.4Hz), 6.80(d, 2H, J=4.4Hz), 6.75(d, 2H, J=4.4Hz), 3.88-4.05(m, 8H), 2.63(d, 1H, J=6.8Hz), 2.39(d, 1H, J=6.8Hz), 2.10(t, 1H, J=6.4Hz), 2.06(t, 1H, J=6.4Hz), 1.95-2.02(m, 1H), 1.91(d, 1H, J=6.4), 1.37(d, 1H, J=5.6Hz), 1.13(t, 1H, J=12.8Hz), 0.96(d, 6H, J=4.0Hz), 0.86(t, 1H, J=12.8Hz), 0.36(s, 3H).



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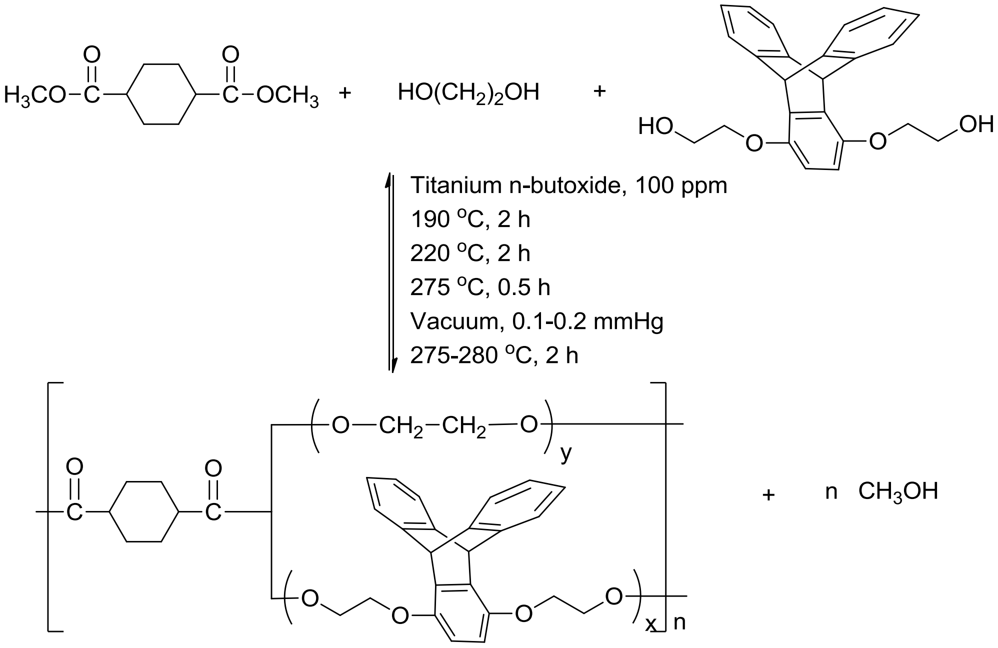
Scheme 5.3 Synthesis of 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) **(5)**

Preparation of catalyst solution. The titanium catalyst solution was obtained by dissolving titanium n-butoxide in n-butanol in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

Abbreviation of polyesters. The polymer nomenclature used in this manuscript is based on a polyester containing 100 mol% of diester and 100 mol% of diol. For example, the polymer designated by poly[100(DMCD)75(EG)25(TD)] means this targeted polymer containing 100 mol% DMCD as the diester units and 75 mol% EG and 25 mol% TD as the diol units. The letters, stand for various monomers′ abbreviation and the numbers indicate targeted mol % of monomers, respectively.

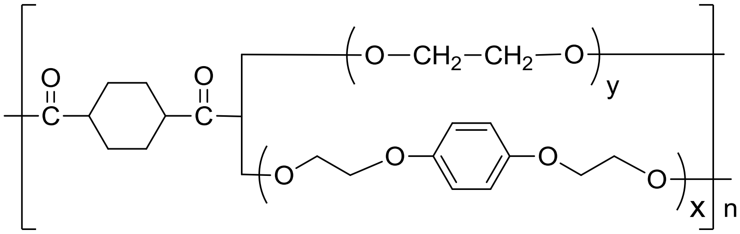
Melt-phase polymerization. The triptycene diol (TD) (**3**) and its comonomer EG were copolymerized with DMCD by melt polycondensation reaction. The detailed procedure in **Scheme 5.4**, which is similar to a published method,[9] is as follows (for poly[100(DMCD)75(EG)25(TD)]): 10 g (0.05 mol) of DMCD consisting of a *trans/cis* (1/3 molar ratio) mixture, 4.66 g (0.075 mol) of EG (100 % excess) and 4.68 g (0.0125 mol) TD were charged to a two-necked 50 mL reaction vessel equipped with a mechanical stirrer, nitrogen inlet, and condenser. The reactor was placed in a molten Belmont metal bath with a temperature controller. Titanium *n*-butoxide catalyst (100 ppm with respect to the targeted polyester) was added via syringe under nitrogen. A multi-step temperature procedure was used for the reaction, i.e. the reaction mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h and 275 °C for 0.5 h. After most of methanol was collected in a receiving flask, low vacuum (1 mmHg) was applied about 10 min and then high vacuum (up to 0.1 mmHg) was used to drive the reaction to high conversion for an additional 2 h. Then the vacuum was discontinued and nitrogen was passed through the system. The polymer was allowed to cool down to room temperature and was removed from the reaction flask. The polymer was dissolved in chloroform, and precipitated into methanol. The solid precipitate was obtained by vacuum filtration and was dried under vacuum at 30-60 °C overnight to yield 12.7 g (92 %) of dry copolyester. The same procedure was employed to prepare poly[100(DMCD)(100-x)(EG)x(TD)] with different composition of triptycene diol (TD).



Scheme 5.4 Synthesis of poly[100(DMCD)y(EG)x(TD)]

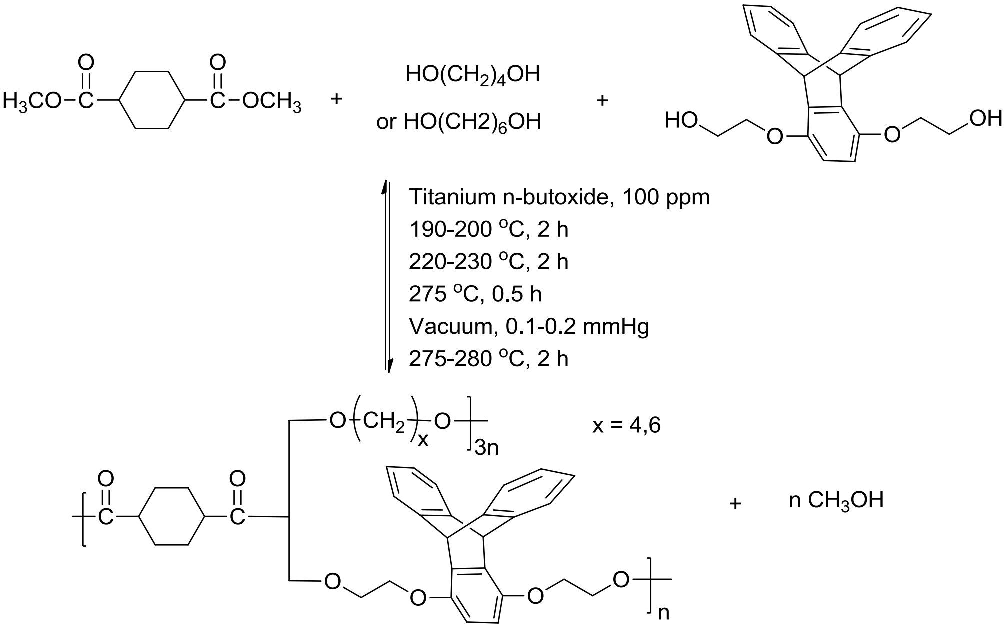
Synthesis of poly[100(DMCD)y(EG)x(HBE)] for comparative purposes. Non-triptycene analogs also were synthesized for comparison. 1,4-bis(2-hydroxyethoxy)benzene (HBE) was used as a corresponding diol shown in **Scheme 5.5**.

The experimental procedures are the same as described above.



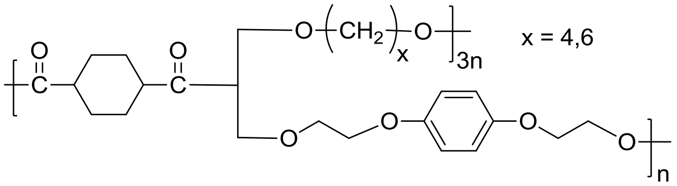
Scheme 5.5 Structures of non-triptycene poly[100(DMCD)(100-x)(EG)x(HBE)]

Synthesis of poly[100(DMCD)75(BD or HD)25(TD)] (**Scheme 5.6**). Copolyesters were prepared by the above mentioned procedure except that the content of TD and straight-chain alkanediols were fixed. In **Scheme 5.6**, ethylene glycol was replaced by 1,4-butanediol or 1,6-hexanediol, which was used in 30 mol% excess.



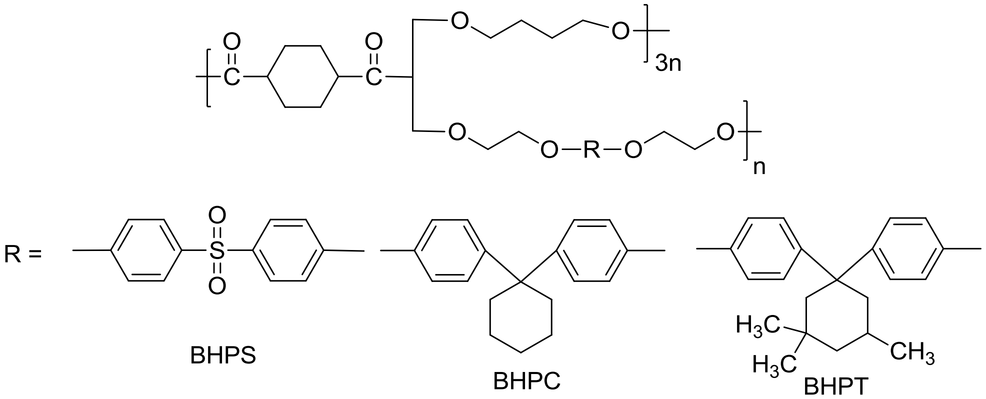
Scheme 5.6 Synthesis of poly[100(DMCD)75(BD or HD)25(TD)]

Synthesis of poly[100(DMCD)75(BD or HD)25(HBE)]. One non-triptycene analog (depicted in **Scheme 5.7**) with the same composition was synthesized for comparative purposes. The same experimental procedures were applied.



Scheme 5.7 Structures of non-triptycene polyesters poly[100(DMCD)75(BD or HD)25(HBE)]

Synthesis of poly[100(DMCD)75(BD)25(BHPS or BHPC or BHPT)]. The other non-triptycene analogs (depicted in **Scheme 5.8**) with the same compositions were synthesized for comparative purposes. The same experimental procedures were applied.



Scheme 5.8 Structures of poly[100(DMCD)75(BD)25(BHPS or BHPC or BHPT)]

5.3.3 Characterization

All measurements were performed at Virginia Tech (Blacksburg, Virginia) except for the elemental analysis, which was done by Atlantic Microlab, Inc. (Norcross, Georgia). NMR spectra were determined at 25 ºC at 400 MHz with an INOVA spectrometer. The elemental analysis was done by Atlantic Microlab, Inc. (Norcross, Georgia). Molecular weights of synthesized polymers were determined using size exclusion chromatography (SEC) with a Waters 410 refractive index (RI) detector and viscometer DP detector. SEC measurements were performed at 30 ^{o}C in chloroform with a sample concentration 5.0 mg/mL at a flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was conducted under nitrogen from 25 to 600 ºC at a heating rate of 10 ºC/min using a TA Instrument TGA Q500. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC Pyris 1 (TA instrument DSC Q2000). DSC data were obtained from -20 °C to 300 °C at heating/cooling rates of 20 °C / min under nitrogen circulation. The glass transition temperature was determined from analysis of the second heating cycle. Dynamic mechanical analysis (DMA) of samples was conducted using a DMA Q800 of TA instruments at a heating rate of 5 ° C/min from -150 °C to 100 °C while they were deformed (10 micrometer amplitude) in the tension mode at a frequency of 1 Hz under nitrogen. Tensile measurements at room temperature (23 °C) were performed on an Instron Model 4400 Universal Testing System equipped with a 1KN load. Tensile measurements at low temperatures (-25 °C or 40 °C) were performed on an Instron 5800R and Thermotron Testing System equipped with a load capacity of 1KN. The film samples were prepared using a PHI Model GS 21-J-C-7 compression molding press at 70 °C above T_g for 15 min. After the film samples were cooled down in ambient air, they were stored in a desiccator at ambient temperature. The molecular weights of the prepared film samples were unchanged from the original samples before compression molding. The film samples were dried in vacuum 24 h and then were cut to a dog bone shape at 40 × 4 × 0.3 mm (length × width × thickness) for tensile tests. The samples were tested at a rate of 15 mm/min using an initial grip-to-grip separation of 15 mm. Young’s modulus was calculated from the linear part of the initial slope. All reported tensile data were averaged from at least three independent measurements and a standard deviation was also reported. An X-ray diffractometer was used to determine if any crystallinity existed within the cast films. For this experiment, the original films or stretched films were fixed on the platform and the X-ray diffraction was observed from the surface of films by use of the reflection mode.

5.4 Results and Discussion

Selection of monomers. The synthetic route to triptycene-1,4-hydroquione-bis (2-hydroxyethyl) ether **(3)** is shown in **Scheme 5.1**. Anthracene was reacted with quinone across the 9,10 position to yield triptycene-1,4-quinone **(1)**.[14, 15] When treated with HBr in glacial acetic acid, triptycene-1,4-quinone **(1)** gives triptycene-1,4-hydroquinone **(2)** with a high yield.**[14]** This bisphenol can be readily and inexpensively converted to the primary alcohol triptycene-1,4-hydroquione-bis(2-hydroxyethyl) ether **(3)** in high yield by reaction of the phenol OH group with ethylene carbonate.[9] To the best of our knowledge, monomer **(3)** has not been reported in the literature and is a new monomer. Triptycene **(3)** with primary alcohol groups is required for polyesters in diol-diester polycondensations because it is well know that the direct melt polycondensation of bisphenols is a low yield reaction.[9] Bis[4-(2-hydroxyethoxy)-phenyl]4,4'-cyclohexylidene (BHPC) **(4)** was obtained in much higher yield than the literature.[17] DMCD (a c*is*/*trans* ratio of 3 to 1) as the diacid unit was used in this study to provide amorphous polyesters with improved solubility, while maintaining the linear 1,4-enchainment mode. Thus the introduction of cyclohexane units to the main chain of the polyesters does not significantly decrease the mechanical properties due to the rigidity of the alicyclic structure.

Copolyester composition by ^{1}H NMR spectroscopic analysis. Figure 5.1 shows the ^{1}H NMR spectrum of a representative copolyester based on DMCD, EG and TD with a targeted molar ratio of 100:75:25. The diols within the copolyester chains are assumed to react in a random fashion. In brief, peak “a”, “a’”, ”b”, “c” are assigned to the protons of the triptycene group. Peaks “d” and “e” are the methylene group adjacent to the oxygen at the TD unit. Peak “f” is assigned to the methylene group adjacent to the oxygen at the EG unit (single peak), and the *cis*/*trans* ratio of DMCD was determined by comparing the α-hydrogens on the *cis* and *trans* isomers. Some isomerization of DMCD from *cis* to *trans* occurred during polymerization (final mole ratio of *cis*/*trans* =1/1). These broad peaks “h” come from the protons on carbons in the rings. The peak area ratio of “f” to “e” give 74 % EG and 26 % TD. ^{1}H NMR spectrum of each of these polymers showed good agreement of its actual composition with the targeted composition.

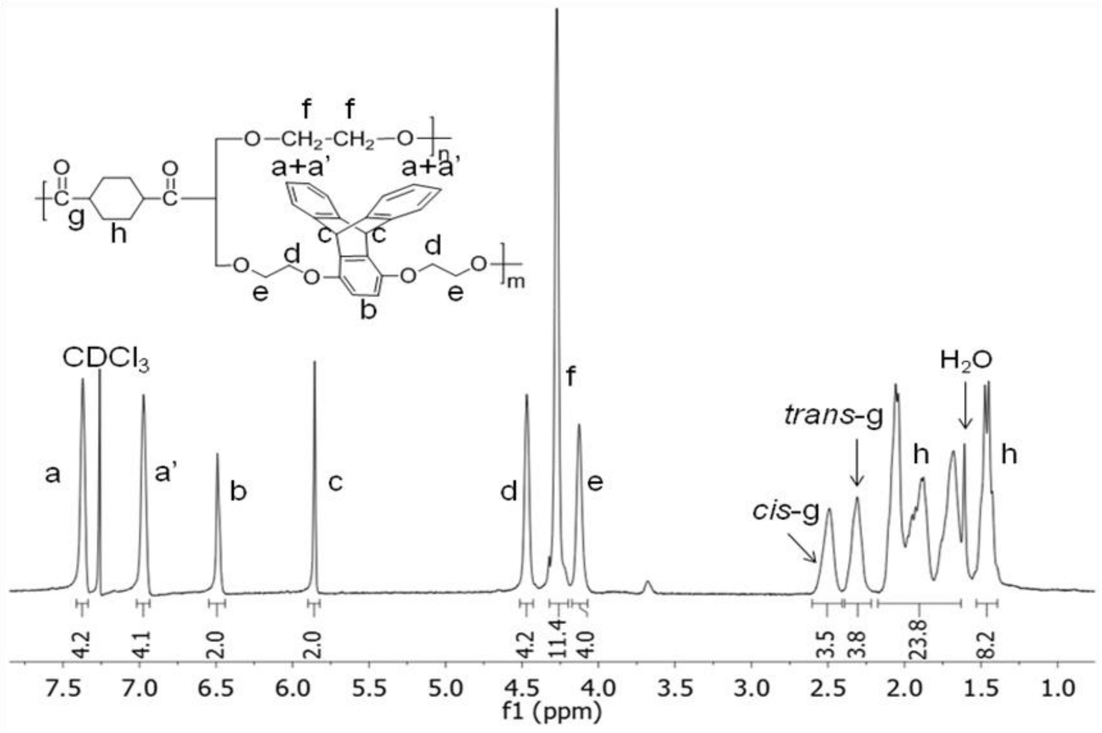


Figure 5.1 ^{1}H NMR spectrum of poly[100(DMCD)(74)(EG)26(TD)]

Thermal property analysis of copolyesters poly[100(DMCD)(100-x)(EG)x(TD)]. All polymers became highly viscous when the polymerization proceeded to high conversion, which typically took about 6 h. Some of the copolyesters started to take on a yellow color due to the titanium catalyst. The semi-aromatic copolyester samples were soluble in common chlorinated solvents, such as dichloromethane and chloroform, as expected from the amorphous polyester structure. In order to minimize the effect of physical aging of the respective polyesters on thermal and mechanical properties, all polyester film samples were run as soon as possible (in 24 h) after they were made by compression molding. The thermal properties, the molecular weights and tensile properties at ambient temperature (23 ^{o}C) are summarized in **Table 5.1**.

Table 5.1 Characterization Results of Triptycene and Non-triptycene Copolyesters

Polyester composition (^{1}H NMR)	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	M_w/M_n	DSC T_g (°C)	Tensile* stress at break (MPa)	Tensile* strain at break (%)	Modulus* (MPa)
100(DMCD)100(EG)	307	51,000	2.7	15	a	a	a
100(DMCD)74(EG)26(TD)	384	54,000	3.1	69	48 ± 4	4.5 ± 0.7	1475 ± 137
100(DMCD)49(EG)51(TD)	384	17,000	2.7	99	b	b	b
100(DMCD)26(EG)74(TD)	385	9,500	2.9	118	b	b	b
100(DMCD)74(EG)26(HBE)	372	43,000	3.1	23	6 ± 0.7	1920 ± 76	0.9 ± 0.1
100(DMCD)49(EG)51(HBE)	372	33,000	2.5	27	a	a	a
100(DMCD)26(EG)74(HBE)	372	106,000	2.6	31	a	a	a
100(DMCD)74(BD)26(TD)	375	25,500	2.2	44	32 ± 2	319 ± 14	1169 ± 21
100(DMCD)74(BD)26(HBE)	368	20,000	1.9	4	0.39 ± 0.03	737 ± 33	1.0 ± 0.2
100(DMCD)75(HD)25(TD)	370	24,000	2.0	25	11 ± 1	494 ± 47	50 ± 3
100(DMCD)65(HD)35(TD)	368	27,800	2.0	47	43 ± 3	10 ± 2	734 ± 27
100(DMCD)50(HD)50(TD)	360	24,300	2.5	77	b	b	b
100(DMCD)75(HD)25(HBE)	346	19,000	2.1	-6	0.24 ± 0.01	339 ± 32	1.4 ± 0.4
100(DMCD)74(BD)26(BHPS)	331	20,100	1.9	32	20 ± 2.0	433 ± 41	316 ± 30
100(DMCD)74(BD)26(BHPC)	359	20,400	2.0	26	15 ± 0.7	608 ± 27	4 ± 0.2
100(DMCD)75(BD)25(BHPT)	357	19,500	2.0	36	19 ± 0.7	249 ± 18	673 ± 46

* Tensile tests were done at 23 ^{o}C; a. Tensile tests were not run; b. Samples failed during preparation of dogbone specimens.

An examination of **Table 5.1** shows that most of the copolyesters displayed high molecular weights as well as PDIs of 2.5 - 3.1, which are typical for melt polymerization polyesters. The SEC trace of poly[100(DMCD)74(EG)26(TD)] by the refractive index detector was shown in **Figure 5.2** as a representative of these samples. The presence of small peaks, following the main sharp peak, suggests the presence of some cyclic oligomers in the polyester.

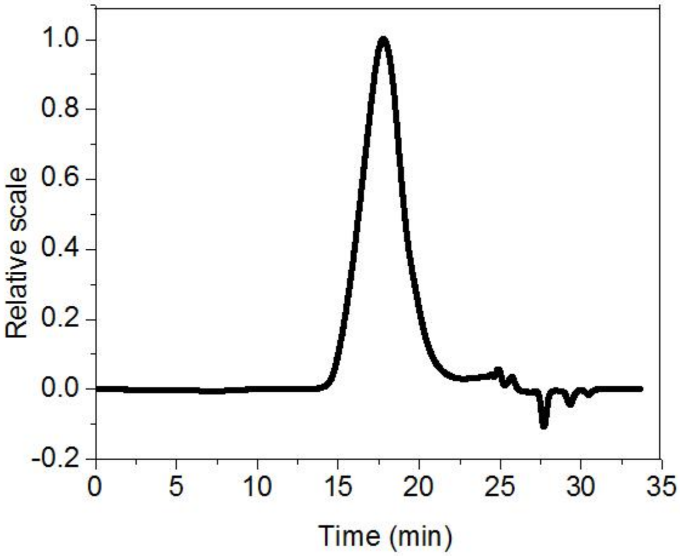


Figure 5.2 SEC trace of poly[100(DMCD)74(EG)26(TD)]

Molecular weights of polyesters, containing DMCD, EG, and TD, decrease with decreasing EG content. However, T_g increases with increasing TD content. As shown in **Table 5.1**, the 5 % weight loss (T_d) for all TD-containing polymers was higher than those of the corresponding non-TD analogs, as expected from the more highly aromatic structure of TD. For example, poly[100(DMCD)74(EG)26(TD)] showed a T_d at 384 ^oC, whereas poly[100(DMCD)74(EG)26(HBE)] displayed a T_d of 372 ^oC. These data indicate that copolyesters containing TD have marginally higher thermal stability than non-triptycene analogs. When the triptycene unit was incorporated into polyester, the T_g values were remarkably increased when compared to those of the non-triptycene polyesters. From **Table 5.1**, the incorporation of 26 mol% HBE into the DMCD/EG backbone only raised the T_g 8 ^oC, whereas TD at the same incorporation level raised the T_g 54 ^oC. This is consistent with the bulky structure of TD. The data in **Table 5.1** also shows that, as expected, the T_g of triptycene copolyesters decreases when the carbon number of the linear aliphatic co-diol increases to 4 (BD) and 6 (HD). Average molecular weights also decreased with the longer chain aliphatic diols because of their lower volatility than EG, making it more difficult to drive the conversion. The TD-containing polymers poly[100(DMCD)75(BD or HD)25(TD)] exhibited higher thermal stabilities than the corresponding non-triptycene analogues poly[100(DMCD)75(BD or HD)25(HBE)]. The absence of a melting peak in all DSC traces indicates that the copolyesters are amorphous, in contrast to the results reported by Swager, Thomas, *et al.*[11] (their triptycene-containing polyesters were semicrystalline). It is difficult to obtain high molecular weight copolyesters with an incorporation level of 70 mol% or more TD due to the non-volatility of TD.

