

Designing Acrylic Block Copolymers with Multiple Hydrogen Bonding or Multiple Ionic Bonding

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Abstract

The dynamic characteristics of hydrogen and ionic bonding contributes to the reversible properties of acrylic polymers, opening new avenues for designing materials with mechanical strength and processability. These non-covalent interactions function as physical crosslinks, which provide enhanced structural and mechanical integrity to acrylic block copolymers. The strong hydrogen bonding or ionic interaction also directs self-assembly to hierarchical microstructures, which enables many applications including thermoplastic elastomers and energy storage devices.

Inspired by complementary hydrogen bonding interactions between nucleobase pairs in DNA, a series of bioinspired nucleobase-acrylate monomers such as adenine acrylate (AdA), thymine acrylate (ThA), cytosine acrylate (CyA) were designed, whose synthesis were afforded by aza-Michael addition. Among those nucleobases, cytosine arises as a unique category. It is not only able to self-associate via weak hydrogen bonds, but also forms quadruple hydrogen-bond bearing units (ureido-cytosine) when functionalized with isocyanates. Reversible addition-fragmentation chain transfer polymerization (RAFT) yielded acrylic ABA triblock copolymers with CyA external hard blocks. A subsequent post-functionalization using hexyl-isocyanate generated the corresponding ureido-cytosine acrylate(UCyA)-containing triblock copolymers. The self-complementary quadruple hydrogen bonding in the UCyA polymers achieved a broader service

temperature window, while the alkyl chain ends of UCyA units allowed tunability of the mechanical strength to apply as thermoplastic elastomers. In addition, quadruple hydrogen bonding induced stronger propensity of self-assembly and denser packing of the polymers, which contributed to a well-defined ordered morphology and enhanced resistance to moisture uptake. A facile 2-step synthesis provided doubly-charged styrenic DABCO salt monomer(VBDC₁₈BrCl) containing an octadecyl tail. RAFT polymerization allowed the preparation of DABCO ABA block copolymers with defined molecular weights and low polydispersity. Thermal analysis revealed a melting transition of the VBDC₁₈BrCl block copolymer resulting from the side-chain crystallization of the long alkyl tail. Systematic mechanical comparisons between DABCO salt-containing copolymers and the corresponding singly-charged polymer controls demonstrated superior mechanical properties attributable to a stronger ionic interaction between the doubly-charged groups. Morphological characterizations revealed a well-ordered lamellar microstructure and a unique three-phase morphology of the DABCO block copolymers, which involve a soft phase, a hard phase, and an ionic aggregates domain dispersed within the hard domain.

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Chapter 1. Hydrogen Bonding in Shape Memory Polymers: Structure-Property Relationships

1.1 Introduction

1.1.1 From Shape Memory Alloy (SMA) to Shape Memory Polymer (SMP)

The discovery of shape memory materials has attracted tremendous research attention in recent decades. Application of external stimuli allows the material to transform into one or several temporary shapes and recover to its original state. Buehler *et al.* first observed shape memory behavior in Ni-Ti alloys, in which a phase change from an austenitic phase to a less symmetric martensitic phase occurred during cold processing of the equiatomic Ni-Ti alloys (Figure 1.1).¹ Above a critical temperature (A_f), the alloys reverted to the original austenitic phase resulting in shape recovery. In addition to the Ni-Ti alloys, other SMAs such as Cu-Al-Ni and Fe-Mn-Si, enable many applications in electrical and medical technologies due to their excellent electrical conductivity and high strength.^{2,3} However, those SMAs suffer from the same disadvantages: high density, high manufacturing cost, and toxicity, which prevent utility in many applications. Therefore, researchers started to search for shape memory materials with superior properties.

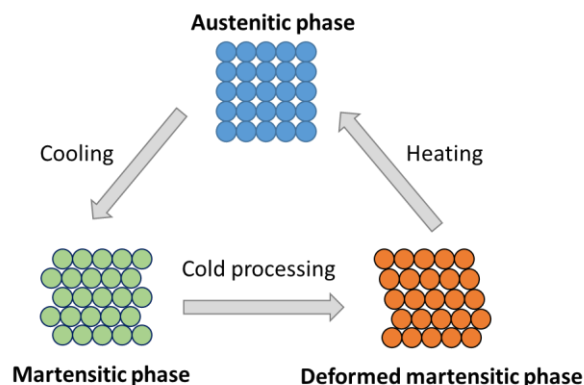


Figure 1.1 Schematic description of shape memory mechanism of the Ni-Ti alloys.