Mechanical property analysis of copolyesters poly[100(DMCD)75(EG or BD or HD)25(TD or HBE)]. Tensile data **in Table 5.1** at ambient temperature revealed that poly[100(DMCD)74(EG)26(TD)] had a higher modulus and yield stress than poly[100(DMCD)74(EG)26(HBE)], which was a flexible material (**Figure 5.3**). But the low elongation to break (14 %) of poly[100(DMCD)74(EG)26(TD)] indicated that this triptycene polyester was brittle under these same conditions. Unlike the polyesters in the paper of Swager, Thomas *et al.*, which used long chain diols, this polyester poly[100(DMCD)74(EG)26(TD)] based on a short chain diol, EG, did not demonstrate ductile behavior.

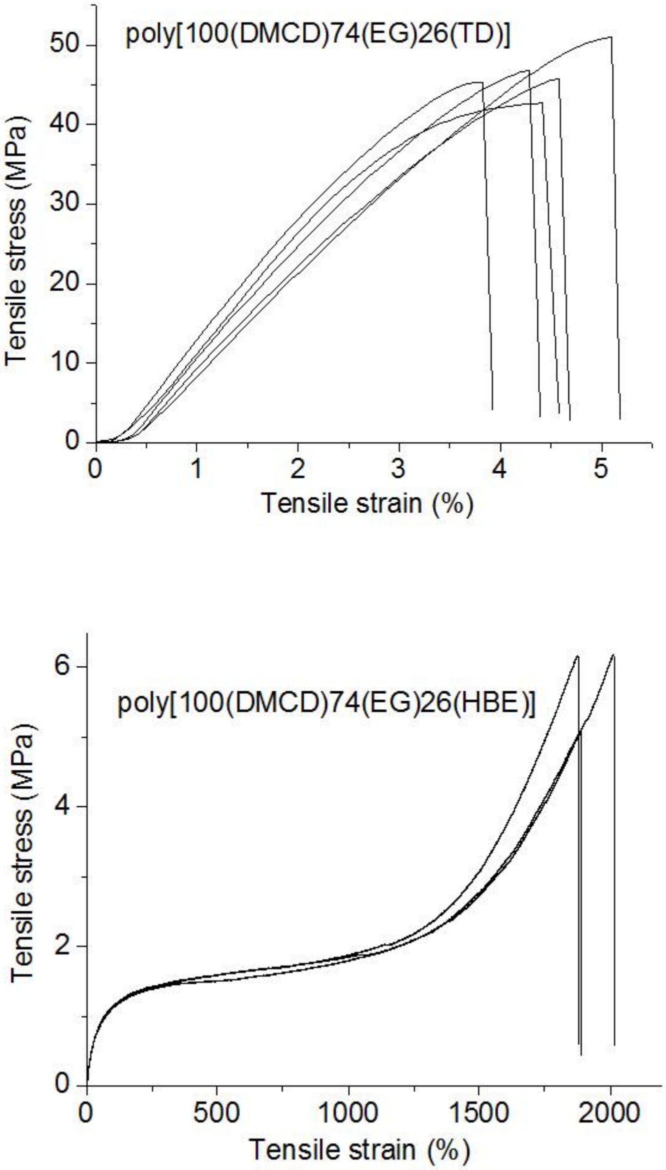


Figure 5.3 Tensile properties of poly[100(DMCD)74(EG)26(TD)] (top) and poly[100(DMCD)74(EG)26(HBE)] (bottom) at 23 ^{o}C

Therefore, we replaced EG with a longer diol, BD, and kept the TD composition the same. A similar polymer was also prepared with a longer diol, HD, so that the effects of the length of aliphatic spacers could be elucidated. We observed significantly different properties with the longer straight chain diols BD and HD.[11] These characterization results are also summarized in **Table 5.1**.

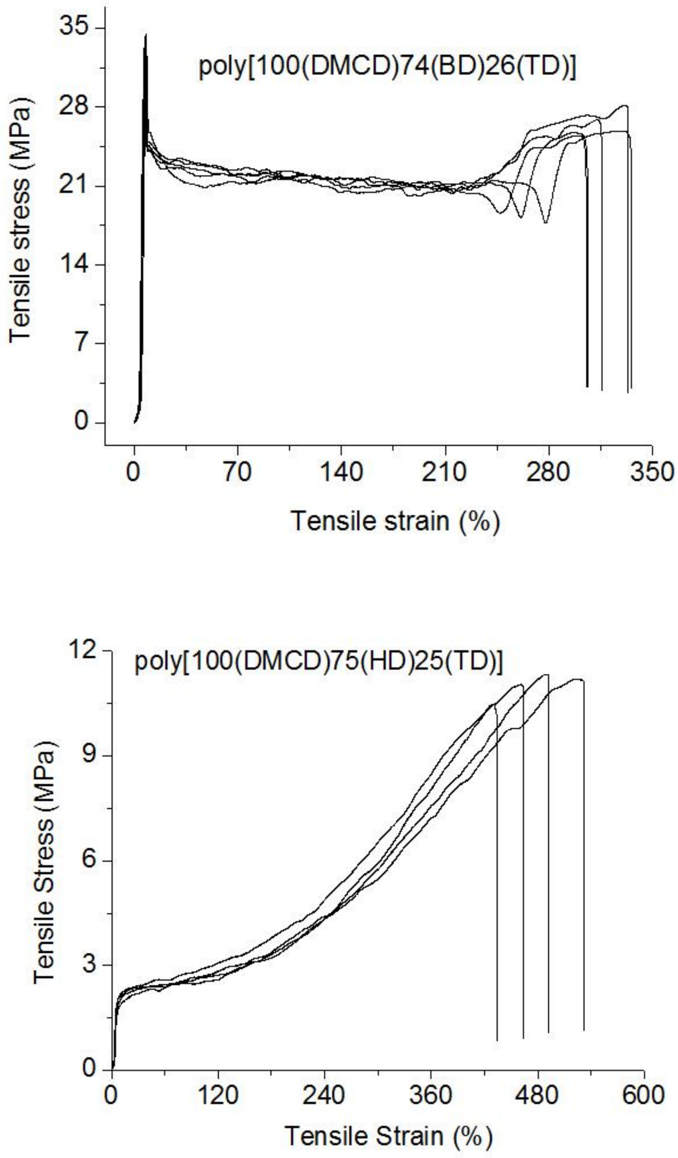


Figure 5.4 Stress-strain properties of poly[100(DMCD)74(BD)26(TD)] (top) and poly[100(DMCD)75(EG)25(TD)] (bottom) at 23 ^{o}C

Tensile data in **Table 5.1** and **Figure 5.4** reveals that poly[100(DMCD)74(BD)26(TD)] had a higher modulus and stress to yield than poly[100(DMCD)75(HD)25(TD)], which had more elastic-like properties. High elongation to break (319 %) and high modulus (1.17 GPa) of poly[100(DMCD)74(BD)26(TD)] indicated that it was ductile and a relatively tough material. Therefore, BD was considered to possess a suitable chain length to demonstrate enhanced ductility and enhanced modulus of triptycene polyesters. A decrease of HD content in triptycene copolyester from 75 mol% to 65 mol% resulted in a brittle material with low elongation to break (10 %) at ambient temperature. When the HD content was lowered to 50 mol%, poor films were obtained and tensile tests were not possible for this triptycene copolyester composition. The TD-containing polyesters poly[100(DMCD)75(BD or HD)25(TD)] also exhibited much higher modulus at 23 ^{o}C when compared to the HBE analogues poly[100(DMCD)75(BD or HD)25(HBE)], which were highly flexible with a modulus of about 1 MPa as shown in **Table 5. 1**.

Mechanical property analysis of copolyesters containing BHPS, BHPC or BHPT. Numerous bisphenol derivatives have been synthesized and incorporated into polymer backbones to increase the T_g for high performance materials.[9, 18] *Bis*[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS) is commercially available; BHPC and BHPT were synthesized as described in the synthesis section. In this study, they were incorporated into identical polyester backbones by replacing the triptycene units with the respective bisphenol derivatives, BHPS, BHPC or BHPT. The properties of their copolyesters are also shown in **Table 5.1**. We can see that poly[100(DMCD)74(BD)26(TD)] still had the highest thermal stability and highest modulus among these copolyesters. The data thus confirms that the incorporation of TD into the polyester backbone can increase T_g due to its rigid structure. Furthermore, poly[100(DMCD)74(BD)26(TD)] had good elongation to break (319 %) and was not brittle. From the tensile curves of poly[100(DMCD)74(BD)26(BHPC)] (**Figure 5.5**), we concluded that it had somel elastic-like properties with a low modulus (only 4 MPa) since T_g was very close to the ambient temperature, at the temperature where the tensile measurements were run.

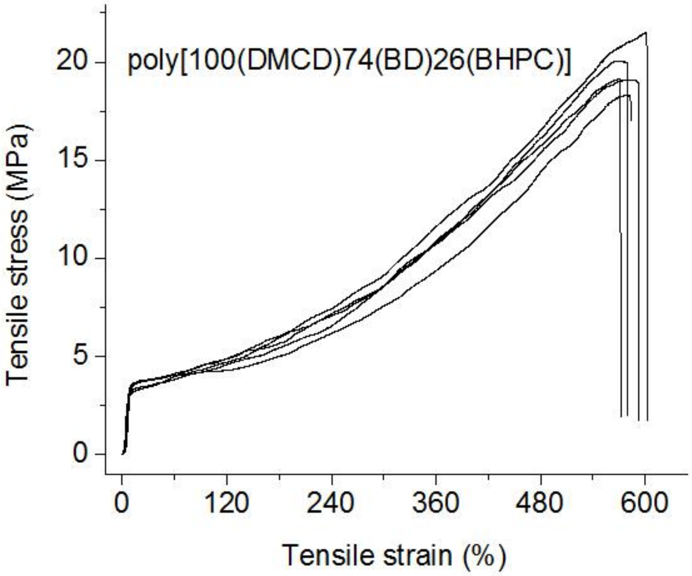


Figure 5.5 Stress-strain properties of poly[100(DMCD)74(BD)26(BHPC)]

The copolyester poly[100(DMCD)74(BD)26(BHPS)] (**Figure 5.6**) had a lower T_g and modulus, but a higher elongation than the corresponding TD copolyester. However, the reproducibility of tensile testing is not good due to the defects of some samples.

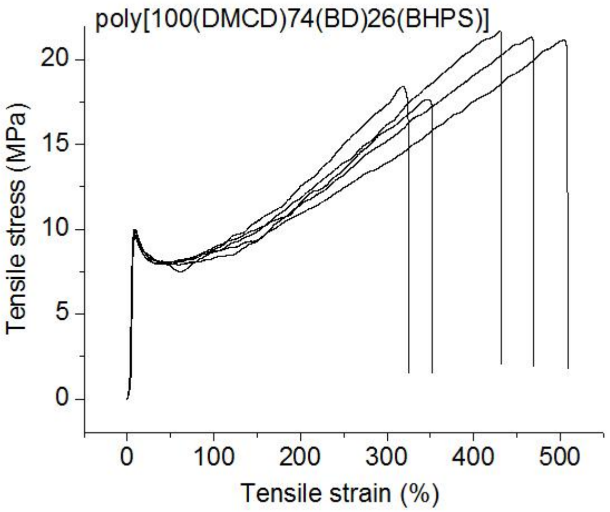


Figure 5.6 Stress-strain properties of poly[100(DMCD)74(BD)26(BHPS)]

The glassy solid BHPT possess an amorphous and bulky structure due to the three pendent methyl groups. No melting endothermic peak was observed in DSC curves of BHPT. When the BHPT concentration was also fixed at 25 mol%, the modulus and T_g values of the corresponding copolyester were significantly less than the triptycene-containing copolyester poly[100(DMCD)74(BD)26(TD)].

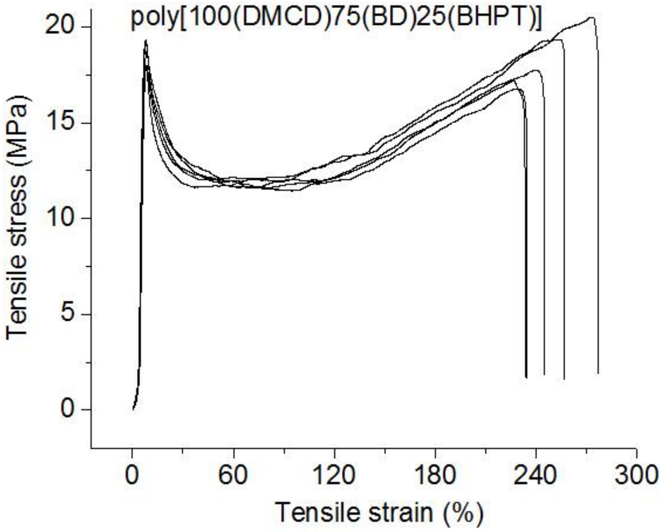


Figure 5.7 Stress-strain properties of poly[100(DMCD)75BD25(BHPT)] at 23 ^{o}C

From the above tensile curves for poly[100(DMCD)74(BD)26(BHPT)] (**Figure 5.7**), the copolyester based on BHPT was found to be a higher modulus and more ductile material with a yield point, although no necking was observed during the deformation. However, when compared to poly[100(DMCD)74(BD)26(BHPT)], the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] exhibited the synergistic effect observed by Swager, Thomas, *et al*. because both the elongation to break and modulus of the triptycene copolyester were improved. The distinct upward turn in tensile curves in **Figure 5.4** was due to strain hardening, which began at a fairly high level of strain. Necking formation was also observed for poly (100(DMCD)74(BD)26(TD) and was similar to the observation of Swager, Thomas, *et al.*[11] However, the polyesters of this study did not show crystallinity in contrast to Swager, Thomas, *et al.*[11]

In order to verify if crystallization was induced during the deformation, we obtained the X-ray diffraction of the elongated polymer film, which was maintained in the stretched condition during the measurement. **Figure 5.8** shows the X-ray diffraction traces for both the original and stretched samples. No significant difference between these films was observed. The broad diffuse peaks (almost across 20 ^{o}) indicated that both samples were amorphous.

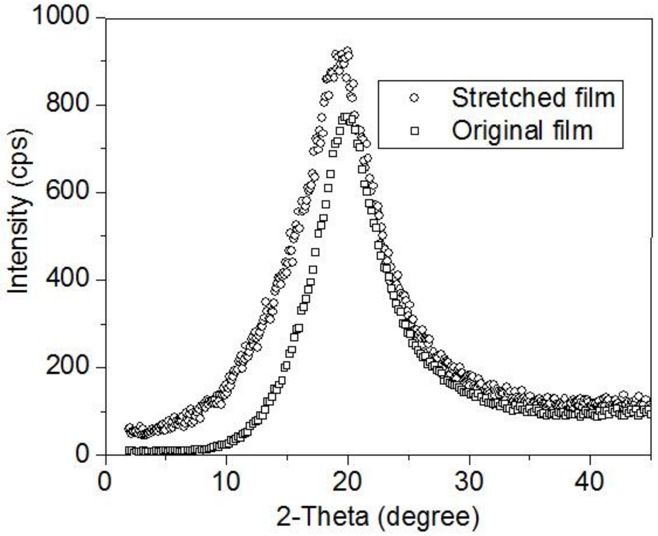


Figure 5.8 X-ray diffraction traces of poly (100(DMCD)74(BD)26(TD) films before and after stretching

In order to better compare the mechanical properties of triptycene polyesters to non-triptycene analogs in their glassy states, tensile measurements at low temperatures were carried out and the results are shown in **Table 5.2**. The tensile properties of these non-triptycene polyesters were measured at -25 ^{o}C except for the HBE-containing polyester, which was measured at -40 ^{o}C due to its low T_g. All copolyesters in **Table 5.2** had comparable glassy modulus values and were brittle at temperatures well below their T_g's. Since the tensile elongation to break of the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] was greatly decreased at -25 ^{o}C, this triptycene polyester did not behave differently in regards to ductility and modulus when compared to the other copolyesters of this study containing rigid and bulky units (BHPS, BHPC and BHPT) measured at well below T_g. These data differ from the earlier results of Swager and Thomas, *et al.*[11] who observed ductile behavior for their triptycene-containing copolyesters at -30 ^{o}C.

Table 5.2 Tensile properties of various copolyesters at -25 ^{o}C or -40 ^{o}C*

Various copolyesters with similar compositions (T_g)^a	Tensile Stress at break/yield (MPa)	Tensile strain at break (%)	Modulus (MPa)
DMCD/BD/BHPS (32) 100/74/26	46 ± 6 (break)	6 ± 1	1406 ± 96
DMCD/BD/BHPC(26) 100/74/26	50 ± 3(yield)	19 ± 2	1448 ± 65
DMCD/BD/BHPT(36) 100/75/25	51 ± 4(yield)	10 ± 1	1526 ± 82
DMCD/BD/TD(44) 100/74/26	69 ± 3(break)	8 ± 0.4	1688 ± 61
*DMCD/BD/HBE(4) 100/74/26	37 ± 4(break)	24 ± 5	952 ± 66

^{a}T_g values are shown in parentheses; The tensile tests of poly(DMCD/BD/HBE) was run at -40 ^{o}C

DMA spectra of triptycene and various non-triptycene polyesters are presented in **Figure 5.9.** The plots of storage modulus versus temperature indicate that all polyesters possessed an expected glassy storage modulus (above 1GPa) except for the HBE-containing polyester. The α peaks in the tan δ curves, accompanied by a sharp decrease in modulus, corresponded to the T_g's of the respective polyesters. The triptycene polyester displayed the highest glassy storage modulus (above 1.8 GPa) and T_g (66 ^{o}C from tan δ), together with the widest glassy plateau well past room temperature among these polyesters, while the HBE-containing polyester showed the lowest glassy DMA modulus of 0.7 GPa and T_g of 21 ^{o}C. The tan δ T_g was about 20 ^{o}C higher than the DSC T_g as expected.

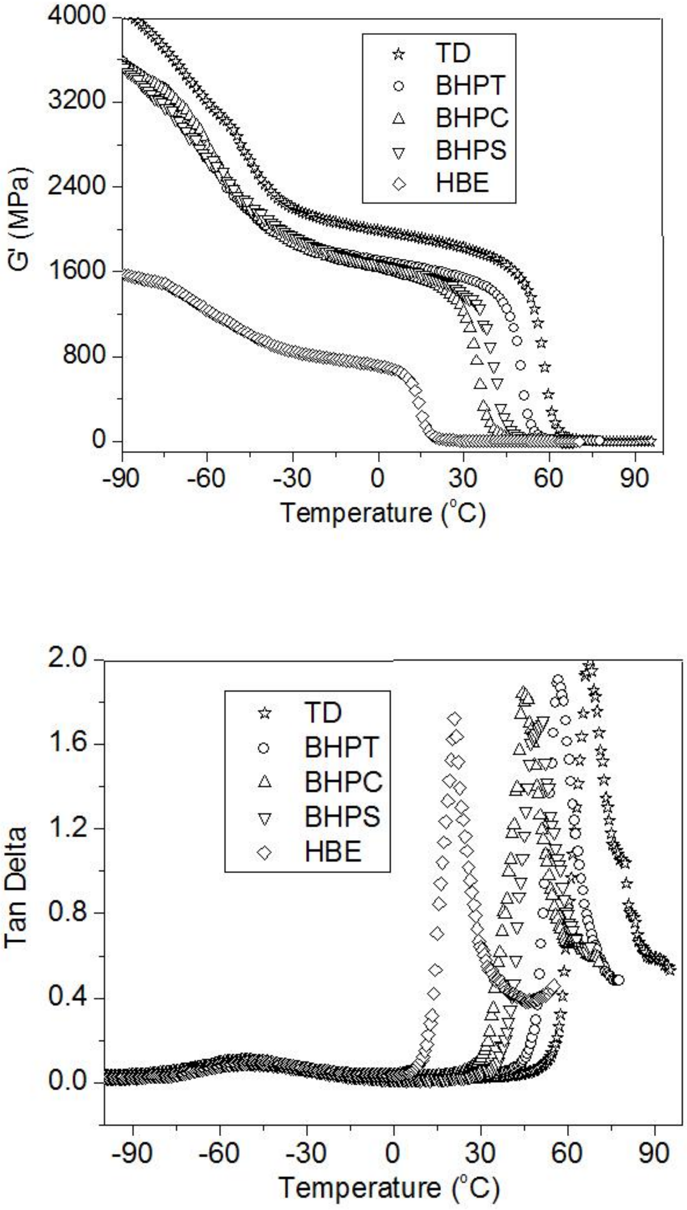


Figure 5.9 DMA of poly[100(DMCD)75(BD)25(TD/BHPT/BHPC/BHPS/HBE)]

All copolyesters exhibit the existence of a secondary relaxation tan δ peak from -57 to -51 °C with about the same intensity. The conformational changes of the cyclohexyl units in the polyester backbones are the origin of sub-T_g loss peaks. It is of interest to note that other cyclohexyl group-containing polyesters, such as the poly(1,4-

cyclohexylenedimethylene terephthalate) (PCT), were confirmed by Yee *et al.* to have a weak transition in this region as well.[19]

5. 5 Conclusions

In summary, we have described the melt-phase synthesis of triptycene-containing polyesters using a new triptycene primary diol and we also characterized some of the properties of these new materials. All TD-containing polymers in this study had higher thermal stability by TGA and higher T_g′s than the corresponding non-triptycene analogs. The T_g of TD-containing polymers increased with increasing TD content. The results from tensile tests revealed that poly[100(DMCD)74(EG)26(TD)] was rigid but brittle at ambient temperature. However, the copolyester poly[100(DMCD)74(BD)26(TD)] was found to simultaneously possess higher modulus and excellent ductility at ambient temperature. This indicates that its short flexible spacer (butane unit) in combination with triptycene units can promote an improved ambient temperature modulus and enhanced ductility. However, our results do not confirm the synergistic effect observed by Swager, Thomas, *et al.* since the triptycene copolyester does not show enhanced ductility when compared to other copolyesters containing rigid and bulky units (BHPS, BHPC and BHPT) at -25 ^oC. These polyesters, including triptycene polyesters, are brittle and display similar modulus values at temperatures well below their DMA (tan δ) T_g's. Poly[100(DMCD)74(BD)26(TD)] differs from the triptycene-containing copolyesters of Swager, Thomas *et al.*[11], which still exhibits ductile behavior at -30 ^oC.

5.6 Acknowledgements

The authors are grateful to Eastman Chemical Company for donating DMCD and Dr. Liang Chen for synthesis of the monomer BHPT. We gratefully acknowledge Prof.

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5.8 Supporting information:

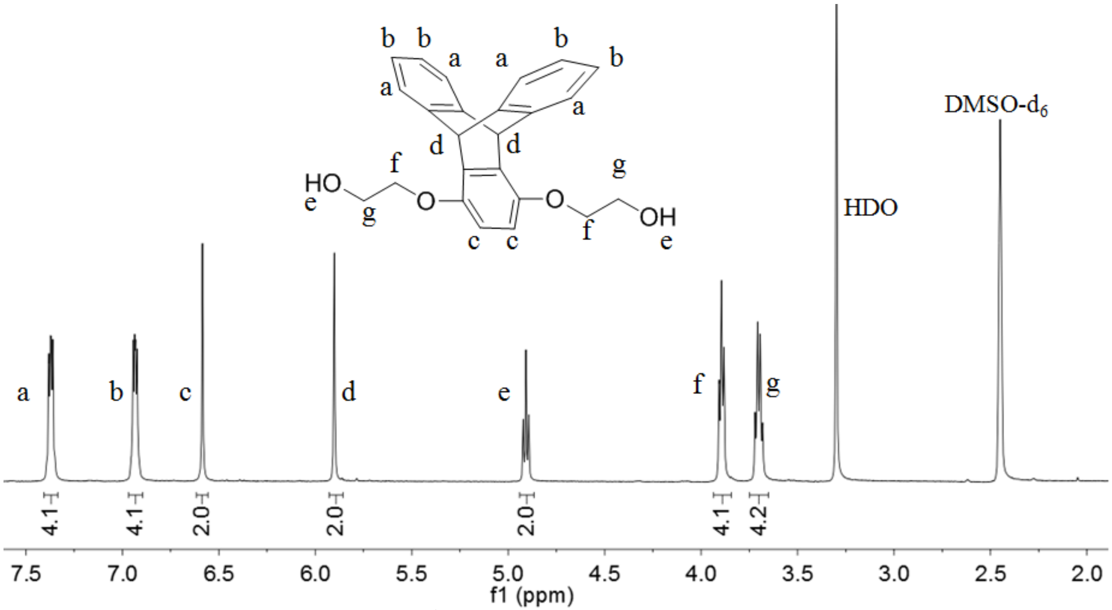


Figure 5.10 ^{1}H NMR of triptycene diol (TD)

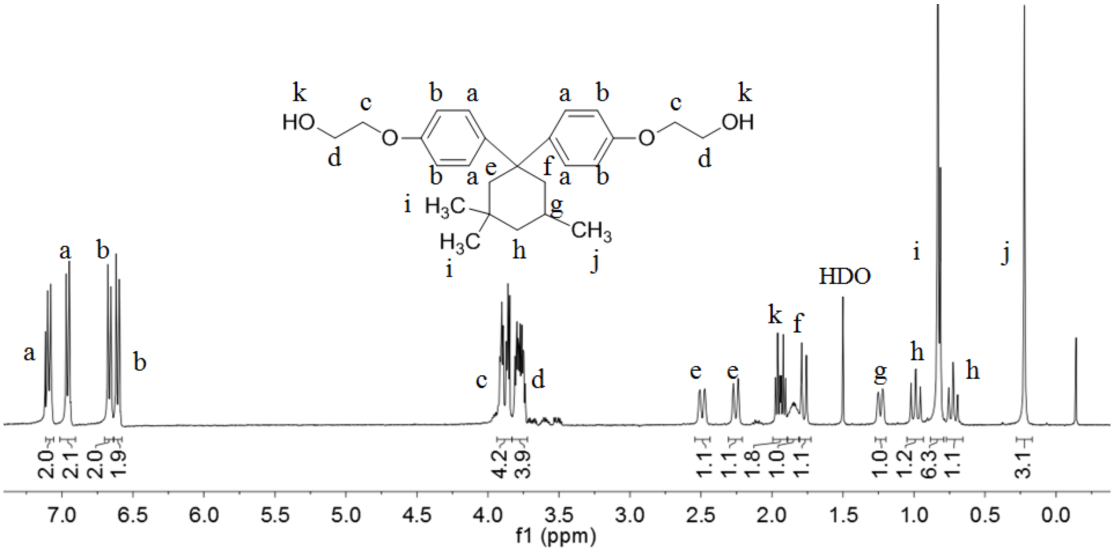


Figure 5.11 ^{1}H NMR of BHPT

Figure 5.12 A film of poly[100(DMCD)74(BD)26(TD)] prepared by a melt press

Figure 5.12 indicates that the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] is transparent due to its amorphous characteristics.

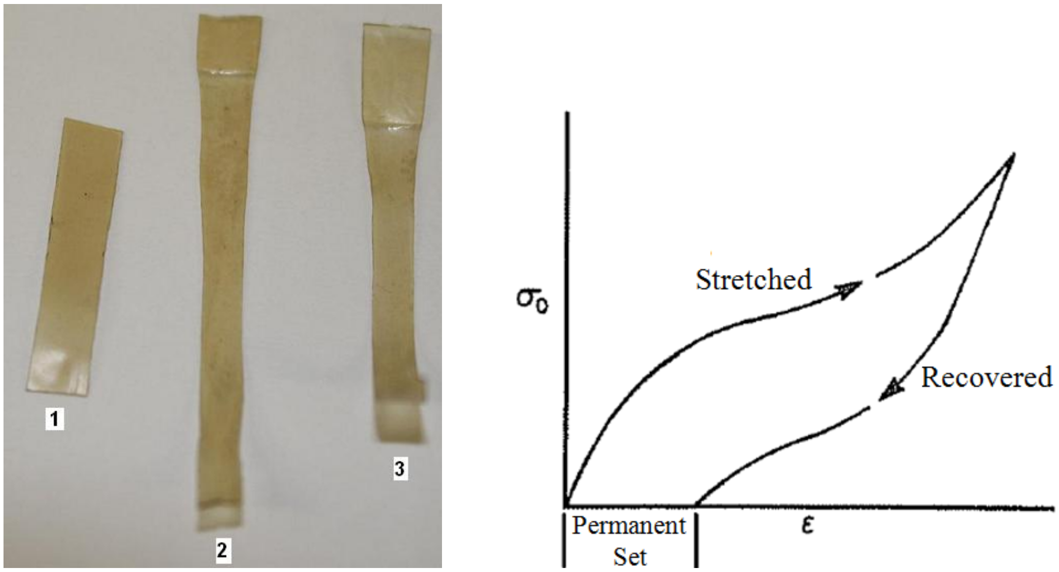


Figure 5.13 Stress-stain behavior of the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] illustrating the phenomenon of permanent set

The initial length of Film **1** in **Figure 5.13** before streching was 15 mm, the film was then stretched to a length of 50 mm, which resulted in breakage on one side of the film. The broken film was measured at 46 mm. After 10 minutes, the film was recovered and measured once again—its length was recorded to be 26.5 mm. We can see from this experiment that the initial dimension of Film 1 was not totally recovered and a permanent set, (i.e., unrecovered strain) was observed.

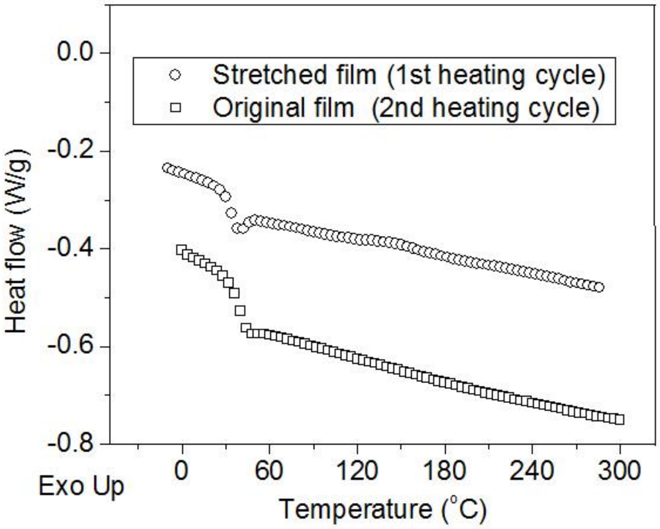


Figure 5.14 DSC traces for the film of the triptycene copolyester poly[100(DMCD)74(BD)26(TD)] before and after stretching

Figure 5.14 confirms very little difference in the T_g of the triptycene polyester poly[100(DMCD)74(BD)26(TD)] film before and after stretching. Therefore, we can again conclude that the polyester sample was still amorphous after stretching and no crystallization was observed.

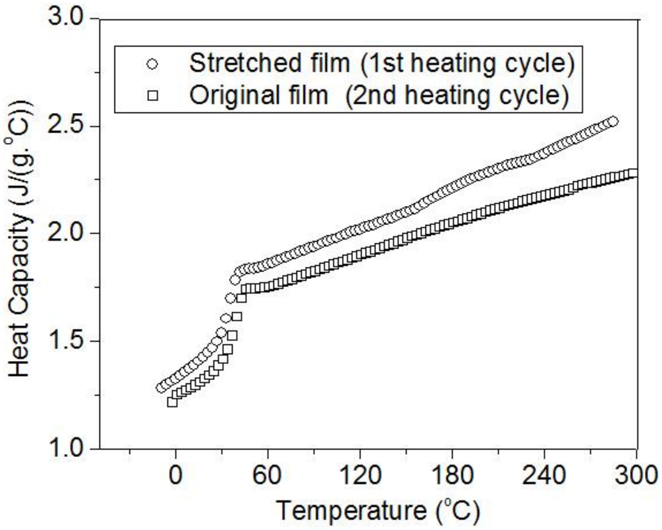


Figure 5.15 Heat capacity versus temperature for triptycene polyester poly[100(DMCD)74(BD)26(TD)] before and after stretching [ΔCp ~ 0.5 J/(g· °C)]

In general, the heat capacity of a given material is constant at a given temperature and pressure. Moreover, the value of Δ*Cp* at glass transition temperature is directly proportional to the weight fraction of a material in its pure amorphous phase. **Figure 5.15** indicates that no apparent difference was observed for the heat capacity of the triptycene polyester poly[100(DMCD)74(BD)26(TD)] film before and after stretching. Therefore, this outcome suggests that the phase behavior of the polyester sample after stretching was not altered.

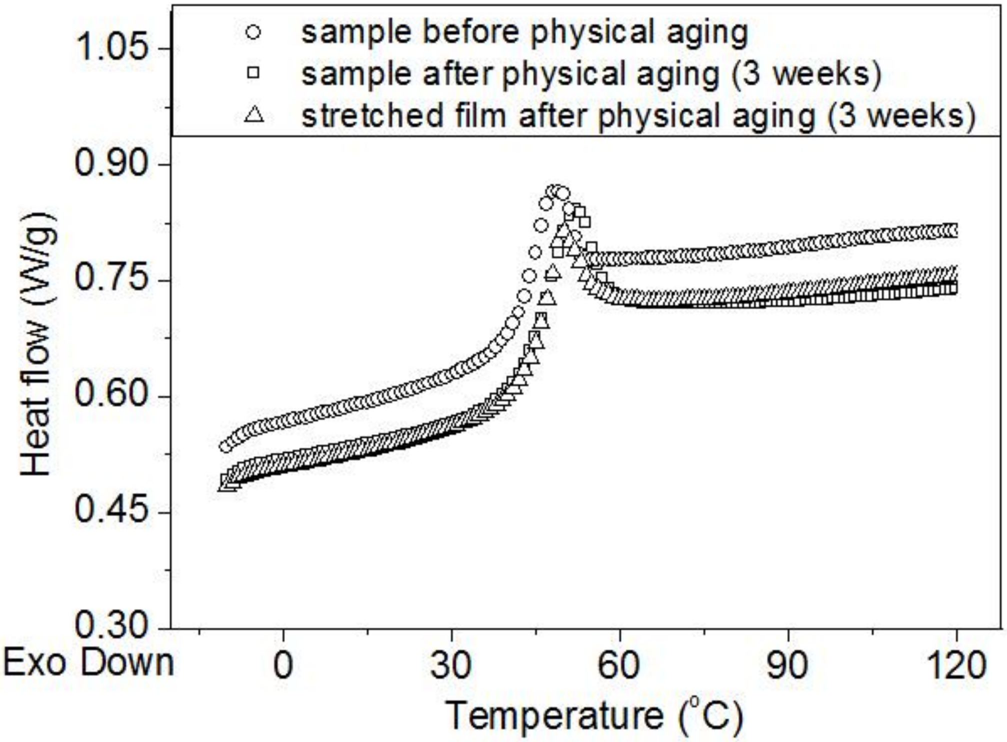


Figure 5.16 Effect of physical aging on the T_g of triptycene polyester poly[100(DMCD)74(BD)26(TD)] before and after stretched

As discussed in this chapter, in most cases we conducted tensile testing 24 h after the polyester film samples were made via compression molding so that the effect of physical aging on the properties of the respective polyesters could be minimized. However, the effects of physical aging on thermal properties were also studied, as shown in **Figure 5.16**. The tensile curves confirm that the T_g values for either the original sample or the stretched film did not change, even after aging the samples for three weeks.

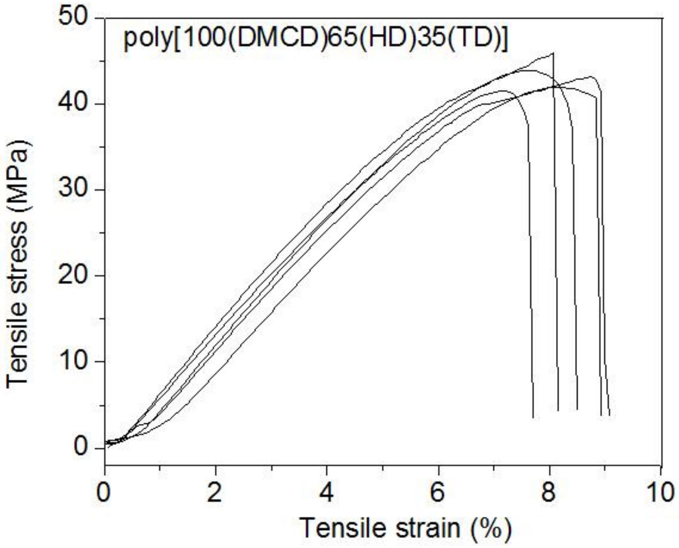


Figure 5.17 Tensile curves for triptycene polyester poly[100(DMCD)65(HD)35(TD)]

The tensile curves shown in **Figure 5.17** confirm that the copolyester based on 65 mol% HD and 35 mol% TD was brittle and it did not exhibit an advantageous combination of enhanced ductility and enhanced modulus. Moreover, we were unable to prepare dogbone specimens of the poly[100(DMCD)50(HD)50(TD)] due to its highly brittle characteristics.

Chapter 6: Melt-phase Synthesis and Properties of Other Triptycene Containing Copolyesters (unpublished)

6.1 Abstract

Other copolyesters based on the triptycene diol (TD) – triptycene-1,4-hydroquinone-bis (2-hydroxyethyl) ether, straight chain aliphatic co-diols – ethylene glycol (EG) or butane diol (BD), and a diester – dimethyl 1,4-cyclohexanedicarboxylate (DMCD), were synthesized via high temperature melt-phase polymerization. For the triptycene-containing PETG copolyesters, their mechanical properties were found to be dependent on the composition of triptycene diol. Some non-triptycene copolyesters based on enhanced contents of bis[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS), 1,1-bis[4-(2-hydroxyethoxy)-phenyl]cyclohexane (BHPC) or 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) were also prepared. These materials were still found to have lower T_gs and modulus at ambient temperature than the triptycene-containing copolyester poly[100(DMCD)74(BD)26(TD)]. However, our results still did not exhibit the synergistic effect observed by Swager *et al,*[1] which we attributed to the fact that the tensile elongation of the triptycene-containing copolyester poly[100(DMCD)74(BD)26(TD)] was not higher than the other analogous copolyesters containing rigid units described in this chapter.

6.2 Introduction

In the previous chapter, we reported the effects of incorporating the new triptycene primary diol (TD) and various hydroxyethoxylated bisphenols into amorphous melt-phase prepared copolyester backbones. The effects of the hydroxyethoxylated bisphenol units on the T_g of copolyesters was compared to the analogous results for the triptycene diol (TD). Although we did observe that the modulus of the poly[100(DMCD)74(BD)26(TD)] went up considerably, we did not observe any increased elongation at room temperature when compared to the copolyesters based on other bulky hydroxyethoxylated bisphenol derivatives, as described in Chapter 5. This difference was likely due to the fact that some non-triptycene copolyesters, such as poly[100(1,4-DMCD)74(BD)26(HBE)], possess a low T_g (4 ^oC), below room temperature. Therefore, we decided it would be interesting to conduct a comparison using a higher glass transition temperature PETG system, which would enable us to increase the diol chain lengths and still maintain the T_g well above room temperature. Moreover, a PETG system based on 1,4-cyclohexane dicarboxylic acid (via DMCD) would not negatively impact the mechanical properties of these materials. In this study, therefore, we varied the composition of TD in the PETG, and then assessed the thermal and mechanical properties of the resulting copolyesters. In addition, some non-triptycene copolyesters based on enhanced content of bis[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS), 1,1-bis[4-(2-hydroxyethoxy)-phenyl]cyclohexane (BHPC) or 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) were also prepared and their properties were compared to those of triptycene-containing copolyesters (described in Chapter 5).

6.3 Experimental

6.3.1 Materials

Dimethyl terephthalate (> 99 %), ethylene glycol (≥ 99 %), 1,4-butanediol (99 %) and 1,4-CHDM were purchased from Aldrich and used as received. Dimethyl 1,4-cyclohexanedicarboxylate (DMCD) (*cis*/*trans* = 3/1) was donated by Eastman Chemical

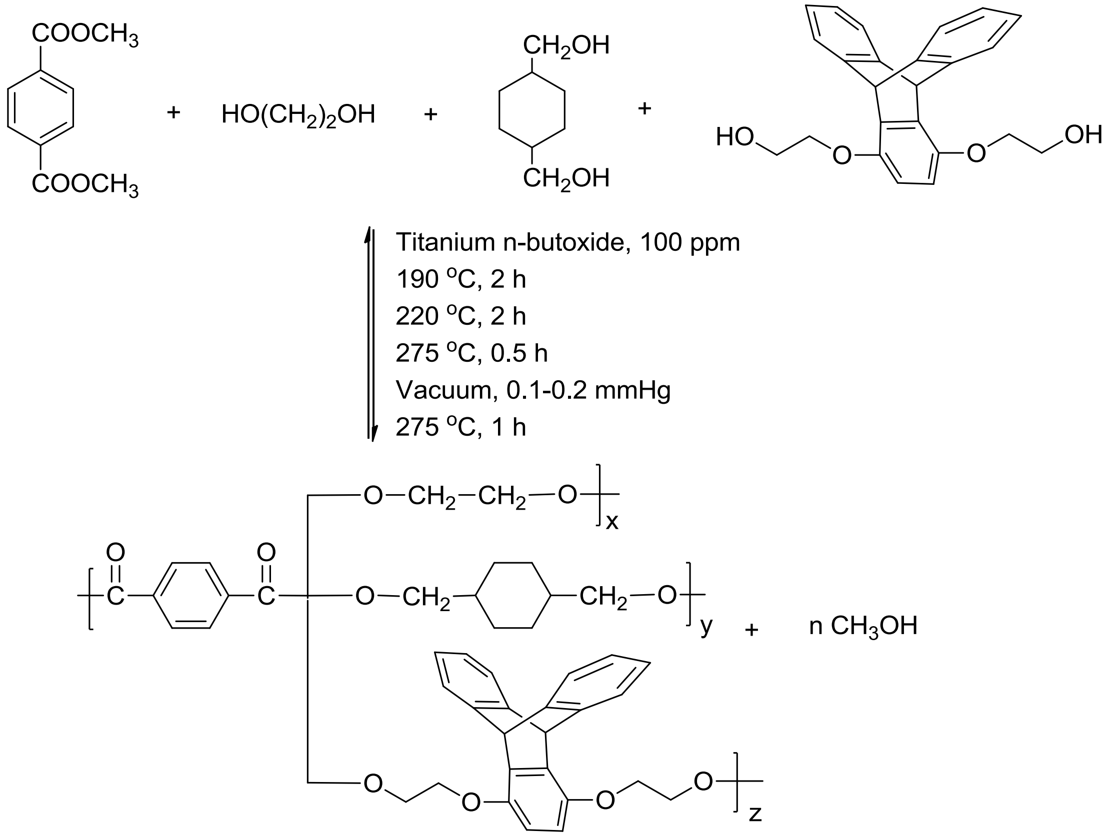
Company. Titanium(IV) n-butoxide (>98 %) was purchased from Alfa Aesar. BHPS, BHPC and BHPT were synthesized, as described in Chapter 5.

6.3.2 Synthesis

Preparation of catalyst solution. The titanium catalyst solution was obtained by dissolving titanium n-butoxide in n-butanol in a dry bottle under nitrogen at a concentration of 0.06 g/mL based on Ti.

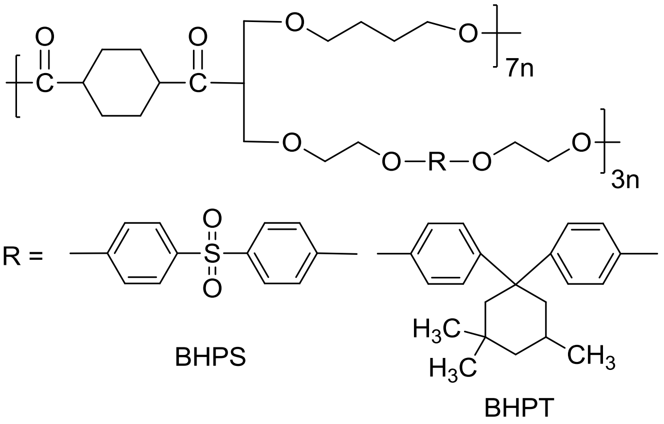
Nomenclature for the polyesters. The polymer nomenclature used in this chapter is based on a polyester containing 100 mol% of diester and 100 mol% of diol. For example, the polymer designated as poly[100(DMT)x(EG)y(1,4-CHDM)z(TD)] means that this targeted polymer contains 100 mol% DMT as the diester units and x mol% EG, y mol% 1,4-CHDM and z mol% TD as the diol units. The letters represent the various monomers, and numbers indicate the targeted mol% of those monomers.

Polymerization. Synthesis of poly[100(DMT)x(EG)y(1,4-CHDM)z(TD)]. The triptycene diol (TD) and its comonomers EG and 1,4-CHDM were copolymerized with DMT by melt polycondensation reaction. The detailed procedure is shown in **Scheme 6.1**, which is similar to a published method,[2] and is described here. To prepare the poly[100(DMT)50(EG)40(1,4-CHDM)10(TD)], 5.83g (0.03 mol) of DMT, 2.24 g (0.018 mol) of EG (100 % excess),1.3 g (0.009 mol) of 1,4-CHDM, and 1.12 g (0.003 mol) of TD were charged to a two-necked 50 mL reaction vessel equipped with a mechanical stirrer, nitrogen inlet, and condenser. The reactor was placed in a molten Belmont metal bath with a temperature controller. Titanium *n*-butoxide catalyst (100 ppm with respect to the targeted polyester) was added via syringe under nitrogen. The reaction mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h and 275 °C for 0.5 h. Methanol was collected in a receiving flask. At the end, high vacuum (0.1 -0.2 mm Hg) was applied to drive the reaction to high conversion for an additional hour. The polymer was allowed to cool to room temperature and then the vacuum was discontinued and nitrogen was passed through the system. The polymer was dissolved in chloroform, and precipitated into methanol. Finally, the solid precipitate was obtained by vacuum filtration and was dried under a vacuum oven at 60 °C overnight before characterization. The same procedure was used to prepare poly[100(DMT)x(EG)y(1,4-CHDM)(z)(TD)] with other compositions.



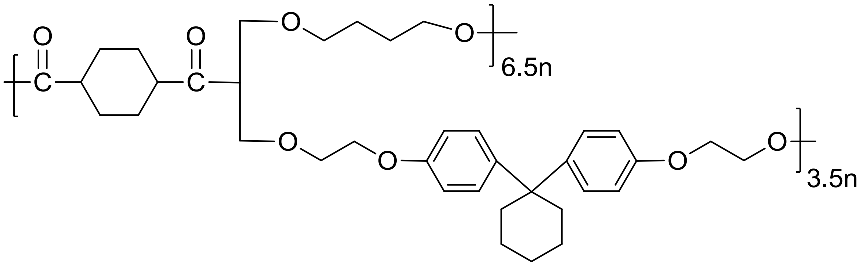
Scheme 6.1 Synthesis of poly[100(DMT)x(EG)y(1,4-CHDM)z(TD)]

Synthesis of poly[100(DMCD)70(BD)30(BHPS or BHPT)]. The non-triptycene polyesters based on BHPS and BHPT (depicted in **Scheme 6.2**) with the same compositions were synthesized for comparative purposes. The above experimental procedures were applied.



Scheme 6.2 Structures of poly[100(DMCD)70(BD)30(BHPS or BHPT)]

Synthesis of poly[100(DMCD)65(BD)35(BHPC)]. The non-triptycene polyesters based on 35 mol% BHPC were depicted in **Scheme 6.3.** The previous experimental procedures were applied to synthesize poly[100(DMCD)65(BD)35(BHPC)] for comparative purposes.



Scheme 6.3 Structure of poly[100(DMCD)65(BD)35(BHPC)]

6.3.3 Characterization

^{1}H NMR spectra were determined at 25 ºC at 400 MHz with an INOVA spectrometer. Molecular weights of synthesized polymers were determined using size exclusion chromatography (SEC) with a Waters 410 refractive index (RI) detector and viscometer DP detector. SEC measurements were performed at 30 ^{o}C in chloroform with a sample concentration 5.0 mg/mL at a flow rate of 1.0 mL/min. Thermogravimetric analysis (TGA) was conducted under nitrogen from 25 to 600 ºC at a heating rate of 10 ºC/min using a TA Instrument TGA Q500. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC Pyris I (TA instrument DSC Q2000). DSC data were obtained from -20 °C to 300 °C at heating/cooling rates of 20 °C/min under nitrogen circulation. The glass transition temperature was determined from analysis of the second heating cycle. Tensile measurements at room temperature (23 ^{o}C) were performed on an Instron Model 4400 Universal Testing System equipped with a 1KN load. The film samples were prepared using a PHI Model GS 21-J-C-7 compression molding press at 50 °C above T_g for 15 min. After the film samples were cooled down in ambient air, they were stored in a desiccator at ambient temperature. The molecular weights of the prepared film samples were unchanged from the original samples before compression molding. The film samples were dried in vacuum 24 h and then were cut to a dog bone shape at 40 × 4 × 0.3 mm (length × width × thickness) for tensile testing. The samples were tested at a rate of 15 mm/min using an initial grip-to-grip separation of 15 mm. Young's modulus was calculated from the linear part of the initial slope. All reported tensile data were averaged from at least three independent measurements and a standard deviation was also reported.

6.4 Results and Discussion

Thermal and mechanical property analysis of PETG copolyesters with different TD contents. Varying compositions (0 to 30 mol%) of the triptycene diol (TD) (0 to 30 mol%) were successfully incorporated into the PETG backbone. All the polyesters became highly viscous when the polymerization proceeded to high conversions, which typically took about 6 h. The copolyesters started to take on a deep yellow color (**Figure 6.1**) due to the titanium catalyst and the extended reaction time at high temperatures.

Figure 6.1 A film for poly[100(DMT)50(EG)30(1,4-CHDM)20(TD)]

The aromatic copolyester samples were soluble in common chlorinated solvents, such as dichloromethane and chloroform, which was expected based on the amorphous characteristic of the polyesters. In order to minimize the effect of physical aging on the thermal and mechanical properties of the respective polyesters, all the polyester films were tested at ambient temperature as soon as they were fabricated via compression molding. The thermal properties, molecular weights and tensile properties of the copolyesters with varying TD content are summarized in **Table 6.1**.

Table 6.1 Characterization results of copolyesters containing different TD contents

Polyester composition (^{1}H NMR)	TGA 5% weight loss at T_d (°C)	SEC M_n (g/mol)	T_g (°C)	Tensile Stress at break (MPa)	Tensile strain at break (%)	Modulus (MPa)
TD/ EG/1,4-CHDM/DMT 0/60/40/100	341	25,700	83	48 ± 1.5	326 ± 34	737 ± 24
TD/EG/1,4-CHDM/DMT 10/50/40/100	346	34,500	100	53 ± 5.7	9 ± 2	846 ± 55
TD/EG/1,4-CHDM/DMT 20/40/40/100	346	29,300	112	51 ± 5.3	8 ± 2	908 ± 51
TD/EG/1,4-CHDM/DMT 30/30/40/100	344	43,000	125	48 ± 2.0	6 ± 1	961 ± 67

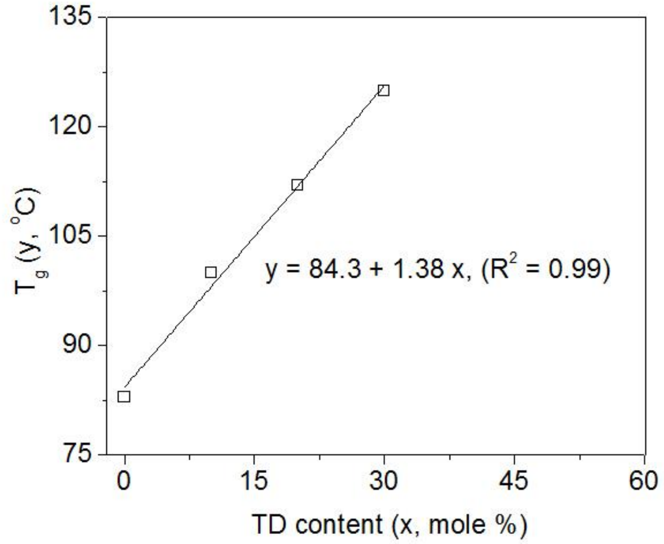


Figure 6.2 The TD content vs T_g of poly[x(TD)(60-x)(EG)40(1,4-CHDM)100(DMT)]

Table 6.1 confirms that all of the copolyesters display high molecular weights as well as high T_g values. These results are expected for the PETG copolyesters, as discussed in the literature review. The commercially available copolyester PETG shows a T_g of 81 °C,[3] which is consistent with our tabular data. It should also be noted that the T_g

of the triptycene-containing PETG increased linearly up to 125 ^{o}C for the poly[30(TD)30(EG)40(1,4-CHDM)100(DMT)] with increasing TD content, as shown in **Figure 6.2**. This data confirms that the triptycene unit can improve the T_g of polymers due to its bulky rigid Y-shaped structure, as shown in **Figure 6.3**.

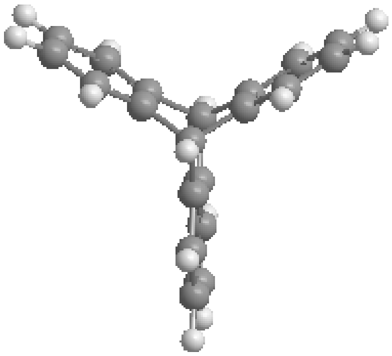


Figure 6.3 3-D structure of the tripycene unit

With respect to the tensile properties of these materials, however, the triptycene-containing PETG was brittle, as shown in **Figures 6.4** to **6.7**. It is likely that the interlocking effects reported by Swager *et al.* may not be operative when there are no simple extended threading units (alkyls).

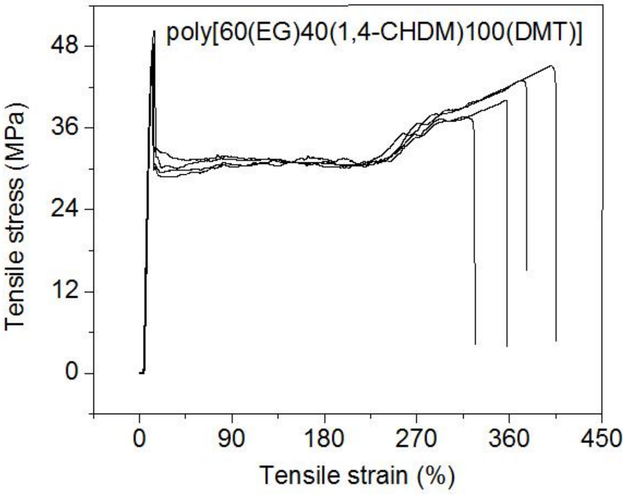


Figure 6.4 Tensile curves of PETG copolyesters without TD

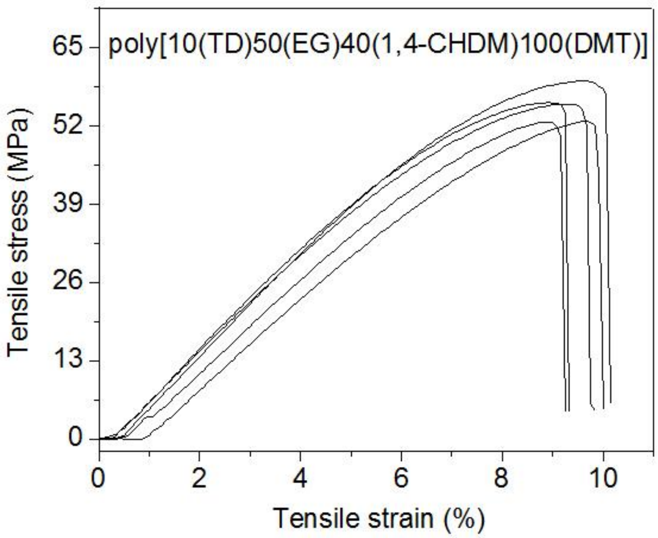


Figure 6.5 Tensile properties of PETG copolyesters with 10 mol% TD

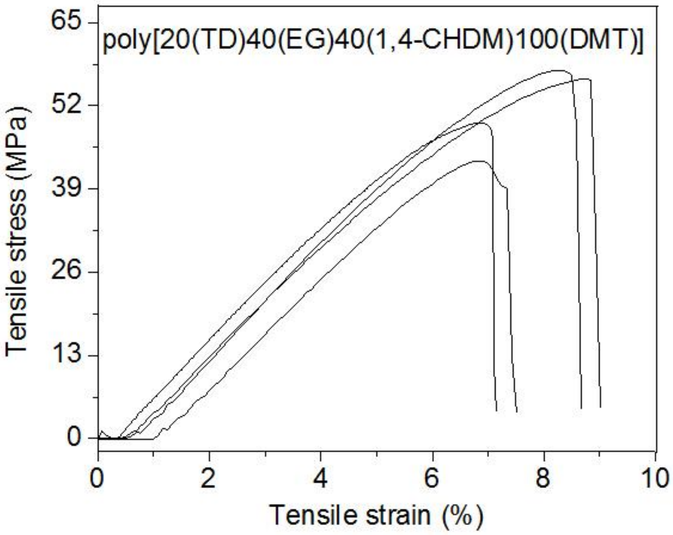


Figure 6.6 Tensile properties of PETG copolyesters with 20 mol% TD

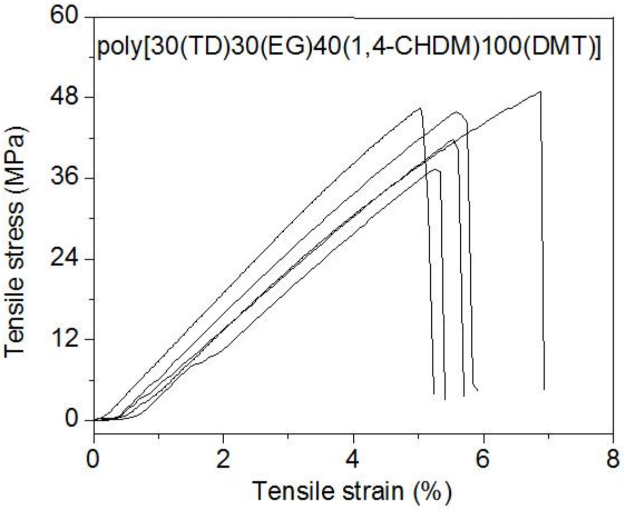


Figure 6.7 Tensile properties of PETG copolyesters with 30 mol% TD

Mechanical property analysis of copolyesters containing BHPS, BHPC or BHPT. The synthesis of BHPS, BHPC and BHPT was described in Chapter 5. This chapter described their incorporation into the polyester backbones by increasing their compositions. The properties of the resulting copolyesters are shown in **Table 6.2**.

Table 6.2 Characterization results of copolyesters containing BHPS, BHPC or BHPT

Copolyester composition (^{1}H NMR)	TGA T_d 5% weight loss (°C)	SEC M_n (g/mol)	T_g (DSC) (°C)	Tensile Stress at break (MPa)	Tensile strain at break (%)	Modulus (MPa)
DMCD/BD/BHPC 100/65/35	367	20,000	36	28 ± 2.0	457 ± 35	573 ± 14
DMCD/BD/BHPS 100/70/30	359	14,300	34	11 ± 2.0	311 ± 34	471 ± 27
DMCD/BD/BHPT 100/70/30	370	17,400	41	24 ± 4.9	320 ± 44	635 ± 36
DMCD/BD/TD 100/74/26	375	25,500	44	32 ± 2	319 ± 14	1169 ± 21

From this table, we can see that the poly[100(DMCD)74(BD)26(TD)] continued to display the highest thermal stability and highest modulus among these copolyesters. This finding confirms that incorporating TD into the polyester backbone can increase T_g due to its rigid structure. Moreover, the poly[100(DMCD)65(BD)35(BHPC)] (see **Table 6.1**) displayed a T_g of 36 ^{o}C and a modulus of 573 MPa, which is 10 times higher than the poly[100(DMCD)74(BD)26(BHPC)] (50 MPa), with a T_g of 26 ^{o}C. This finding was expected since the modulus typically experiences a significant drop at the glass transition temperature.[4] The tensile curves shown in **Figure 6.8** indicate that the poly[100(DMCD)65(BD)35(BHPC)] was a typical tough plastic with a yield point. Furthermore, this copolyester exhibited an enhanced elongation at break, in comparison to the triptycene-containing copolyester poly[100(DMCD)74(BD)26(TD)], which was discussed in Chapter 5.

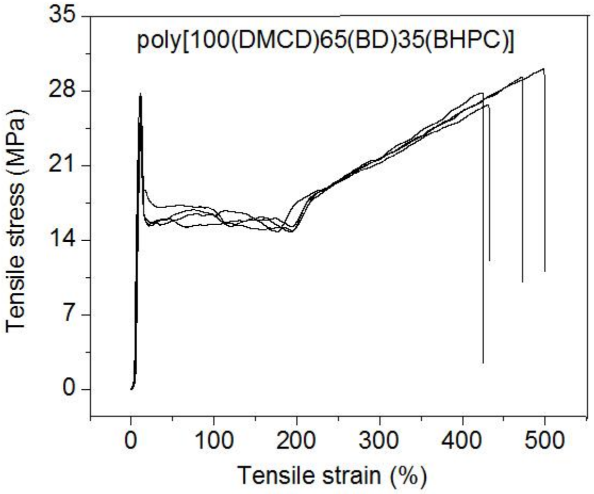


Figure 6.8 Tensile curves for poly[100(DMCD)65(BD)35(BHPC)]

The copolyester based on BHPS, the poly[100(DMCD)70(BD)30(BHPS)], displayed a higher modulus than the poly[100(DMCD)74(BD)26(BHPS)] (discussed in Chapter 5) due to the higher BHPS content of the former. However, the poly[100(DMCD)70(BD)30(BHPS)] also displayed lower molecular weights than the latter copolyester probably in that the non-volatility of BHPS renders it more difficult to push the melt phase polymerization to high conversion. However, the poly[100(DMCD)70(BD)30(BHPS)] showed good ductility, as shown in **Figure 6.9**.

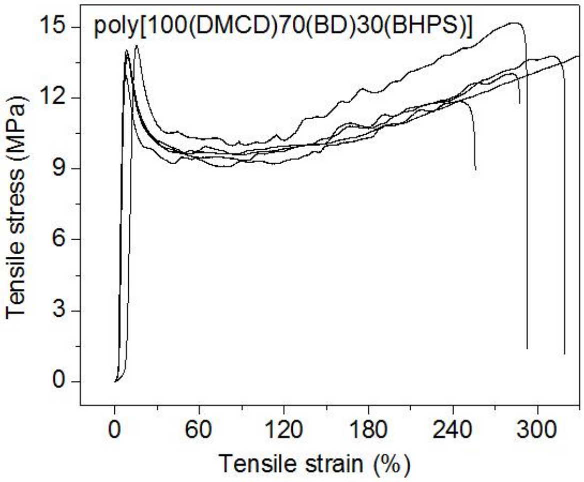


Figure 6.9 Stress-strain properties of poly[100(DMCD)70(BD)30(BHPS)] at 23 ^{o}C

Glassy solid BHPT possesses a bulky structure due to the pendant cyclohexylene ring and the three side methyl groups, as shown in **Figure 6.10**.

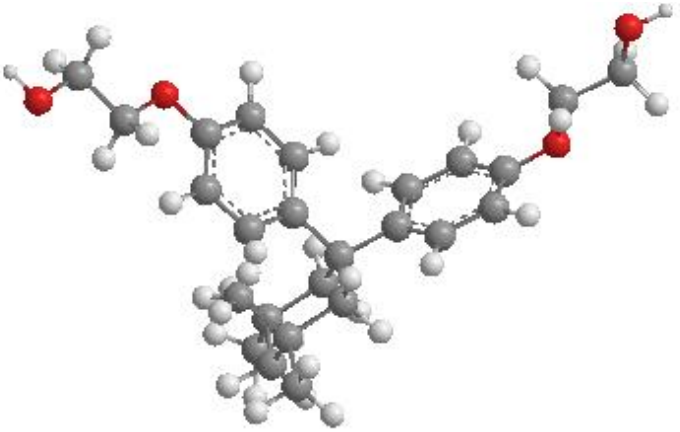


Figure 6.10 3-D structure of BHPT

To achieve a T_g level equivalent to the TD copolyester, the BHPT concentration was increased to 30 mol%. At this level, the poly[100(DMCD)70(BD)30(BHPT)] possessed a T_g of 41 ^{o}C, very close to that of the tripycene copolyester (**Table 6.2**).

However, the modulus of the poly[100(DMCD)70(BD)30(BHPT)] was still significantly less than that of the 25 mol% TD copolyester. This indicates that the rigidity of the triptycene unit is higher than that of the BHPT unit in our study. As shown in the tensile curves in **Figure 6.11**, we can see that the copolyester poly[100(DMCD)70BD30(BHPT)] was also a tough material, featuring a yield point (neck formation) and an upward curve (stress hardening). Moreover, this copolyester exhibited an excellent ductility. Once again, our results did not exhibit the synergistic effects observed by Swager *et al.*[1], since the tensile elongation of the TD-based copolyester was even lower than the other analogous non-triptycene-based copolyesters described in this chapter. For the present study, the polymer chain may not have threaded through the triptycene cavities as efficiently as the polymers containing ten carbons linear aliphatic components, as described in Swager's studies.

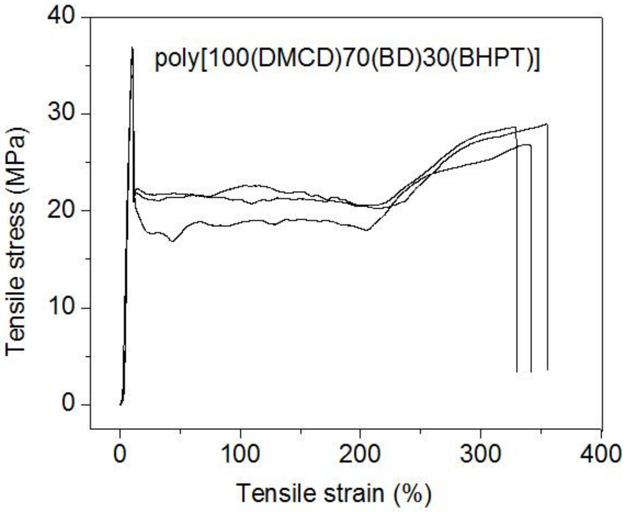


Figure 6.11 Stress-strain properties of poly[100(DMCD)70BD30(BHPT)] at 23 ^{o}C

6. 5 Conclusions

In summary, we synthesized triptycene-containing PETG polyesters based on the triptycene diol (discussed in Chapter 5) and characterized their resulting properties. The T_g of the TD-containing PETG copolyesters increased linearly with increasing TD content. Tensile test results revealed that the PETG copolyesters with 10 mol% to 30 mol % TD were rigid; however, they were also brittle. Again, it indicates that the interlocking effects that were reported by Swager *et al.* may not be operative when there are not some simple extended threading units. Copolyesters based on various hydroxyethoxylated bisphenols with increased mole percents still possessed lower T_gs and modulus than the copolyester poly[100(DMCD)74(BD)26(TD)] at ambient temperature. Therefore, our results still do not exhibit the synergistic effect observed by Swager *et al.* due to the fact that the tensile elongation of the TD-based copolyester was not as high as analogous copolyesters containing rigid units.

6.6 Acknowledgements

We are grateful to the Eastman Chemical Company for donating the DMCD. We gratefully acknowledge Prof. Timothy Long's group for allowing us to use their TGA, DSC and INSTRON equipment. We would also like to thank Mark Flynn in Prof. Judy Riffle's group for performing essential SEC measurements.

6.7 References

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Chapter 7: Synthesis and Properties of All-aliphatic Block Copolyesters Containing Neopentyl Glycol (NPG) and Cycloaliphatic Units

(Manuscript in preparation)

7.1 Abstract

Melt polycondensation was used to prepare a series of all-aliphatic block and random copolyesters containing the following aliphatic monomers: *trans*-dimethyl-1,4-cyclohexane dicarboxylate (*trans*-DMCD), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), neopentyl glycol (NPG), diethylene glycol (DEG), and dimethyl succinate (DMS). Polymer end group functionality was determined by NMR; molecular weight was determined via size exclusion chromatography (SEC). The oligomers and copolyesters were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and by tensile tests. The block copolyester containing DMCD-2 and NPG was observed to have a higher glass transition temperature than the block copolyester based on *trans*-DMCD and NPG. Although no microphase separation was observed from DSC traces, the block copolyester containing DMCD-2 was found to possess better mechanical properties than the block copolyester based on *trans*-DMCD. Furthermore, these block copolyesters were found to possess better mechanical properties than the corresponding random copolyesters.

7.2 Introduction

It is well known that block copolyesters possess better properties, such as improved barrier properties, higher impact, and higher heat distortion temperature, in comparison to random copolyesters of the same composition.[1] A number of block copolymers have been synthesized and studied. For example, block copolymers based on polycaprolactone (PCL) have been successfully synthesized in the presence of anionic coordination catalysts, which resulted in new materials with a broad range of controllable molecular parameters.[2] In contrast, block copolyesters intend to undergo rapid transesterification under typical processing conditions (e.g., extrusion and injection molding), often resulting in the loss of the desirable properties mentioned above. In order to reduce the degree of transesterification, which leads to adverse ester interchange reactions, researchers have explored various methods such as the use of transesterification reaction inhibitors and the selection of moderate processing conditions.[3, 4] For example, in 1966, Quisenberry[5] described a process for the production of segmented linear copolyesters containing poly(ethylene 2,5-dimethyl terephthalate) blocks. He claimed that segmented copolyesters were stable in the melt (up to 280 ^{o}C) for several hours, and thus were highly suitable for melt processing without undergoing randomization within the process time period. Quisenberry asserted that the 2,5-substitution process resulted in steric hinderance, which could inhibit the transesterification. It has also been reported that “transesterification-resistant” polymers could be produced by simply capping all reactive end groups. For example, poly(ethylene adipate) (PEA) could be blended with PET and then capped with phenyl ester groups to obtain a transesterification-resistant polymer.[6] Another approach for achieving the same goal involved the incorporation of alkyl side groups into polymer chains. According to the Newman’s principle, introducing alkyl side groups into polyester chains improved the hydrolytic stability and weatherability of polymers.[7] Research has also suggested that the incorporation of neopentyl glycol (NPG) with two methyl side groups could be effective in improving the hydrolytic stability of polyesters. Accordingly, Moad, *et al.* designed and synthesized segmented block copolyesters based on PET and poly (neopentyl isophthalate) (PNPIP).[8, 9] Initially, oligoesters from isophthalic acid (IPA) and NPG were synthesized by standard melt-phase polycondensation in the presence of a catalyst (butylhydroxyoxostannane), and were then copolymerized with PET to obtain multiblock copolyesters. The resulting block copolyesters were shown to have a number of desirable properties, including a high gas barrier and improved hydrothermal stability due to the steric hindrance of the methyl side groups. Furthermore, these materials were less likely to suffer structural randomization and property degradation as a result of transesterification during processing. A later patent awarded to Turner *et al.*[10] (US patent 7026027 B2) described the synthesis of amorphous copolyesters prepared from terephthalic acid (TPA), 1,4-CHDM and NPG. These copolyesters were claimed to have potentially valuable for the manufacture of medical devices, which have improved resistance to degradation when exposed to lipids. However, since these copolyesters contain aromatic groups, they are, in fact, not suited to many biomedical applications due to toxicity concern.

To the best of our knowledge, no experiments have been performed on all-aliphatic "transesterification-resistant" block copolyesters. The main objective of this project, therefore, is to synthesize all-aliphatic block copolyesters that display both desirable properties and structural integrity. An aliphatic diol NPG and a cycloaliphatic diester – *trans*-DMCD or DMCD-2 (instead of aromatic TPA or IPA) were selected to prepare block copolyesters. The incorporation of the rigid bicyclic diester DMCD-2 into block copolyesters was expected to increase the T_g of their hard segment. The effects of different cyclic diesters on thermal and mechanical properties of block copolyesters were investigated with the goal of achieving a balance between synthetic facilitation and transesterification resistance. These all-aliphatic block copolyesters were thought to possess excellent properties, which could make them useful for biomedical applications—for example, in the manufacture of cardiac-assist devices.

7.3 Experimental

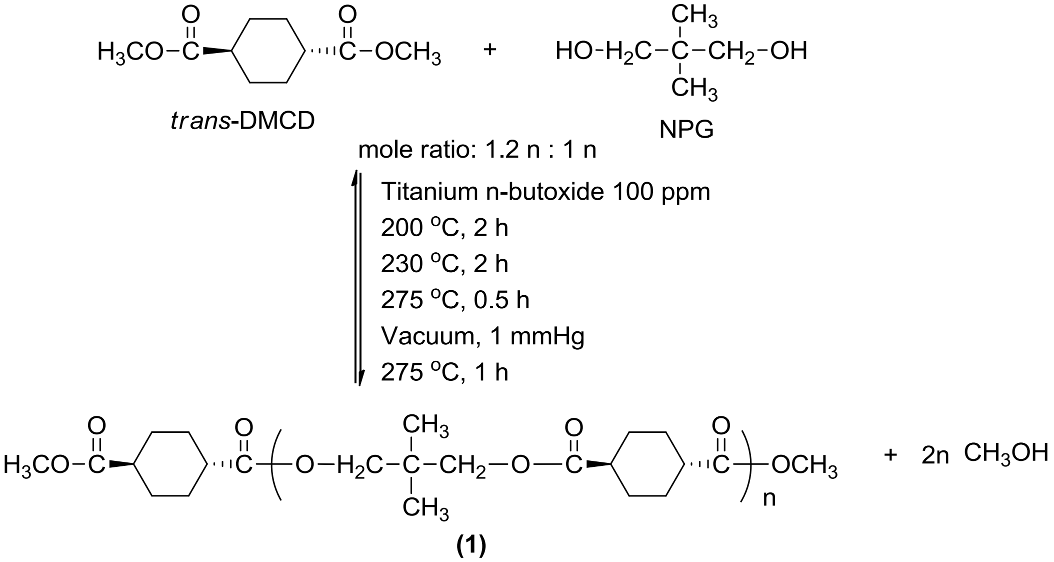
7.3.1 Materials

All reagents were used without further purification. Neopentyl glycol (NPG, 99 %), diethylene glycol (DEG, ≥ 99 %), dimethyl succinate (DMS, ≥ 98 %), dimethyl adipate (≥ 99 %), and tin (II) 2-ethylhexanoate (95 %) were purchased from the Aldrich Chemical Co. Titanium(IV) butoxide (98 %) was purchased from Alfa Aesar Chemical Co. *Trans*-DMCD was donated by Eastman Chemical Co.

7.3.2 Synthesis

Preparation of the catalyst solutions. A titanium catalyst solution was obtained by dissolving titanium n-butoxide in dry n-butanol in a dry bottle under nitrogen at a concentration of 0.08 g/mL based on Ti. A tin catalyst solution was prepared by mixing stannous octoate with dry toluene in a dry bottle under nitrogen at a concentration of 0.133 g/mL.

Model Reaction for oligoester (1) based on *trans*-DMCD and NPG (Scheme 7.1). 8.8 g *trans*-DMCD (44 mmol) and 4.16 g (40 mmol) of NPG (mole ratio of -$COOCH_3$ to -OH is 1.1:1) were added to a 50 mL round-bottom glass flask; the titanium catalyst solution (0.12 mL) was added under nitrogen. The reaction mixture was heated and stirred at 200 °C for 2 h, 235 °C for 2 h and 275 °C for 0.5 h. After that, a low vacuum was applied for about 10 min, followed by the use of a high vacuum (about 0.1 mm Hg) for an additional hour. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 3,600 g/mol, M_w: 7,000 g/mol; M_n from ^{1}HNMR: 3,100 g/mol (ester groups are the end ones). TGA: 5 % weight loss occurred at 275 °C, DSC: T_g: 17 °C, T_c: 79 °C, T_m: 183 °C.

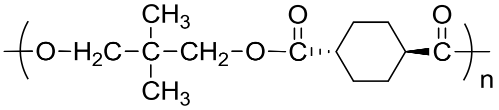


(1)

Scheme 7.1 Synthesis of oligoesters **(1)** based on *trans*-DMCD and NPG

Synthesis of homopolyester (2) based on *trans*-DMCD and NPG (as hard segment) (Scheme 7.2). 8.01 g *trans*-DMCD (40 mmol) and 4.16 g (40 mmol) of NPG (mole ratio of $-COOCH_3$ to -OH is 1:1) were added to a 50 mL two-necked round-bottom glass flask; the titanium catalyst solution (0.11 mL) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 200 °C for 2 h, 230 °C for 2 h and then 275 °C for 0.5 h. After that, a low vacuum was applied for about 10 min. Finally, a high vacuum (about 0.1 mm Hg) was applied for an additional 2 h. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 8,900 g/mol, M_w: 20,300 g/mol; PDI: 2.3.

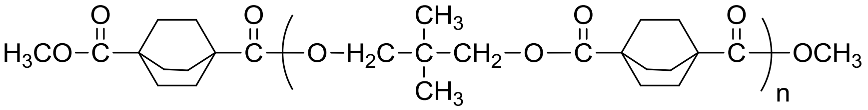
TGA: a 5 % weight loss occurred at 366 °C, DSC T_g: 26.4 °C, T_c: 108 °C (the first cooling cycle), T_m: 178 °C.



(2)

Scheme 7.2 Structure of a homopolyester **(2)** based on *trans*-DMCD and NPG

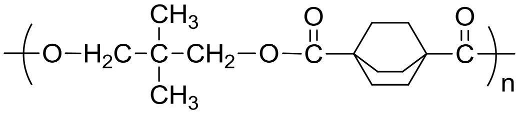
Oligoesters (3) with diester end groups based on DMCD-2 and NPG. 7.06 g DMCD-2 (31.2 mmol) and 2.71 g (26 mmol) of NPG (mole ratio of -$COOCH_3$ to -OH was 1.2:1) were added to a two-necked 100 mL round-bottom glass flask; the titanium n-butoxide catalyst (0.08 mL catalyst solution) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 200 °C for 2 h, 240 °C for 2 h and 275 °C for 0.5 h. After that, a low vacuum was applied for about 10 min. Finally, a high vacuum (0.1 mmHg) was applied for an additional 90 min. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 2,200 g/mol, M_w: 4,000 g/mol; M_n from ^{1}H NMR: 1,822 g/mol. TGA: 5 % weight loss at 310 °C, DSC: T_g: 36.5 °C, no T_c and T_m were observed.



(3)

Scheme 7.3 Structure of the oligoester **(3)** based on DMCD-2 and NPG

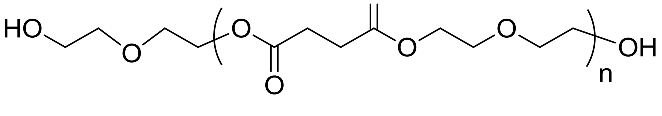
Synthesis of a homopolyester (4) based on DMCD-2 and NPG (as hard segments) (Scheme 7.4). 5.66 g DMCD-2 (25 mmol) and 2.60 g (25 mmol) of NPG (mole ratio of -$COOCH_3$ to -OH was 1:1) were added to a 50 mL two-necked round-bottom glass flask; titanium catalyst solution (0.08 mL) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 200 °C for 2 h, 240 °C for 2 h and 275 °C for 1.5 h. Then, a low vacuum was applied for about 10 min. Finally, a high vacuum (about 0.1 mmHg) was applied for an additional 2 h. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 2,500 g/mol, M_w: 4,400 g/mol; PDI: 1.8. M_n from ^{1}HNMR: 2,880 g/mol (ester groups are the end ones). T_g: 51 ^oC.



(4)

Scheme 7.4 Structure of the homopolyester based on DMCD-2 and NPG

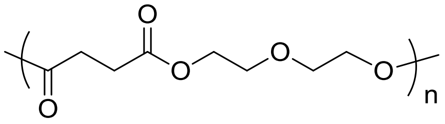
Synthesis of polyesters (5) with OH end groups based on dimethyl succinate (DMS) and diethylene glycol (DEG) (as soft segments) (Scheme 7.5). 8.77 g DMS (60 mmol), 9.54 g (90 mmol) of DEG (mole ratio of $-COOCH_3$ to -OH is 1:1.5) were added to a 50 mL two-necked round-bottom glass flask; the titanium catalyst solution (0.11 mL) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 180 °C for 2 h, 210 °C for 2 h and 230 °C for 0.5 h. Then, low vacuum was applied for about 10 min. Finally high vacuum (about 0.1 mmHg) was applied for an additional hour. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 47,000 g/mol, M_w: 83,300 g/mol; PDI: 1.8. TGA: 5 % weight loss at 255 ^oC, DSC: T_g: -20 ^oC, no T_c and T_m were observed.



(5)

Scheme 7.5 Structure of polyesters **(5)** with OH end groups based on DEG and DMS

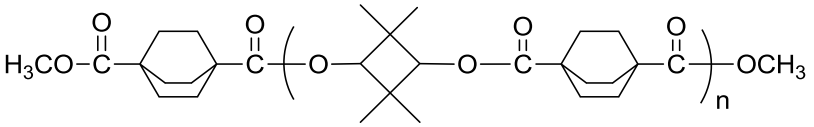
Synthesis of homopolyesters (6) based on dimethyl succinate (DMS) and diethylene glycol (DEG) (as soft segments) (Scheme 7.8). 7.31 g DMS (50 mmol) and 5.3 g (50 mmol) of DEG (mole ratio of -$COOCH_3$ to -OH was 1:1) were added to a 50 mL two-necked round-bottom glass flask, then the titanium catalyst solution (0.11 mL) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 170 °C for 2 h, 200 °C for 2 h and 230 °C for 0.5 h. Then a low vacuum was applied for about 10 min. Finally, the high vacuum (about 0.1 mm Hg) was applied for an additional 90 min. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 28,100 g/mol, M_w: 58,100 g/mol; PDI: 2.07. TGA: 5 % weight loss at 276 ^{o}C, DSC: T_g: -21 ^{o}C, no T_c and T_m were observed.



(6)

Scheme 7.6 Structure of homopolyesters **(6)** based on DMS and DEG

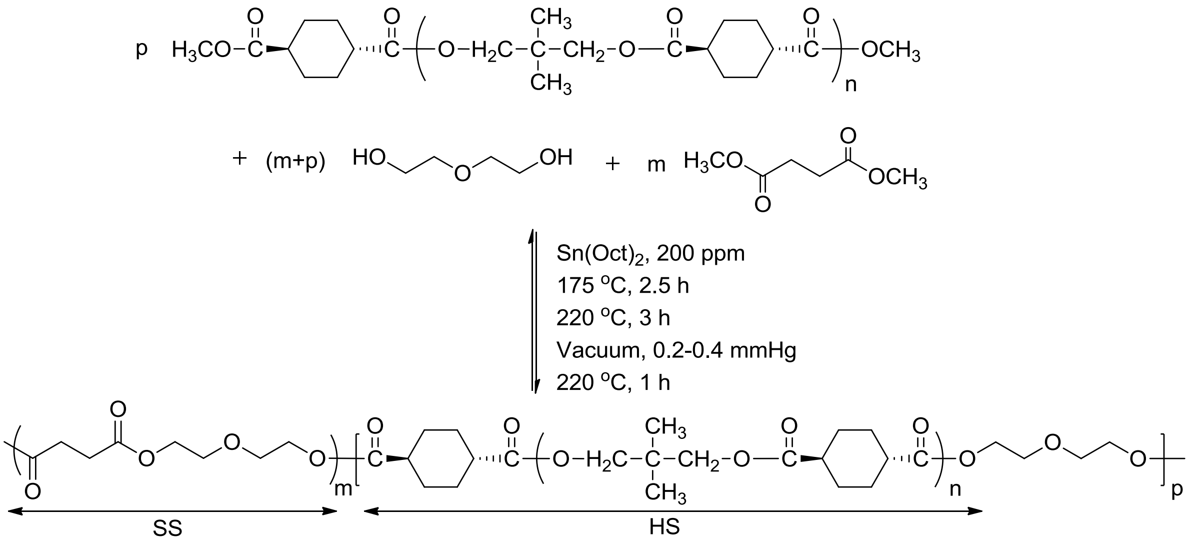
Oligoesters (7) based on DMCD-2 and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) (Scheme 7.9). 4.98 g DMCD-2 (22 mmol) and 2.88 g (20 mmol) of TMCBD (mole ratio of -$COOCH_3$ to -OH was 1.1:1) were added to a two-necked 100 mL round-bottom glass flask; the catalyst dibutyltin oxide (200 ppm based on polyester) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 200 °C for 1 h, 240 °C for 5 h and 275 °C for 1 h. After that, a low vacuum was applied for about 10 min, followed the application of the high vacuum (0.1 mmHg) for an additional hour. The final product was removed from the reaction flask without further purification. SEC in $CHCl_3$: M_n: 600 g/mol, M_w: 1,100 g/mol; DSC: T_g: 23.4 ^oC, no T_c and T_m were observed.



(7)

Scheme 7.7 Expected structure of oligoesters based on DMCD-2 and TMCBD

Synthesis of all-aliphatic block copolyesters (8) from the oligoester (1) (Scheme 7.8). 4 g (1.29 mmol) of the oligoester **(1)** as hard segments (40 wt%), 2.89 g (27.29 mmol) of diethylene glycol (DEG), and 3.80 g (26 mmol) dimethyl succinate (DMS) as soft segments (60 wt%) (mole ratio of -OH to $-COOCH_3$ was 1: 1), were added to a 100 mL round-bottom glass flask; the stannous octoate ($Sn(Oct)_2$) catalyst solution (0.05 mL) was then added under nitrogen. The reaction mixture was heated and stirred at 175 °C for 2.5 h, 220 °C for 3 h. After that, a low vacuum was applied for about 10 min, and then a high vacuum (0.1 mmHg) was applied for an additional hour. The final product was removed from the reaction flask without further purification.

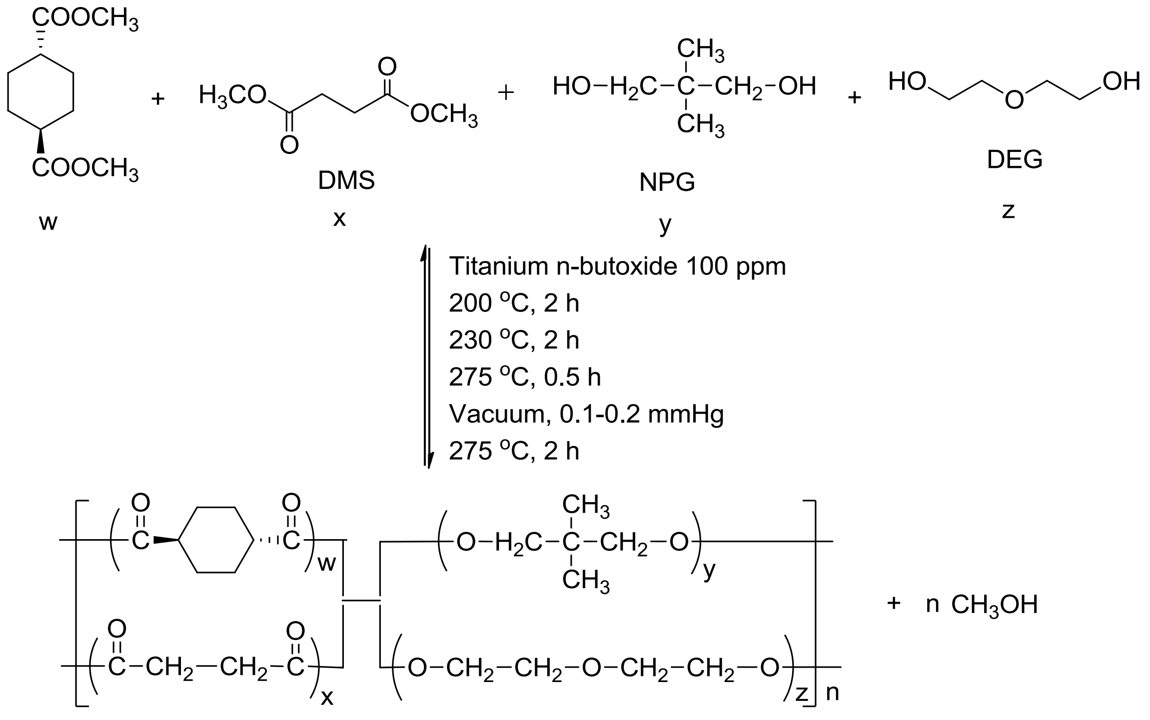


(8)

Scheme 7.8 Synthesis of block copolyesters based on *trans*-DMCD and NPG

This resulting copolyester was partially soluble in $CHCl_3$, THF, DMF, toluene and chlorobenzene, but it was completely soluble in 1,2-dichloroethane. SEC in $CHCl_3$: M_n: 21,300 g/mol, M_w: 78,100 g/mol; PDI: 3.66. TGA: a 5 % weight loss occurred at 294.4 ^oC. T_g from DSC: -11 ^oC.

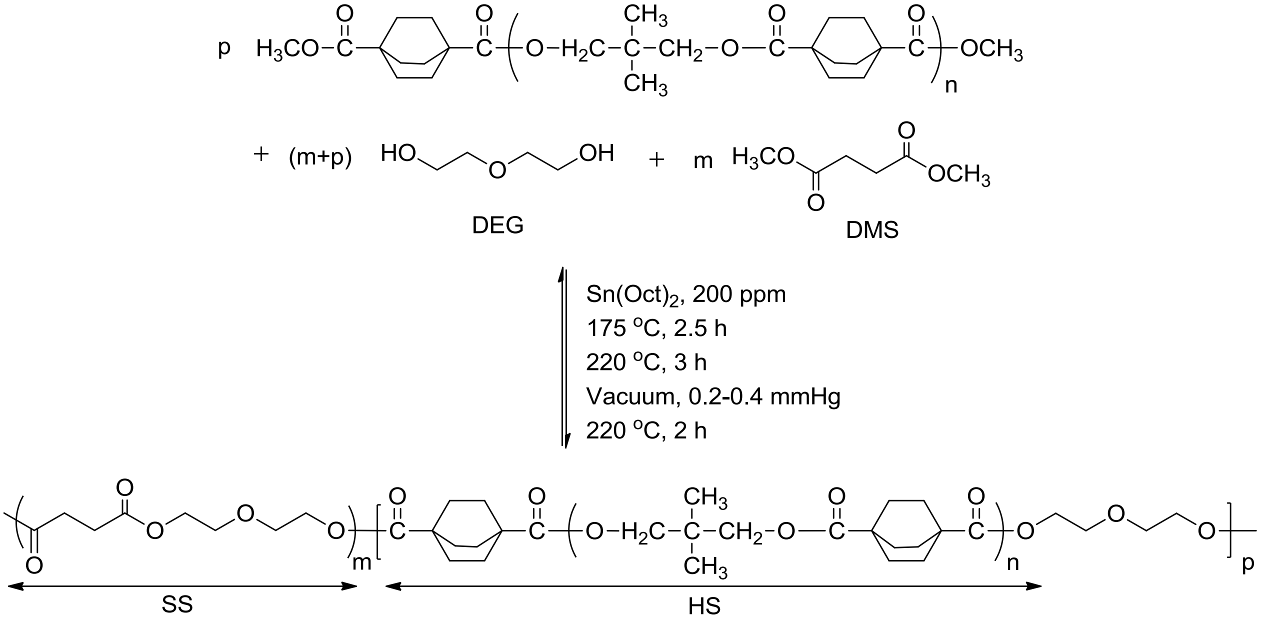
Synthesis of all-aliphatic random copolyesters (9) based on *trans*-DMCD, NPG, DMS and DEG (Scheme 7.9). A random copolyester based on *trans*-DMCD, NPG, DMS and DEG was synthesized for comparison. 8 g *trans*-DMCD (40 mmol), 6.43 g (44 mmol, 10 % in excess) dimethyl succinate (DMS), 4.24 g (40 mmol) of diethylene glycol (DEG), and 4.17 g (40 mmol) of NPG were added to a 100 mL round-bottom glass flask, followed by the addition of the catalyst titanium solution (0.05 mL) under nitrogen. A multi-step temperature procedure was used for the polymerization, i.e., the mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h and 275 °C for 0.5 h. After that, a low vacuum was applied for about 10 min, followed by the application of a high vacuum (0.1 mm Hg) for an additional 2 h. Finally, the product with a deep color was removed from the reaction flask without further purification. This random copolyester was a weak elastomer and was soluble in $CHCl_3$, M_n from SEC: 22,000 g/mol, M_w: 53,000 g/mol; PDI: 2.40. T_g: -7 ^oC. This experiment was repeated by replacing dimethyl succinate (DMS) with dimethyl adipate. However, a deep color product was obtained and it was still a very weak elastomer.



(9)

Scheme 7.9 Synthesis of random copolyesters containing *trans*-DMCD and NPG

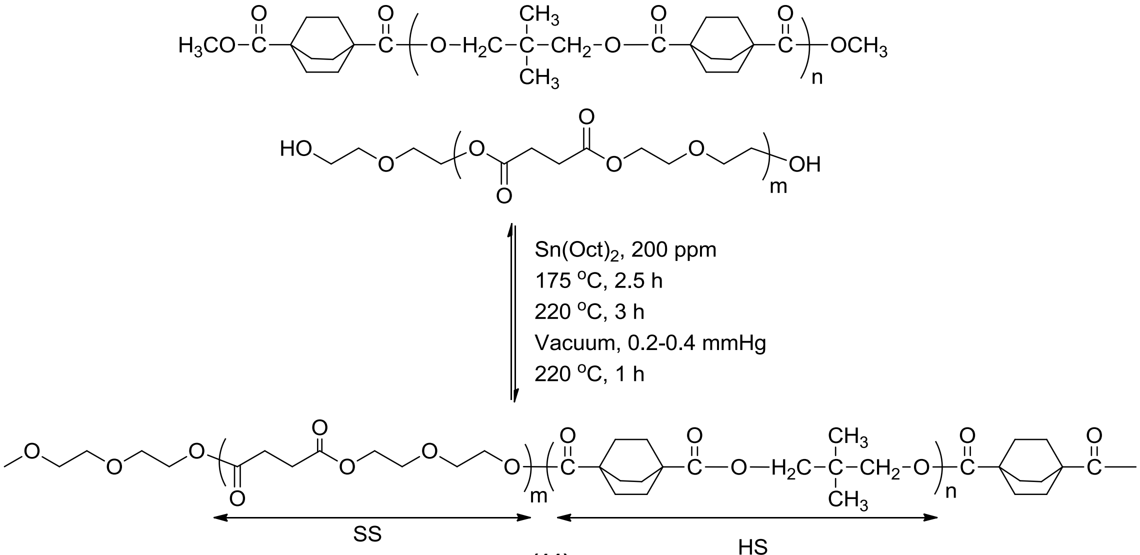
Synthesis of block copolyesters (10) from oligoester (3) containing DMCD-2 unit (Scheme 7.10). 4 g (1.39 mmol) oligoester **(3)** as hard segment (40 wt%), 2.89 g (27.3 mmol) of diethylene glycol (DEG), and 3.79 g (25.91 mmol) dimethyl succinate (DMS), as soft segment (60 wt%) (mole ratio of -OH to -$COOCH_3$ was 1 :1), were added to a two-necked 100 mL round bottom flask; stannousoctoate catalyst solution (0.05 mL) was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 175 °C for 2.5 h, 220 °C for 3 h. After that, low vacuum was applied for about 10 min. Finally, a high vacuum (0.2 mmHg) was applied at 240 °C for an additional 2 h. The mixture was viscous at the end of polymerization. The final product was cooled down to room temperature and was removed from the reaction flask without further purification. This block copolyester was soluble in $CHCl_3$, M_n from SEC: 26,400 g/mol, M_w: 82,100 g/mol; PDI: 3.10. T_g from the second heating cycle of DSC is -3 ^oC. No T_c and T_m were observed.



(10)

Scheme 7.10 Synthesis of block copolyesters **(10)** containing DMCD-2 and NPG units

An alternate synthetic method for obtaining block copolyesters (11) from hard segments (3) and soft segments (5). 4 g hard segment oligoesters **(3)** based on DMCD-2 and NPG (M_n = 2,200 g/mol) (40 wt%), 6 g soft segments **(5)** based on diethylene glycol (DEG) and dimethyl succinate (DMS) (M_n = 46,500 g/mol) (60 wt%) were added to a two-necked 100 mL round bottom flask; then the catalyst stannousoctoate solution (0.05 mL) was added under nitrogen. The mixture was heated and stirred at 175 °C for 2.5 h, 220 ^oC for 3 h. After that, a low vacuum was applied for about 10 min followed by the application of a high vacuum (0.1 mmHg) at 220 °C for an additional hour. The mixture was viscous at the end of polymerization. After the metal bath was removed, the final product was cooled to room temperature and was removed from the reaction flask without further purification. This block copolyester was not soluble in $CHCl_3$, thus molecular weight data were not available. T_g from DSC is 0 ^oC. No T_c and T_m were observed. Unfortunately, a limited amount of DMCD-2 prevented an optimization of polymerization conditions and compositions of block copolyesters.

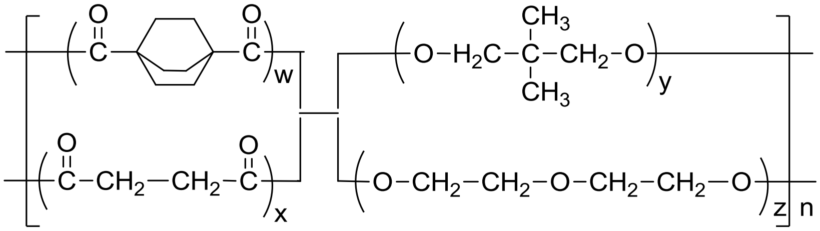


(11)

Scheme 7.11 Alternate synthetic method for obtaining block copolyesters **(11)** containing DMCD-2 and NPG units

Synthesis of all-aliphatic random copolyesters (12) based on DMCD-2, NPG, DMS and DEG (Scheme 7.12). Random copolyesters based on DMCD-2, NPG, DMS and DEG was also synthesized for comparison. 4.52 g DMCD-2 (20 mmol), 6.14 g (42 mmol) dimethyl succinate (DMS), 4.45 g (42 mmol) of diethylene glycol (DEG), and 2.08 g (20 mmol) of NPG (mole ratio of -OH to $-COOCH_3$ was 1 :1) were added to a two-necked 100 mL round-bottom glass flask, and 0.15 mL of the titanium catalyst solution was added under nitrogen. A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 190-200 °C for 2 h, 220-230 °C for 2 h and 275-280 °C for 0.5 h. After that, a low vacuum was applied for about

10 min, followed the application of a high vacuum (0.1 mmHg) for an additional 90 min at 280 ^{o}C. After the product was cooled to room temperature and the vacuum was stopped, the final product was removed from the reaction flask without further purification. This random copolyester was partially soluble in $CHCl_3$, THF, DMF, toluene, and chlorobenzene, but was soluble in 1,2-dichloroethane. M_n from SEC: 33,500 g/mol, M_w: 151,600 g/mol; PDI: 4.53. A 5 % weight loss occurred at 307 ^{o}C. T_g from DSC: -6 ^{o}C.



(12)

Scheme 7.12 Structure of random copolyesters **(12)** containing DMCD-2 and NPG units

Preparation of blends from the homopolyester (4) (hard segments) and the homopolyester (6) (soft segments). Two homopolyesters (40 wt% of hard segments **(4)**) were dissolved in chloroform. Blends were then prepared by precipitating the chloroform solution into a large amount of methanol. The precipitates were dried in a vacuum oven at 60 ^{o}C for 24 h and then were compression molded at 100 ^{o}C for 10 min.

7.3.3 Characterization

^{1}HNMR spectra were determined at 25 ºC at 400 MHz with an INOVA spectrometer. Molecular weights of synthesized polymers were determined using SEC with a Waters 410 refractive index (RI) detector and viscometer DP detector. SEC measurements were performed at 30 ^{o}C in chloroform with a sample concentration 5.0 mg/mL at a flow rate of 1.0 mL/min. TGA was conducted under nitrogen from 25 to 600 ºC at a heating rate of 10 ºC/min using a TA Instrument TGA Q500. DSC was conducted using a TA instrument

DSC Q2000 from -20 °C to 300 °C at heating/cooling rates of 20 °C / min under nitrogen circulation. DMA of samples was conducted using a DMA Q800 of TA instruments at a heating rate of 5 °C/min from -150 °C to 100 °C while they were deformed in the tension mode at a frequency of 1 Hz under nitrogen. Tensile measurements at room temperature (23 ^{o}C) were performed on an Instron Model 4400 Universal Testing System equipped with a 500 N load. The film samples were prepared using a PHI Model GS 21-J-C-7 compression molding press at 70 °C above T_g for 10 min. The samples were tested at a rate of 50 mm/min using an initial grip-to-grip separation of 15 mm. Young's modulus was calculated from the linear part of the initial slope. All reported tensile data were averaged from at least three independent measurements and a standard deviation was also reported. SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1603 m, and q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 hour. All SAXD data were analyzed using the SAXSGUI software package to obtain radically integrated SAXS intensity versus scattering vector q, where $q=(4\pi/\lambda)\sin\theta$, θ is one half of the scattering angle and λ is the wavelength of X-ray.

7.4 Results and Discussion

Selection of monomers. DMCD-2-containing random copolyesters with high T_gs were synthesized as previously described (Chapter 3). For the investigation described here, DMCD-2 was selected for incorporation into the hard segment of the block copolyesters since the rigidity of bicyclo[2.2.2]oactane rings is comparable to that of phenyl rings. Therefore, we anticipated that it might be possible to increase the microphase separation of block copolyesters, thereby improving their mechanical properties. Due to the limited availability of DMCD-2, commercially available *trans*-DMCD was used to synthesize model reactions for these block copolyesters. NPG with two methyl side groups was used to improve the hydrothermal stability of the block copolyesters and reduce property degradation as a result of transesterification. The commercially available aliphatic monomers DEG and DMS were used as soft segments for the block copolymers.

Synthesis of oligoesters and their composition by ^{1}H NMR spectroscopic analysis. Oligoesters were prepared from DMCD-2 and NPG by standard melt-phase polymerization, and were subsequently used as hard segments for the block copolyesters. Model reactions based on *trans*-DMCD and NPG were also conducted for comparison. Their end group functionality was controlled by adjusting the mole ratio of the starting materials. The degree of polymerization and end group functionality were determined by ^{1}H NMR spectra. **Figure 7.1** shows the ^{1}H NMR spectra of the oligoester based on *trans*-DMCD and NPG (the feed ratio of *trans*-DMCD to NPG was 1.2:1). The single peak “a” is assigned to protons on the end methyl group. The single peak “b” represents the methylene unit adjacent to the oxygen at the NPG unit. Peaks “c” and “c’” are the α-hydrogens of *trans*-DMCD; Broad peaks “d”, “d’”, “e” and “e’” come from protons on the carbons in the cyclohexylene rings. The single peak “f” corresponds to protons at the methyl groups of the NPG. The peak area ratio of “c’” to “c” gives the degree of polymerization n = 11. The ^{1}H NMR spectrum of this oligomer showed good agreement of its actual molecular weight with the corresponding targeted molecular weight.

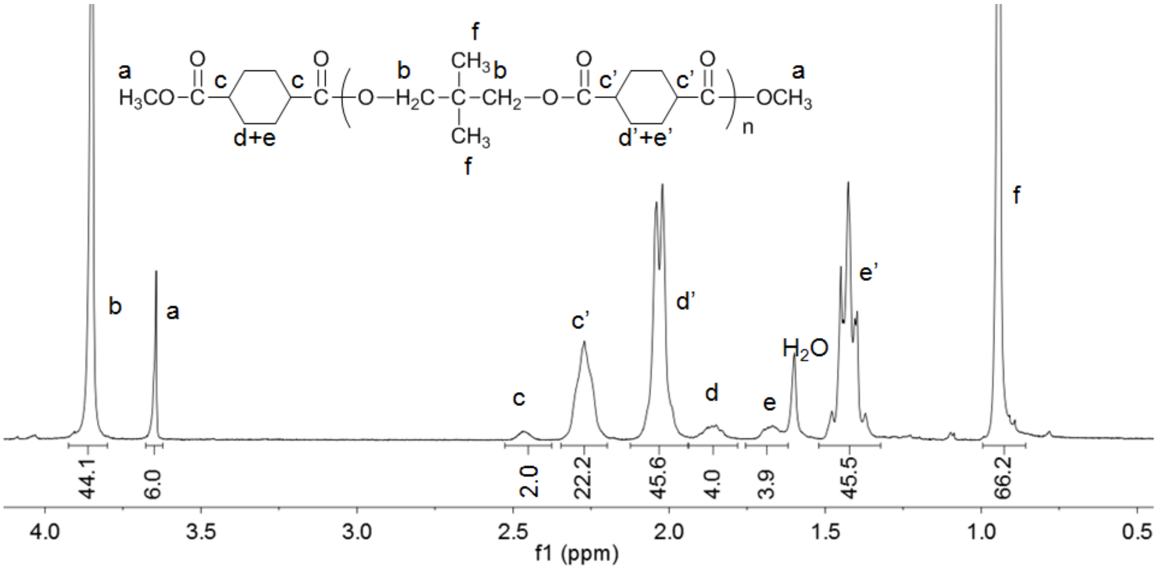


Figure 7.1 ^1H NMR spectrum of oligoester **(1)** based on *trans*-DMCD and NPG

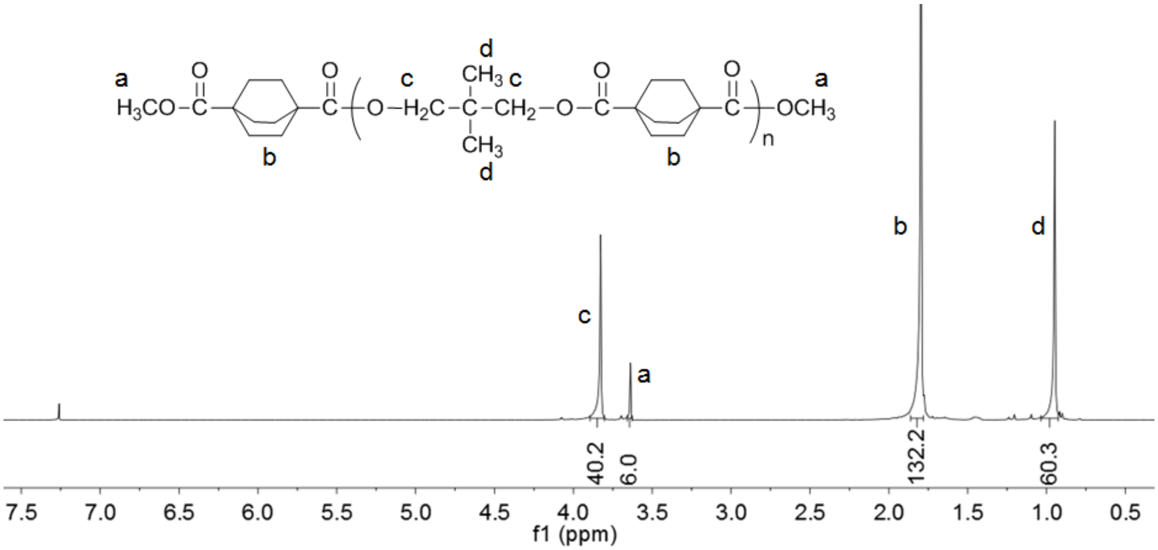


Figure 7.2 ^1H NMR spectrum of oligoester **(3)** based on DMCD-2 and NPG

Figure 7.2 shows the ^1H NMR spectra of the oligoester with diester end groups based on DMCD-2 and NPG. The relative peak area of "d" divided by 6 (i.e. the numbers of protons on two methyl groups in one repeat unit) affords the degree of polymerization n = 10. Therefore, the calculated average molecular weight is 2880 g/mol, which matches well with the M_n from SEC (2500 g/mol). However, we find it difficult to determine if the copolyesters are block or random from the ^{1}H NMR spectra due to the overlapping of some proton peaks. ^{1}H NMR spectrum of homopolyester **(6)** based on DEG and DMS is very clear, as shown in **Figure 7.3**.

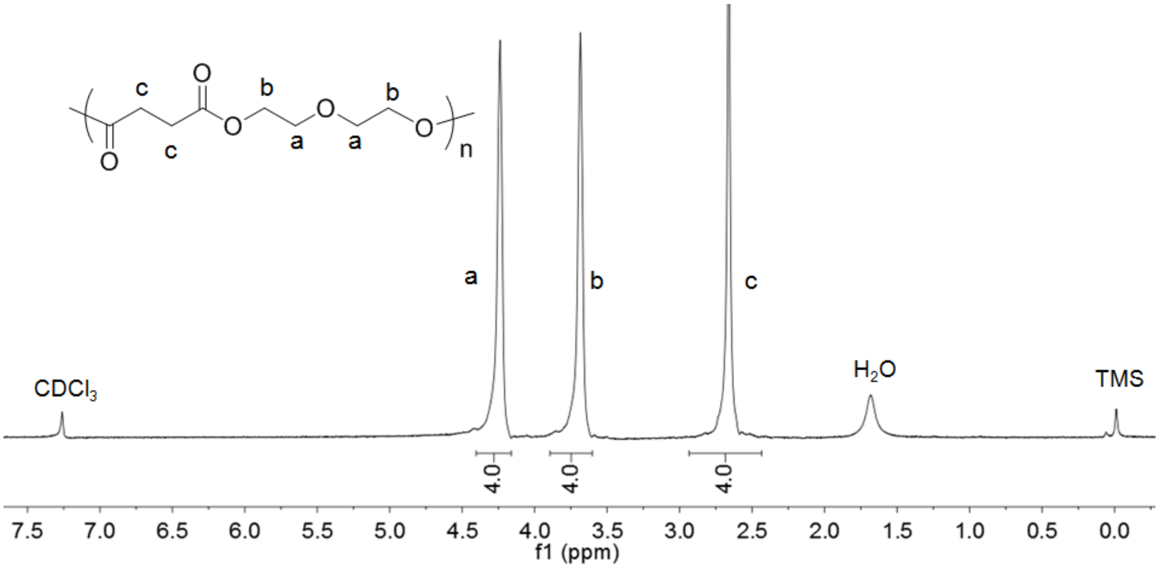


Figure 7.3 ^{1}H NMR spectrum of homopolyester **(6)** of DEG and DMS

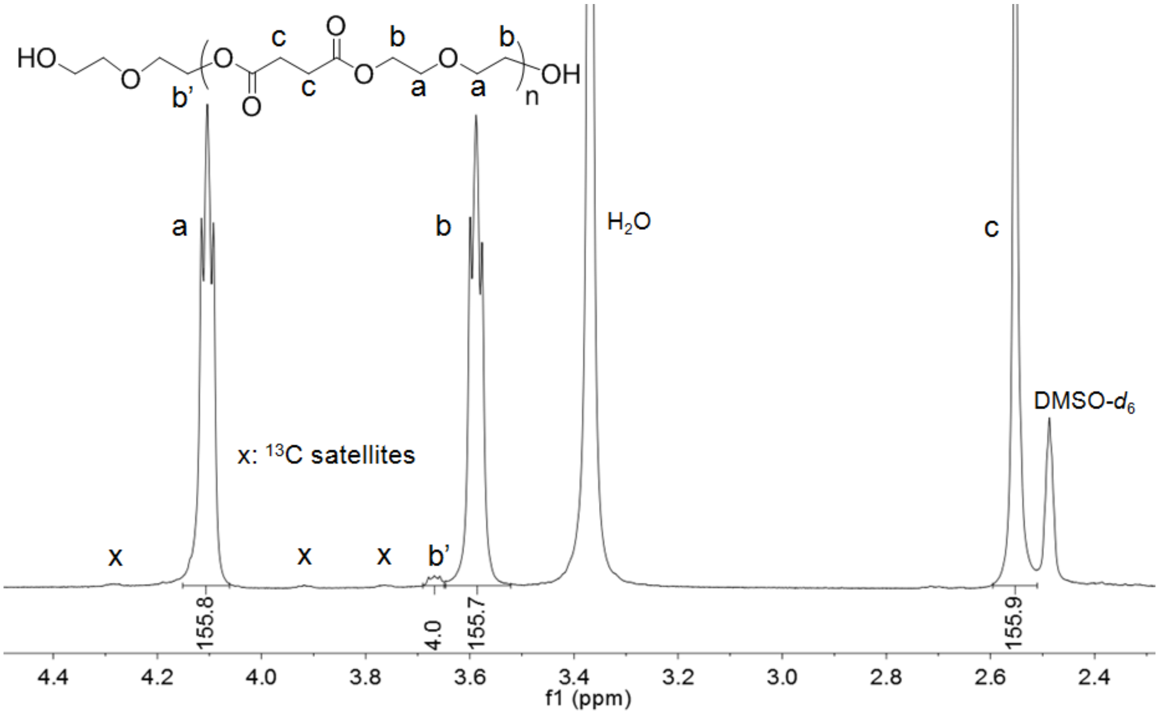
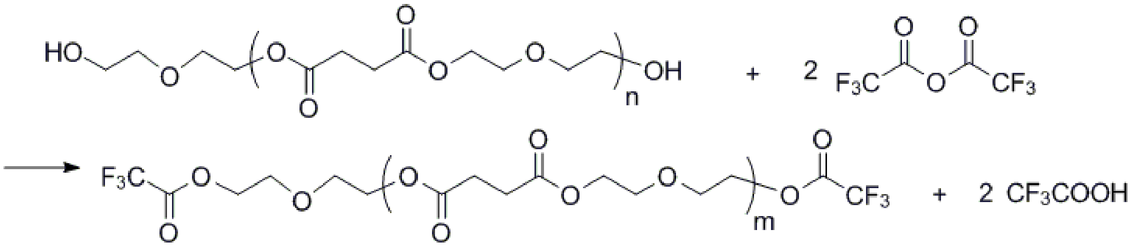


Figure 7.4 ^{1}H NMR spectrum of oligoester **(5)** of DEG and DMS with OH end groups

Although the presence of OH end groups is expected for the polyester **(5)** prepared from DEG and DMS, their corresponding peaks are not observed in the ^{1}H NMR spectra, as shown in **Figure 7.4**. We attribute this to the possible formation of hydrogen bonding, which prevents the appearance of proton peaks. Therefore, in order to confirm the existence of OH end groups, the oligoester **(5)** is reacted with trifluoroacetic anhydride (TFAA) according to the literature,[11] and then ^{1}H NMR analysis is used to evaluate the product **(13)**.


(13)

Scheme 7.13 Reaction of oligoester **(5)** with TFAA

^{1}H NMR spectra of the product **(15)** is shown in **Figure 7.5**. Multiple peaks "e" are assigned to protons on the end methylene group according to the reference, which confirmed the presence of OH end groups in the oligoester **(5)**. The single peak "a" in **Figure 7.5** represents the methylene unit adjacent to the carbonyl group at the DMS unit. The single peak "b" corresponds to the methylene unit adjacent to the central oxygen at the DEG unit. Peak "c" is the methylene unit adjacent to the side oxygen at the DEG unit. The multiple peaks shown as "x" are the ^{13}C satellites. The peak area ratio of "b" to "e" affords the degree of polymerization m = 257. Thus, the calculated average molecular weight for the oligoester **(5)** is 48,000 g/mol, which matches well with the M_n from SEC (47,000 g/mol).

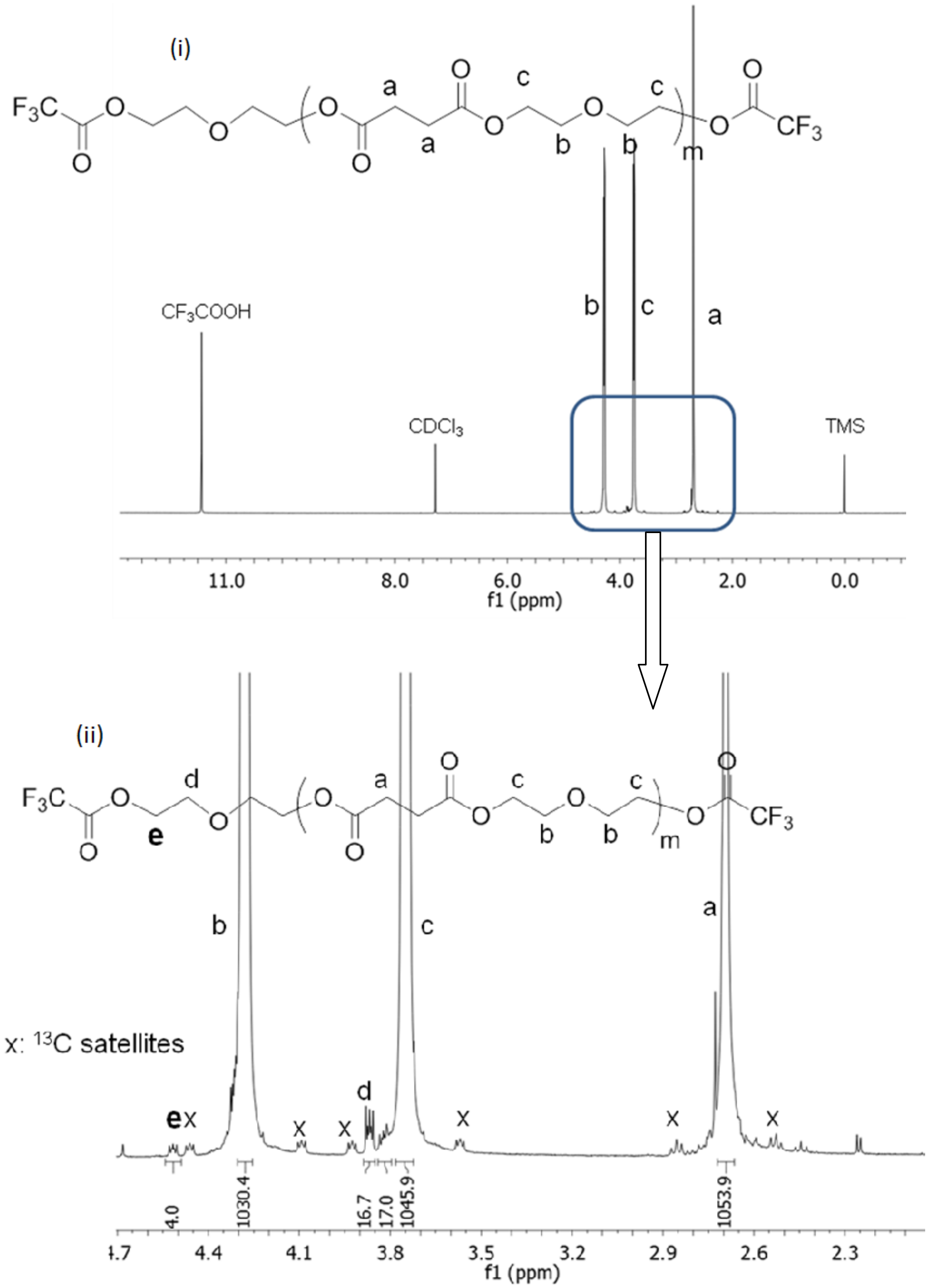


Figure 7.5 Full ^{1}H NMR spectrum (i) and partial enlargement (ii) of the product **(13)**

IR spectrum of oligoester (3) based on DMCD-2 and NPG. The IR spectrum of the oligoester **(3)** based on DMCD-2 and NPG in **Figure 7.6** indicates that no OH end groups were observed as expected. This outcome is consistent with the results from ^{1}H NMR spectra analysis, from which diester end groups were identified.

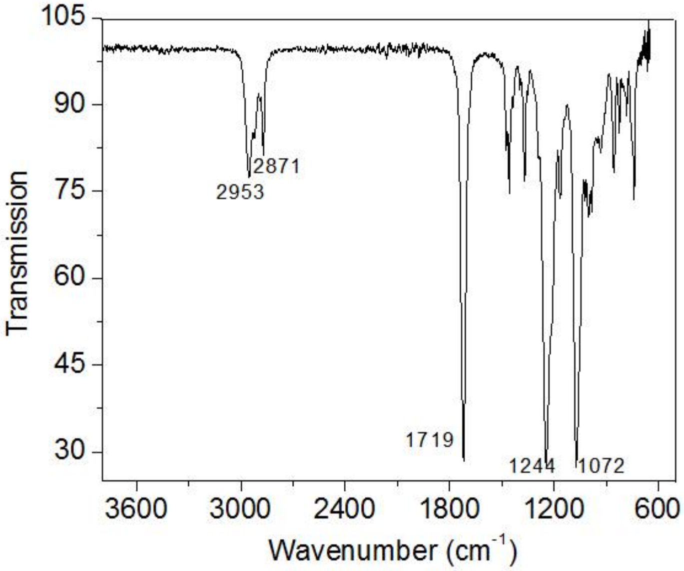


Figure 7.6 IR spectrum of oligoester **(3)** based on DMCD-2 and NPG

Thermal property analysis of the oligoesters and random/block copolyesters. Due to the limited availability of the DMCD-2 monomer, we were unable to ascertain the optimum content of hard segments; therefore, for this study the content of the hard segment was fixed at 40 wt%. At this level, most of polyesters became viscous when the polymerization proceeded to high conversions, which typically took about 5-6 h. Some of the copolyesters started to take on a yellow color due to the titanium catalyst and the long reaction time at high temperatures. Most of the all-aliphatic oligoesters and copolyesters were soluble in common chlorinated solvents, such as dichloromethane and chloroform. Resulting thermal properties and molecular weights are summarized in **Table 7.1**.

Table 7.1 Characterization results of all-aliphatic oligoesters and homopolyesters

Polyester samples	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (g/mol)	DSC T_g (°C)	DSC T_c (°C)	DSC T_m (°C)
(1)	261	3,600	7,000	17	79	183
(2)	366	8,900	20,300	26	108	178
(3)	310	2,200	4,000	37	N/A	N/A
(4)	318	2,500	4,400	51	N/A	N/A
(5)	255	47,000	83,300	-20	N/A	N/A
(6)	276	28,100	58,100	-21	N/A	N/A
(7)	290	645	1180	23	N/A	N/A

From **Table 7.1**, we can see that oligomers **(1)** with diester end groups or homopolyesters **(2)** based on *trans*-DMCD and NPG are semi-crystalline materials due to the ease of chain packing of polyester chains. Both T_c and T_m peaks are clearly observed in the DSC traces (on the second heating cycle) of homopolyester **(2)** prepared from *trans*-DMCD and NPG, as shown in **Figure 7.7**.

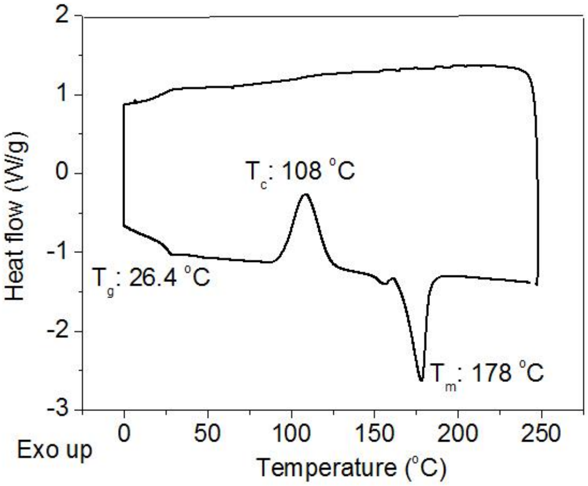


Figure 7.7 DSC trace of homopolyester **(2)** of *trans*-DMCD and NPG

As is well known, T_g and T_c values are highly dependent on the molecular weights of a polymer, with higher molecular weights leading to high T_g and T_c values. In the case of oligoester **(1)** prepared from *trans*-DMCD and NPG, it displayed a lower M_n (3,600 g/mol) and had lower T_g and T_c values in comparison to the corresponding homopolyester **(2)**. Conversely, both the oliogoester **(3)** and the homopolyester **(4)** prepared from DMCD-2 and NPG were amorphous, but they had low molecular weights due to the poor reactivity between DMCD-2 and NPG. Despite the fact that the molecular weights of **(3)** and **(4)** were lower than **(1)** and **(2)** (based on *trans*-DMCD and NPG), the former materials had higher T_g values. This outcome was expected since DMCD-2 is more rigid than *trans*-DMCD. The polyester **(5)** with OH end groups and the homopolyester **(6)** prepared from DEG and DMS also displayed high molecular weights due to the good reactivity of their monomers. Low T_gs, however, were obtained as expected due to the flexible structures of **(5)** and **(6)**. As a result, the polyester **(5)** with OH end groups based on DEG and DMS was used as soft segment for the preparation of all-aliphatic block copolyesters. We also tried to synthesize oligomers **(7)** based on DMCD-2 and TMCBD (the targeted MW was 4000 g/mol), but very low molecular weights were obtained due to the low reactivity of TMCBD (a secondary diol with steric hindrance) towards DMCD-2. Correspondingly, a low T_g was reported due to the low molecular weight of **(7)**. The products still contained some monomers, which were identified from the ^{1}H NMR spectra of **(7)**.

Block copolyesters based on the above oligomers and random copolyesters based on the corresponding monomers were also prepared, as described earlier. The thermal properties and molecular weights of these copolyesters are listed in **Table 7.2**.

Table 7.2 Characterization results of all-aliphatic random or block copolyesters

Copolyester samples	TGA T_d. 5% weight loss (°C)	SEC M_n (g/mol)	SEC M_w (g/mol)	M_w/M_n	DSC T_g (°C)
(8)	294	21,300	78,100	3.7	-11
(9)	309	22,000	53,000	2.4	-7
(10)	315	26,400	82,100	3.1	-3
(11)	320	24,500	61,200	2.5	0
(12)	307	33,400	151,600	4.5	-6

As indicated in **Table 7.2**, all of the copolyesters displayed sufficiently high molecular weights, as well as a polydispersity index (PDI) of 2.4 to 4.5. Some copolyesters possessed broad PDIs due to the presence of some low molecular weight cyclic oligomers. All of the copolyesters in **Table 7.2** showed good solubility in 1,2-dichloroethane, indicating that they were non-crosslinking. The SEC trace of block copolyester **(10)** with a broad PDI based on DMCD-2 is shown in **Figure 7.8**.

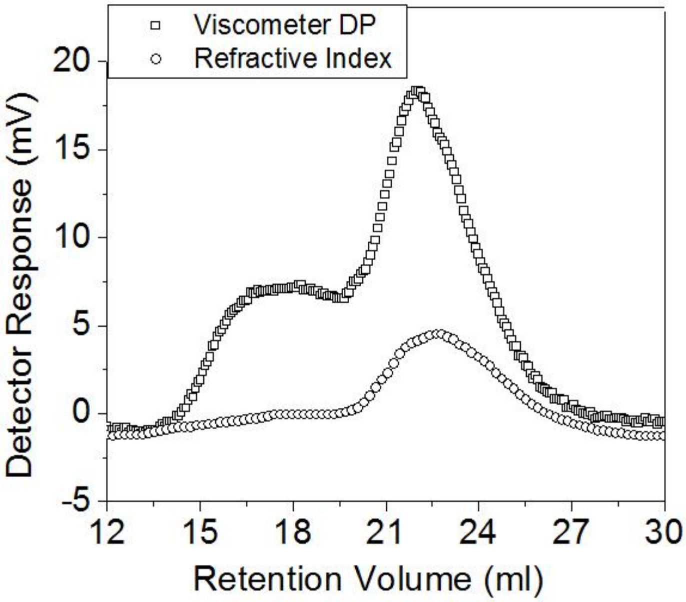


Figure 7.8 SEC trace of the block copolyester **(10)** based on DMCD-2

This study also confirms that the thermal properties of these block copolyesters are highly dependent on molecular weights of the oligoester **(3)** based on DMCD-2 and NPG ester end groups. However, it is difficult to achieve a targeted molecular weight for this oligoester **(3)** due to the fact that the DMCD-2 sublimes above its melting point, particularly in the presence of a vacuum. Specifically, when a vacuum is applied, the unreacted DMCD-2 sublimes and then attaches to the wall of a glass four-way adapter, as shown in **Figure 7.9**.

Figure 7.9 Sublimation of DMCD-2

Due to the loss of DMCD-2, the reaction stoichiometry was disturbed. As a result, lower molecular weights than expected were obtained. In response, it was necessary to melt DMCD-2 and allow most of it to react with NPG before the sublimation point. By controlling polymerization conditions, such as extending the reaction time of the first step from 4 h to 6 h, we were then able to obtain relatively higher molecular weights for the oliogesters based on DMCD-2. However, it remained difficult to obtain high molecular weight homopolyester **(4)** prepared from DMCD-2 and NPG (1:1 mole ratio) due to their low reactivity to each other. The ^{1}H NMR spectra of homopolyester **(4)** indicated the presence of ester end groups, which are due either to the existence of unreacted DMCD-2, or to the stoichiometric variations of the starting materials DMCD-2 and NPG during polymerization. We believe, however, that the low molecular weights we obtained were likely due to the fact that partial unreacted starting materials were pulled out by vacuum, since they did not react completely with each other. The block copolyester **(10)** was prepared from the oligoester **(3)** containing DMCD-2 and NPG, as well as the monomers DEG and DMS; however, the block copolyester **(11)** was prepared from the oligoester **(3)** containing DMCD-2 and NPG, as well as the polyester **(5)** containing DEG and DMS. The latter **(11)** displayed a higher T_g in comparison to the former **(10)**.

With respect to the T_gs of two block copolyesters, the block copolyester **(11)** containing DMCD-2 displayed a higher T_g value than the block polyester **(8)** containing *trans*-DMCD, as shown in **Table 7.2**.

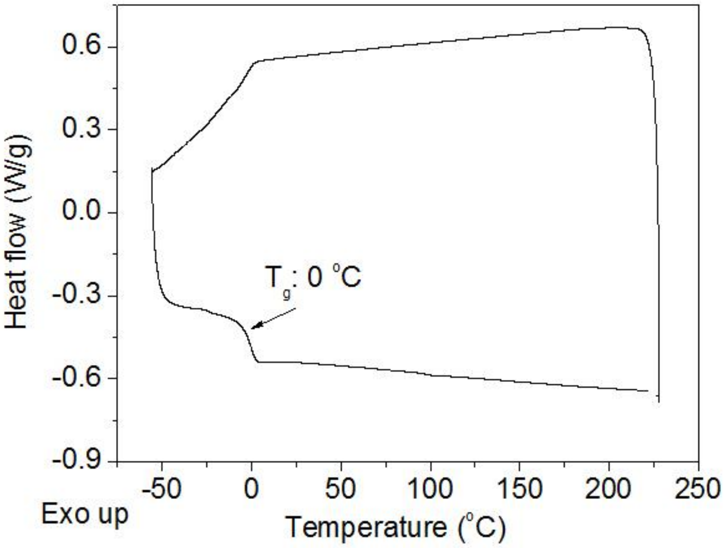


Figure 7.10 Full DSC trace of block copolyester **(11)** based on DMCD-2

Only one T_g was observed via DSC for the block copolyester **(11)**, as shown in **Figure 7.10**, indicating the absence phase separation for this block copolyester. We attributed this outcome to the occurrence of transesterification during polymerization. Small angle X-ray scattering (SAXS) experiments were also performed to examine the possible phase separation and the corresponding SAXS spectra of intensity versus scattering vector q are exhibited in **Figure 7.11**.

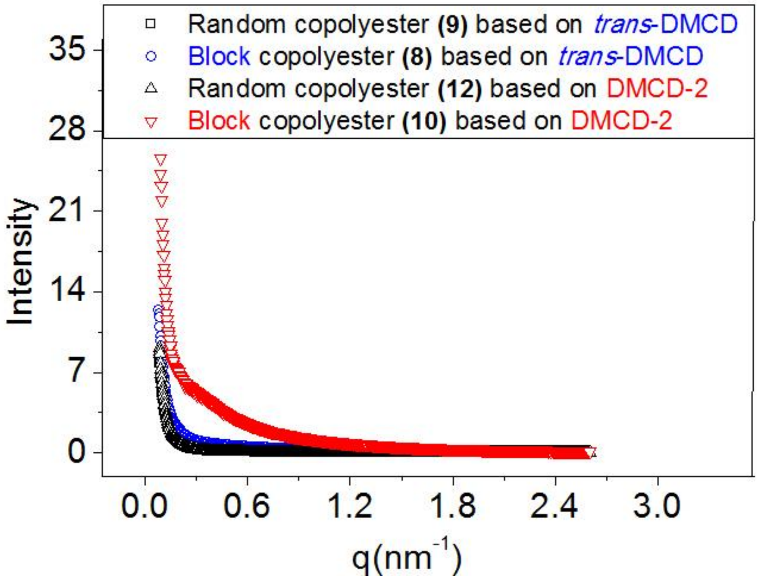


Figure 7.11 SAXS spectra of random and block copolyesters

No really peaks were observed in **Figure 7.11**, indicating no apparent microphase separation for these copolyesters. However, a shoulder was found for the block copolyester **(10)** based on DMCD-2 and this may suggest a low degree of microphase seperation of the block copolyester **(10)**. We also tried to study phase separation by AFM, but were unsuccessful due to the sticky properties (corresponding to low T_g) of the copolyester films.

Therefore, polyester blends were prepared from the homopolyester **(4)** synthesized from DMCD-2 and NPG (hard segments) and the homopolyester **(6)** prepared from DEG and DMS (soft segments). Two T_gs were observed for this polyester blend from the DSC trace shown in **Figure 7.12**. One represents the T_g of the soft segment, while the other is related to the T_g of the hard segment. This outcome indicates the phase separation of the hard segment and the soft segment in the polyester blends.

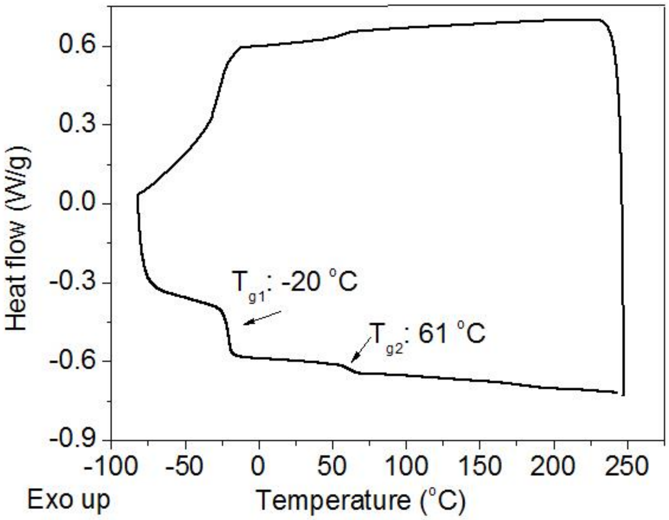


Figure 7.12 DSC traces of polyester blends based on **(4)** and **(6)**

Mechanical property analysis of copolyesters. Tensile data obtained at ambient temperature reveal that the DMCD-2-containing block copolyester **(11)** has a higher tensile modulus and a higher yield stress in comparison to the *trans*-DMCD-containing block copolyester **(8)**, which is a weak elastic material (see **Figure 7.13**). Moreover, tensile curves in **Figure 7.14** indicate that the DMCD-2-containing block copolyester **(11)** displayed higher tensile stress than the corresponding random copolyester **(12)**.

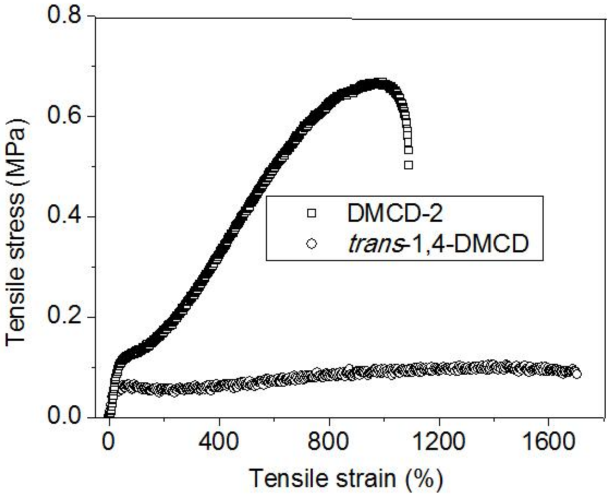


Figure 7.13 Tensile curves of block copolyesters based on DMCD-2 or *trans*-DMCD

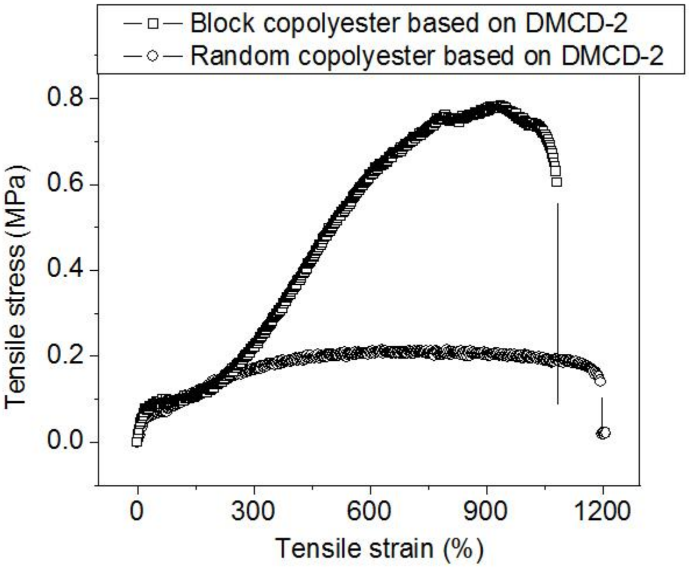


Figure 7.14 Tensile properties of the block copolyester **(11)** and random copolyester **(12)** based on DMCD-2

DMA spectra of the block copolyester **(11)** based on DMCD-2 and the block copolyester **(8)** based on *trans*-DMCD are presented in **Figure 7.15.** The plots of storage modulus versus temperature indicate that both copolyesters possess an expected glassy storage modulus. The α peaks in the tan δ curves, accompanied by a sharp decrease in modulus, correspond to the T_gs of the respective polyesters. The DMCD-2-containing block copolyester **(11)** displays a higher glassy storage modulus (above 1.2 GPa) and T_g (15 ^oC from tan δ) when compared to the *trans*-DMCD-containing block copolyester **(8)**, which displayed a relatively low glassy DMA modulus of 0.7 GPa and a T_g of 7 ^oC. The tan δ T_g was found to be about 18 ^oC higher than the T_g observed via DSC T_g, as expected.

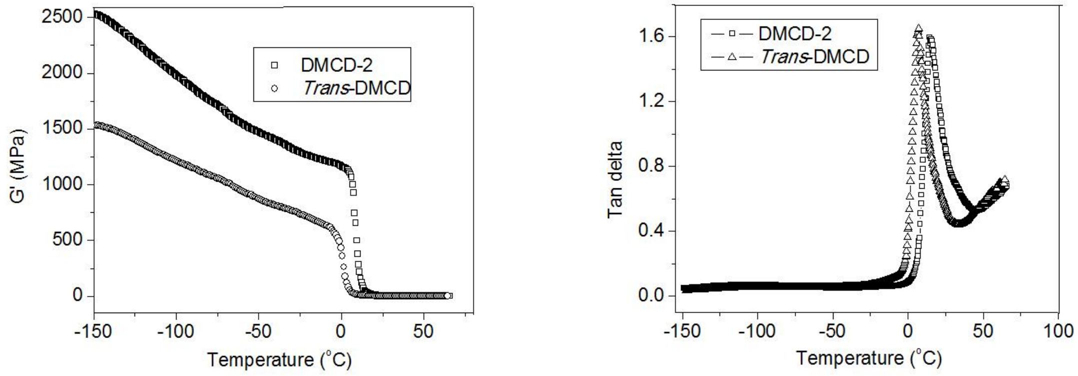


Figure 7.15 DMA traces of block copolyesters based on DMCD-2 or *trans*-DMCD

7.5 Conclusions

To summarize, block copolyesters were prepared based on cycloaliphatic diesters (*trans*-DMCD and DMCD-2), NPG, and other aliphatic monomers. Corresponding random copolyesters were also synthesized for comparison purpose. The block copolyester based on *trans*-DMCD and NPG possessed a higher T_g and better mechanical properties than the random copolyesters. Similarly, the block copolyesters based on DMCD-2 and NPG also possessed a higher T_g and better mechanical properties than the corresponding random copolyesters. Additionally, block copolyesters based on DMCD-2 and NPG displayed a higher T_g and better mechanical properties in comparison to block copolyesters based on *trans*-DMCD and NPG. The sublimation and low reactivity of DMCD-2 toward NPG resulted in hard segments of low molecular weights. This finding could explain why the block copolyesters did not exhibit microphase separation.

7.6 Suggested Future Work

As discussed in Section **7.4**, even though oligomers **(3)** and **(4)** displayed low molecular weights, they may have contained some starting materials, which continued to react with DEG/DMS or with the polyester **(5)** containing OH end groups. Therefore, it is likely that random copolyesters can be obtained instead of multiple block copolyesters. Thus, suggested future work should begin by re-synthesizing oligomers **(3)** and **(4)**, and then purifying them by removing any unreacted monomers. These oligomers should then be dissolved in chloroform and precipitated from a large amount of methanol. After the precipitates dry completely in a vacuum oven, those oligomers could be used to synthesize the block copolyesters **(8)** and **(11)**. However, it may be necessary to repeat the synthesis of the soft segments with OH end groups **(5)** to obtain lower average molecular weights than before. In addition, future work should also involve synthesizing block copolyesters at relatively lower temperatures, which can minimize structural randomization during polymerization. Finally, the thermal and mechanical properties of those block copolyesters should be re-investigated, with the goal of achieving microphase separation and improved performance parameters.

7.7 Acknowledgements

We are grateful to the Eastman Chemical Company for donating *trans*-DMCD and TMCBD. We gratefully acknowledge Prof. Timothy Long’s group and Prof. James E.

McGrath's group for allowing us to use their TGA, DSC, DMA and INSTRON equipment. We also thank Mark Flynn in Prof. Judy Riffle's group for SEC measurements.

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Chapter 8: Overall Summary

The synthesis and characterization of various cycloaliphatic polyesters with novel structures and architectures were described.

The first two chapters described the rationale, synthetic processes, general structure-property relationships, and various polyesters containing different cycloaliphatic rings (from four-member rings to six-member rings). In general, the properties of cycloaliphatic polyesters are influenced by (i) the ratio of ring units to linear units in the chain, (ii) the position of the ester groups, (iii) stereochemistry (*cis* or *trans* forms) of the rings, and (iv) symmetry alterations of cycloaliphatic monomers. Many specific cycloaliphatic monomers and the corresponding polyesters were described; their properties and potential applications were briefly highlighted.

In the subsequent chapter, the synthesis and properties of a systematic series of random and amorphous cycloaliphatic polyesters with different types of rings were described. These polyesters were prepared in melt phase by the reaction between different cycloaliphatic diesters—dimethyl-1,4-cyclohexane dicarboxylate (DMCD), dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate (DMCD-1), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3), 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M)—and the aliphatic diols, ethylene glycol (EG) and 1,4-cyclohexane dimethanol (1,4-CHDM). The copolyester compositions were analyzed by ^{1}H NMR and were close to the targeted compositions. The copolyesters based on DMCD-2 were found to have higher glass transition temperatures (up to 115 ºC) than any of the other cycloaliphatic polyesters and the terephthalate analog synthesized in this chapter. For poly[x(DMCD-2)y(DMCD)30(EG)70(CHDM)], the T_g increased linearly with the increase of DMCD-2 content. Poly[50(DMCD-2)50(DMCD)29(EG)71(CHDM)] was also found to possess the highest T_g and modulus among these copolyesters containing DMCD due to the rigidity of DMCD-2 units in the backbone. Using DMA, all of the cycloaliphatic copolyesters showed similar secondary relaxations, resulting from the conformational transitions of the cyclohexylene rings in the backbone. The polyester based on DMCD-3 underwent the fastest hydrolytic degradation in PBS solution at 37 ^{o}C among these cycloaliphatic polyesters in Chapter 3. In Chapter 4, melt polycondensation was also used to prepare a series of other random and amorphous copolyesters including the following cycloaliphatic monomers: dimethyl-1,4-cyclohexane dicarboxylate (DMCD), dimethyl spiro[3.3]heptanes-2,6-dicarboxylate (DMSHD), bicyclo[2.2.2]octane-1,4-dimethanol (BODM), 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD), 1,1-cyclohexanedimethanol (1,1-CHDM) or 1,4-cyclohexane dimethanol (1,4-CHDM). The copolyester containing DMCD-2 and BODM units was observed to have a high glass transition temperature (up to 115 ºC), which is higher than the other copolyesters in this chapter.

In Chapter 5, a new triptycene primary diol monomer (TD) --- triptycene-1,4-hydroquinone-bis (2-hydroxyethyl) ether was synthesized and used to prepare a series of copolyesters with dimethyl 1,4-cyclohexanedicarboxylate (DMCD) by melt-phase polymerization. Straight chain aliphatic spacers, including ethylene glycol (EG), 1,4-butanediol (BD) and 1,6-hexanediol (HD), were used as co-diols with TD to explore the effects of flexible spacers on copolyester properties. For triptycene-containing copolyesters, the mechanical properties were found to be dependent on the types and compositions of the comonomer diols. The T_g of the TD-containing polymers increased with increasing TD content when the same aliphatic diol was used. Tensile results revealed that poly[100(DMCD)74(EG)26(TD)] was rigid yet brittle at ambient temperature. However, the copolyester poly[100(DMCD)74(BD)26(TD)] was found simultaneously to possess high modulus and excellent ductility at ambient temperature. It indicated that its short flexible spacer (butane unit) in combination with triptycene units can also promote an improved ambient temperature modulus and enhanced ductility. A concomitant series of non-triptycene copolyesters based on hydroquinone bis(2-hydroxyethyl) ether (HBE), bis[4-(2-hydroxyethoxy)phenyl] sulfone (BHPS), 1,1-bis[4-(2-hydroxyethoxy)-phenyl]cyclohexane (BHPC) or 1,1-bis(2-hydroxyethoxy)phenyl-3,3,5-trimethylcyclohexane (BHPT) were prepared for comparison. The results demonstrated that the triptycene-containing copolyesters in this chapter had higher thermal stability and higher glass transition temperatures (T_gs) than the corresponding non-triptycene analogs. However, our results did not confirm the synergistic effect observed by Swager, Thomas, *et al*. because the triptycene copolyester did not show enhanced ductility when compared to other copolyesters containing rigid and bulky units (BHPS, BHPC and BHPT) at -25 ^oC or -40 ^oC. These polyesters, including triptycene polyesters, were brittle and displayed similar modulus values at temperatures well below their DMA (tan δ) T_g's.

In Chapter 6, we incorporated triptycene diol to PETG polyesters and characterized some of the properties. The T_g of the TD-containing PETG copolyesters increased with increasing TD content. The results from tensile testing revealed that PETG copolyesters with 10 mol% to 30 mol % TD were rigid yet brittle. Again, it indicated that the interlocking effects that were reported by Swager et al. may not be operative if there are not some simple extended threading units. Copolyesters based on various hydroxyethoxylated bisphenols with increased mole percentage of hydroxyethoxylated bisphenols still had lower T_gs and modulus than the poly[100(DMCD)74(BD)26(TD)] copolyester. However, our results still did not exhibit the synergistic effect observed by Swager *et al.* because the tensile elongation of the copolyester based on TD was not higher than other the analogous non-triptycene copolyesters.

Lastly, a series of all-aliphatic block and random copolyesters were prepared based on the following aliphatic monomers: *trans*-dimethyl-1,4-cyclohexane dicarboxylate (*trans*-DMCD), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), neopentyl glycol (NPG), diethylene glycol (DEG) and dimethyl succinate (DMS). The block copolyester containing DMCD-2 and NPG was observed to have a higher glass transition temperature and a higher tensile stress than the block copolyester based on *trans*-DMCD and NPG. Tensile testing and DMA showed these block copolyesters were found to have better mechanical properties than the corresponding random copolyesters. The sublimation and low reactivity of DMCD-2 toward NPG resulted in hard segments with low molecular weights. This was probably one reason that the block copolyesters did not exhibit microphase separation.

Chapter 9: Preliminary Results and Suggested Future Work for the Project on high T_m Polyesters for LED Applications

9.1 Introduction

High power light emitting diodes (LEDs) are becoming more and more important for many lighting applications, such as signaling, signage, automotive and solid state lighting. Some materials with high thermal conductivities and thermal expansion properties are required to enable high power electronic device packaging.[1] Currently, the injection molded plastics are being used as LED packaging materials for power applications. Typically, the injection molded plastics are used for lower power (1 W) packages. Depending on the temperature needed, mold compounds with higher service temperatures like liquid crystal polymers (LCP) are required. Such materials are melt-processed and compounded with additives to form injection molded parts or extruded films at high temperatures of up to 300 ^{o}C. However, many commercial engineering polymers, such as PCT, are not sufficiently thermally stable for LED packaging applications. Therefore, our goal is to synthesize more thermally stable polyesters or copolyesters with high T_ms (> 300 ^{o}C) for LED packaging applications.

Dimethyl 2,6-naphthalene dicarboxylate (DMN) is a good candidate for the preparation of high T_m polyesters due to its rigidity structures. Previously, DMN was incorporated into certain polyester backbones and their thermal properties were studied.[2, 3] For example, it was found that the T_g increased with increasing DMN content for the copolyester PCT modified with DMN. The T_m of the DMN modified PCT copolyesters also increases with increasing DMN content in the range of 40 mol% to 75 mol%, as discussed in the chapter of literature review. The T_g and T_m of poly(1,4-cyclohexylene-dimethylene 2,6-naphthalate) (PCN) were 110 ^oC and 320 ^oC, respectively.[3] However, it is difficult to process PCN in melt due to these high transition temperatures. Therefore, it is necessary to lower T_g and T_m to some extent in order to improve processability. We are interested in copolymerizing DMN with PCT at high contents of DMN (80 mol% to 95 mol%) to control the thermal and mechanical properties. In this chapter, strategies and preliminary results on the synthesis of thermally stable polyesters with high T_m's that are currently investigated in our lab are reported. Also, possible future work for the preparation of high T_m polyesters in melt phase is discussed. Other rigid difunctional monomers such as dimethyl biphenyl-4,4'-dicarboxylate (DMBP) and p-terphenyl-4,4'-dicarboxylic acid will also be investigated and incorporated into polyester backbones if possible.

9.2 Experimental

9.2.1 Materials

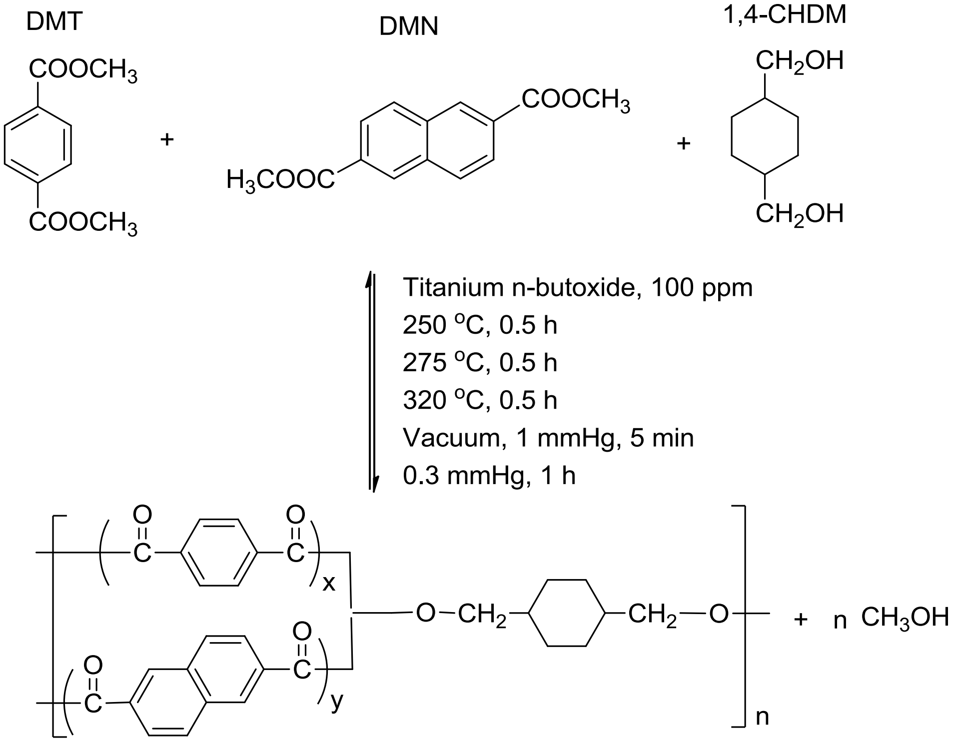
Dimethyl 2,6-naphthalene dicarboxylate (DMN) was supplied by Solvay Specialty Polymers Company. 1,4-CHDM with a 70/30 *cis/trans* isomer mixture, dimethyl terephthalate (DMT) and dimethyl biphenyl-4,4'-dicarboxylate (DMBP) were purchased from Aldrich. Titanium(IV) butoxide (98 %) was purchased from Alfa Aesar Chemical Co. All chemicals were used as supplied without further purification.

9.2.2 Synthesis

Preparation of catalyst solution. The Ti catalyst solution was obtained by mixing titanium n-butoxide with n-BuOH in a dry bottle under nitrogen at a concentration of 0.08 g/ml based on Ti.

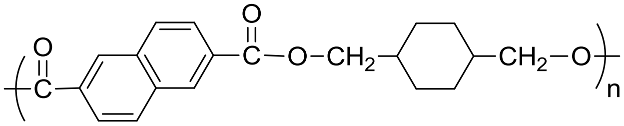
Abbreviation of polyesters. The polymer nomenclature used in this manuscript is based on a polyester containing 100 mol% of diester and 100 mol% of diol. For example, the polymer designated by poly[80(DMN)20(DMT)100(1,4-CHDM)] means this targeted polymer containing 80 mol% DMN and 20 mol% DMT as the diester units and 100 mol% 1,4-CHDM as the diol units. The letters, stand for various monomers' abbreviation and the numbers indicate targeted mol % of monomers, respectively.

Preparation of poly[80(DMN)20(DMT)100(1,4-CHDM)]. 9.77 g (40 mmol) DMN, 1.94 g (10 mmol) of DMT, 7.21 g (50 mmol) of 1,4-CHDM, and 0.14 mL (100 ppm) of a titanium n-butoxide solution (0.08 g/mL in butanol) was placed a 100 ml one-necked, round-bottom glass flask equipped with a N_2 inlet and a mechanical stirrer. The reaction flask was immersed into a molten Belmont metal bath that was pre-heated to 250 °C. The mixture was stirred at 250 °C for 1 h to remove the side product methanol by nitrogen. Then the oligomers formed and solidified at 250 ^{o}C. The oligomers could not melt until the temperature was increased to 320 ^{o}C. Then the temperature was kept at 320 °C for 30 min. The pressure then was gradually reduced and the temperature was raised to 330 °C. A high vacuum (up to 0.1 mmHg) was applied for an additional 1 h at 330 °C and the highly viscous copolyester was obtained. The metal bath was lowered and the temperature controller was turned off. After the mixture cooled down to the room temperature, the vacuum was stopped and nitrogen was bled into the flask. The polyester samples were obtained by breaking the glass flask since they are not soluble in common organic solvents. The polyester samples were characterized without further purification. The similar procedure was employed to prepare poly[85(DMN)15(DMT)100(1,4-CHDM)] and poly[90(DMN)10(DMT)100(1,4-CHDM)]. The synthetic scheme of poly[x(DMN)y(DMT)z(1,4-CHDM)] is shown in **Scheme 9.1**.



Scheme 9.1 Synthesis of poly[x(DMT)y(DMN)z(1,4-CHDM)]

Preparation of poly[100(DMN)100(1,4-CHDM)]---PCN (Scheme 9.2). 19.5 g (80 mmol) DMN, 13.8 g (96 mmol) of 1,4-CHDM (20 mol% in excess), and 0.12 mL (50 ppm) of a titanium n-butoxide solution (0.08 g/ml in butanol) was placed a 100 mL one-necked, round-bottom glass flask equipped with a N_2 inlet and a mechanical stirrer. The reaction flask was immersed into a molten Belmont metal bath that was pre-heated to 220 °C. The mixture was stirred at 220 °C for 30 min. Then the temperature controller was adjusted to 320 °C and the temperature in metal bath was gradually increased at a heating rate of 5 °C/min. The oligomers solidified again and melted gradually when the temperature was increased to 320 °C. Then the temperature was kept at 320 °C for 30 min. The pressure then was gradually reduced and the temperature was raised to 340 °C. A high vacuum (up to 0.1 mmHg) was applied for an additional 30 min at 350 °C and the highly viscous copolyester was obtained. The metal bath was lowered and the temperature controller was turned off. After the mixture cooled down to the room temperature, the vacuum was stopped and nitrogen was bled into the flask. The polyester samples were obtained by breaking the glass flask since they are not soluble in common organic solvents. The polyester samples were characterized without further purification.



Scheme 9.2 Structure of PCN

9.2.3 Characterization

^{1}H NMR analysis was done in C_6F_5OH–$CDCl_3$ solvents by Gary Juneau at NMR Analysis and Consulting Company. Differential Scanning Calorimetry (DSC) was run from 25 °C to 320 ˚C by Perkin Elmer Pyris1 under nitrogen with a flow rate of 50 mL/min and a heating rate of 20 ˚C/min. T_g was determined from the mid-point of an endothermic shift of the second heating cycle. TGA was run at a heating rate 10 °C/min from room temperature to 600 °C under nitrogen on a TA Instrument TGA 2950. For compression molding, the sample was sandwiched between two pieces of 3 mm thick aluminum plate and was centered in a mold of desired thickness. The samples were heated 10 °C above their T_m and a pressure of about 500 PSI was applied. The pressure was released after 10 min and these films were then utilized for thermal and mechanical analyses. Polyester samples were sent to Solvay for inherent viscosity measurements.

9.3 Preliminary Results and Possible Future Work

9.3.1 Preliminary results for poly[x(DMN)y(DMT)100(1,4-CHDM)]

DMN is a difunctional aromatic diester and was incorporated into the polyester backbone, which were discussed in the chapter of literature review. Our preliminary results showed that this monomer, together with DMT, was also polymerizable with 1,4-CHDM to give polyesters with high melt viscosity. During the polymerization, the oligomers solidified due to crystallization and they did not melt when the temperature was increased to 310 ^{o}C. This was the maximum temperature that the old temperature controller could reach, therefore the initial polymerization failed. After a new temperature controller was used, which can reach above 500 ^{o}C, we synthesized the polyesters successfully by modifying the synthetic method used in previous chapters.

Figure 9.1 shows the ^{1}H NMR spectrum of representative copolyester based on DMN, DMT and 1,4-CHDM with a targeted molar ratio 90/10 of DMN/DMT. The correlations between the various structural components and the observed NMR peaks are shown. Peak ‘a’, ‘b’, ‘c’ and ‘d’ are assigned to the protons at DMN and DMT units (some peaks overlapped), and peaks “e” is the methylene group adjacent to the protons at 1,4-CHDM unit (*cis*/*trans* = 30/70). The broad peaks “f” come from the protons on the cycloaliphatic rings. The polymer composition calculated from this ^{1}H NMR spectrum matches well with the feed ratio. In fact, the ^{1}H NMR spectrum of each of these polymers showed that its actual composition was in good agreement with the targeted composition.

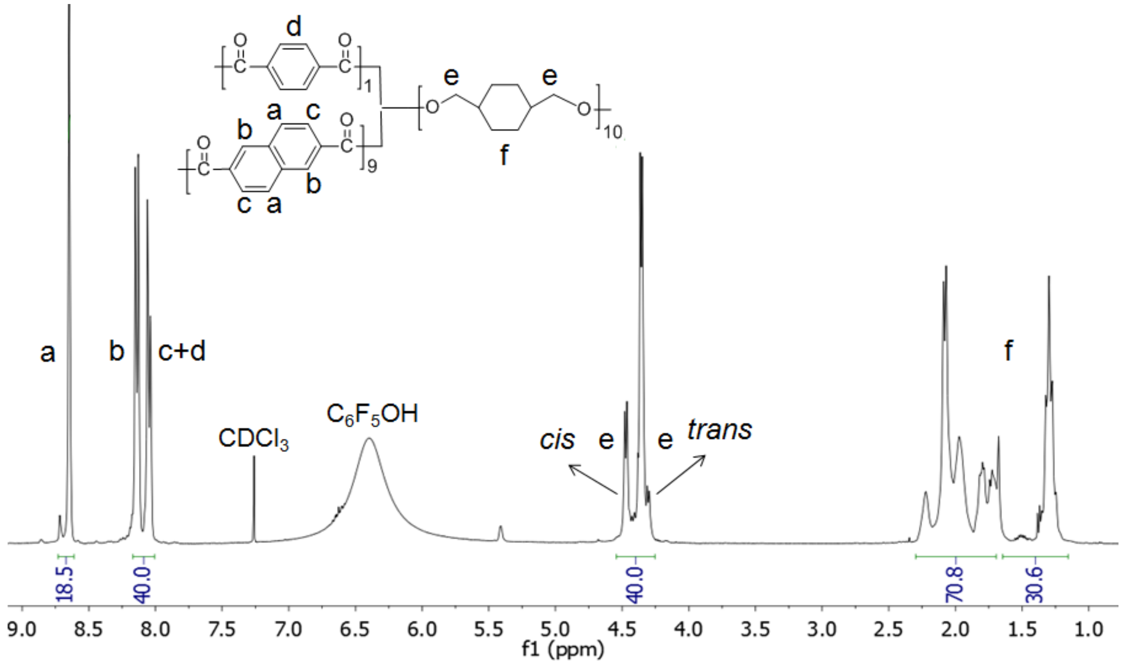


Figure 9.1 ^{1}H NMR spectrum of poly[90(DMN)10(DMT)100(1,4-CHDM)]

The calculated copolyester composition values from peak areas and thermal properties of P(CN-co- CT) are reported in **Table 9.1**.

Table 9.1 Thermal properties of P(CN-co- CT) with different compositions

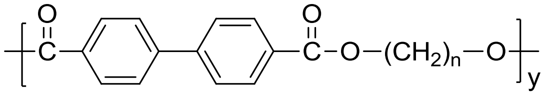
DMN/DMT/1,4-CHDM x/y/z (^{1}H NMR analysis)	TGA T_d. 5% weight loss (°C)	T_c (°C) (1st cooling)	T_m (°C) (1st heating)
0/100/100	381	237	298
80/20/100	384	199	295
90/10/100	386	255	311
100/0/100	383	284	328

As shown by the data, the incorporation of DMN into the main chain of the P(CN-co-CT) copolyester results in high melting temperatures. At high content (≥ 80 mol%) of

DMN, the T_m increases with increasing DMN content. Moreover, P(CN-co-CT) possesses good thermal stability during the entire composition. Therefore, it is effective to enhance the T_m of copolyesters by introducing DMN into the polyester backbone.

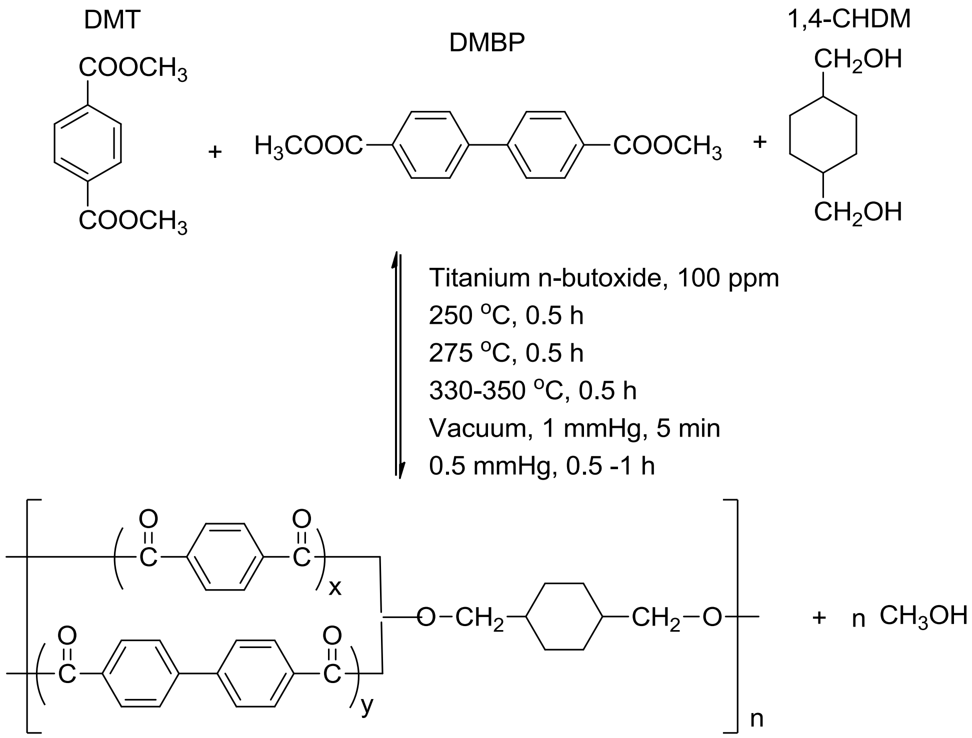
9.3.2 Preliminary results for the diphenyl-containing copolyesters

Dimethyl biphenyl-4,4'-dicarboxylate (DMBP) is a rigid aromatic diester and it has been widely incorporated into polyester backbones to obtain liquid crystal polyesters.[4-7] Effects of different numbers of methylene unit in poly(alkylene *p,p*'-bibenzoate) (**Scheme 9.3**) on the transition temperatures and liquid crystalline properties of polyesters were studied.[7] The homopolyester poly(pentamethy1ene 4,4'-bibenzoate) (PPB) and poly(hexamethy1ene 4,4'-bibenzoate) (PHB) exhibited a smectic phase. The crystalline properties of these two polyesters were significantly affected when they were modified by the non-mesogenic rigid phthalate units, such as DMT and dimethyl isophthalate (DMI).[7] As far as the T_m is concerned, poly(pentamethy1ene 4,4'-bibenzoate) has a T_m of 210 °C,[4] which is not sufficiently high for LED applications.



Scheme 9.3 Structure of poly(alkylene *p,p*'-bibenzoate)

Therefore, we are interested in incorporating DMBP into PCT with different compositions of DMBP. The preparation method of poly[x(DMBP)y(DMT)100(1,4-CHDM)] is shown in **Scheme 9.4**. The thermal properties of P(CB-co- CT) with different content of DMBP are exhibited in **Table 9.2**.



Scheme 9.4 Synthesis of poly[x(DMBP)y(DMT)100(1,4-CHDM)]

Table 9.2 Thermal properties of P(CB-co- CT) with different compositions

DMBP/DMT/1,4-CHDM x/y/z	TGA T_d. 5% weight loss (°C)	T_g (°C) (2st heating)	T_c (°C) (1st cooling)	T_m (°C) (1st heating)
50/50/100	385	107	201	236
80/20/100	388	124	234	297
90/10/100	386	132	242	317
100/0/100	387	---	298	330, 341

As shown by the data in **Table 9.2**, the T_m increases with increasing DMBP content at high content (≥ 50 mol%) of DMBP. Particularly, the polyester poly[100(DMBP)100(CHDM)] has a very high T_m and looks like a liquid crystal polymer. Its morphology need to be confirmed by hot stage polarizing optical microscopy.

Moreover, all of diphenyl-containing copolyesters possess good thermal stability throughout the entire composition. Therefore, the incorporation of biphenyl units into the polyester backbone can effectively enhance the T_m of copolyesters.

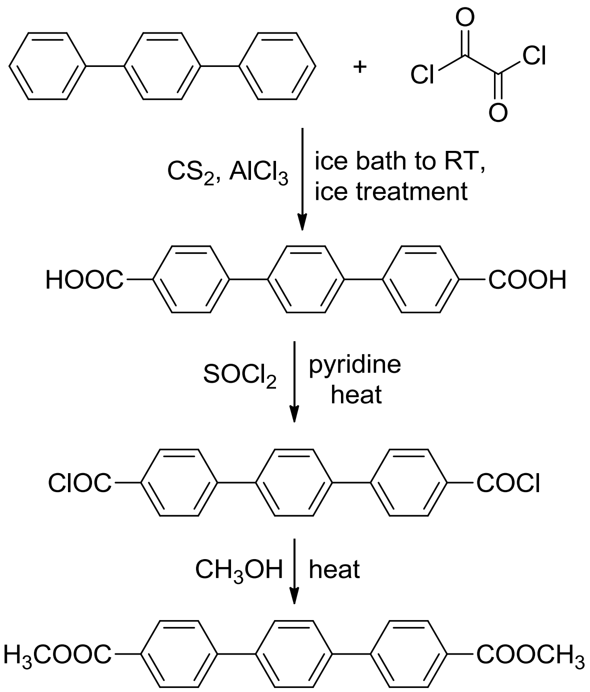
9.3.3 Future work on the terphenyl-containing copolyesters

Another possible future effort is to incorporate terphenyl-containing difunctional monomers in the polyester backbone since terphenyl unit is a very rigid aromatic structure. *p*-Terphenyl-4,4'-dicarboxylic acid or its derivatives are good candidates although they are not commercially available. However, they can be prepared following the synthetic method in literature, as shown in **Scheme 9.5**.[8] This method was found to be a high-yield route. The detailed synthetic procedures for terphenyl-containing difunctional monomers are described as follows.

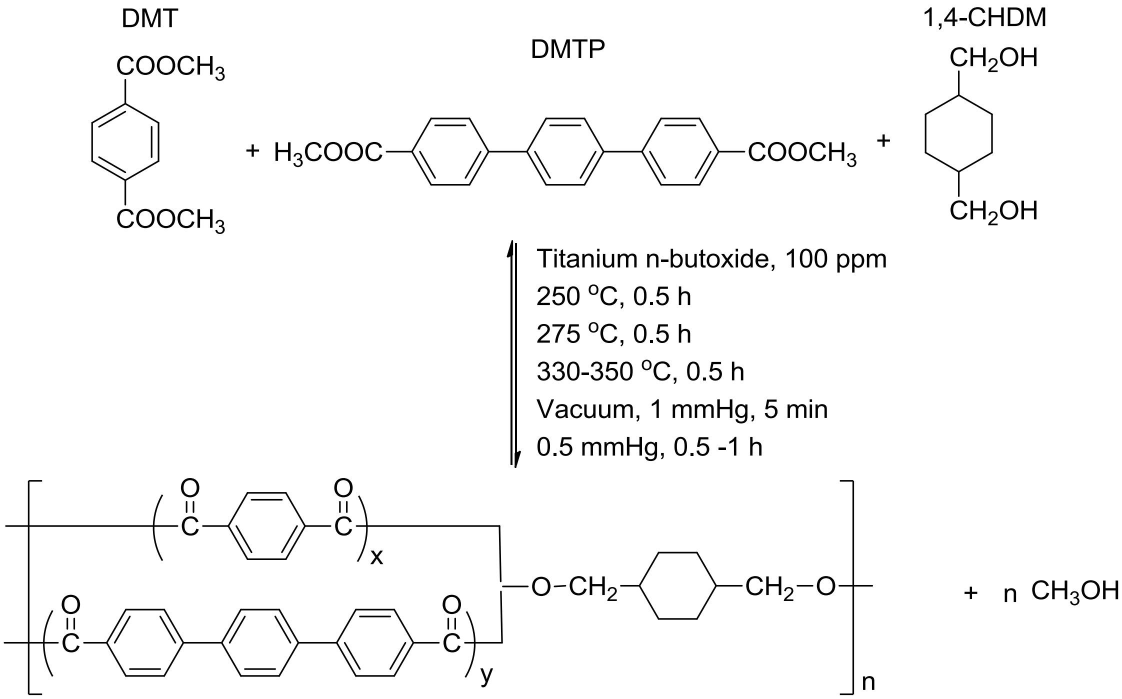
Proposed preparation of 4,4'-terphenyldicarboxylic acid.[8] A mixture of terphenyl and oxalyl chloride dissolved in carbon disulfide is stirred and is treated with anhydrous powdered aluminum chloride. The mixture color immediately turns to brownish-black, and then the mixture is stirred in an ice-bath for 1 h. After an additional amount of anhydrous powdered aluminum chloride is added, the ice-bath is removed. The mixture is continued to be stirred overnight at room temperature and then is poured into cracked ice so that the complex can be decomposed. After the carbon disulfide is evaporated and removed by the nitrogen stream, the solids is filtered, washed several times with dilute hydrochloric acid, and dried in the vacuum oven. It is expected to obtain a pale yellow solid, which will not completely soluble in 10 % aqueous lithium hydroxide, sodium hydroxide, potassium hydroxide and ammonia.

Proposed preparation of 4,4'-terphenyldicarbonyl chloride.[8] The corresponding diacid chloride can be prepared by refluxing the crude dicarboxylic acid with thionyl chloride in small amounts of pyridine. The reaction is assumed to be done when the solids dissolve completely. The excess thionyl chloride can be removed by distillation. The crude product is dissolved in boiling benzene and the undissolved solids are removed by filtration. Then the solution is treated with a small amount of carbon black to remove the color. After filtration to remove the carbon, a yellow precipitate is obtained on cooling from hot benzene. The product can be purified by an easy sublimation.

Proposed preparation of dimethyl 4,4'-terphenyldicarboxylate (DMTP).[8] The dimethyl diester can be easily obtained by reacting the diacid chloride with a small amount of methanol at reflux temperature. Then the solid is recrystallized from dimethylformamide (DMF) to obtain yellow crystals.



Scheme 9.5 Proposed synthesis of *p*-terphenyl-4,4'-dicarboxylic acid and its derivatives[8]



Scheme 9.6 Proposed synthesis of poly[x(DMT)y(DMTP)100(1,4-CHDM)]

Later dimethyl *p*-terphenyl-4,4'-dicarboxylate (DMTP) will be copolymerized with DMT and 1,4-CHDM to obtain the copolyesters, as shown in **Scheme 9.6**. The content of dimethyl terphenyl-4,4'-dicarboxylate (DMTP) can be altered from 0 mol% to 100 mol% to investigate the thermal and mechanical properties of the copolyesters.

9.4 Acknowledgements

We would like to thank Solvay Specialty Polymers for financial support and the supply of the monomer DMN. We also thank Gary Juneau at NMR Analysis and Consulting Company for the ^{1}H NMR measurements. We are also grateful to Dr. Timothy Long's group for allowing our group to use their TGA and DSC.

9.5 References

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