Shape memory polymers (SMPs) have the greatest potential for future applications among all the shape memory materials. They are lightweight, low cost, ductile, and access a wide range of manufacturing temperatures.⁴ Moreover, the biocompatibility and biodegradability^{3–18} highlight these materials for biomedical applications such as self-expandable stents for drug delivery¹⁸ and self-tightening sutures⁸.

1.1.2 Mechanisms and Processing Technologies of SMPs

SMPs exhibit two types of phases, i.e. permanent and temporary phases. Incorporating chemical or physical crosslinking into polymer structures promotes stabilization of the permanent shape, and prevents chain slippage during deformation. Programming of SMPs begins with heating the polymer above its transition temperature T_s (such as T_g and T_m), and applying a tensile load to achieve the required deformation. Cooling below the transition temperature kinetically traps the

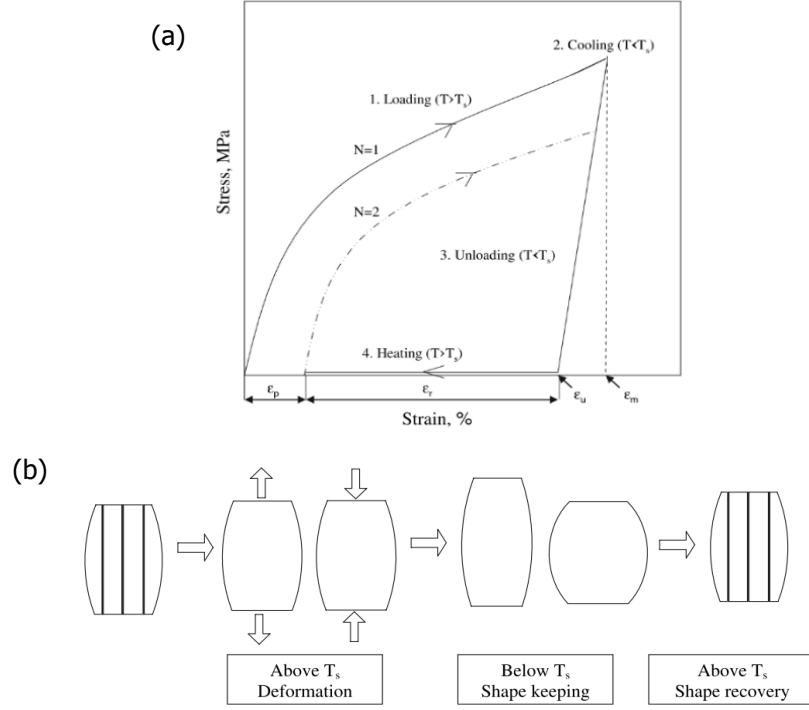


Figure 1.2 Schematic description of thermomechanical test of material in stress-strain relationship (a) and macroscopic shape memory effect (b). The images were reproduced from Reference 6.

stress, providing a temporary shape. (Figure 1.2). At the molecular level, loss of conformational entropy facilitates the recovery of the original shape upon application of external stimuli (such as heat). Shape fixity (R_f) and recovery ratio (R_r) are two important parameters to assess the performance of a material during processing cycles, which are defined as follows:¹⁰

$$R_f = \frac{\varepsilon_u(N)}{\varepsilon_m(N)} \quad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \quad (2)$$

Shape fixity (R_f) describes the ability of a material to retain its shape after removal of the tensile stress. $\varepsilon_m(N)$ is the imposed strain in the N^{th} cycle, and $\varepsilon_u(N)$ is the remaining strain after stress

retraction. Usually, $\varepsilon_m(N)$ and $\varepsilon_u(N)$ have different values, and $\varepsilon_u(N)$ is no larger than $\varepsilon_m(N)$. The formation of a secondary network during cooling helps to restrict chain mobility and immobilize the strained state. The R_f value approaching unity implies a better ability of the polymer to maintain its temporary shape. Recovery ratio (R_r) is the measurement of the extent to which a SMP returns to its permanent shape at the end of each programming cycle. $\varepsilon_p(N - 1)$ and $\varepsilon_p(N)$ are the corresponding residual strains after the SMP reverts to its permanent state at the $(N-1)^{th}$ and N^{th} cycle, respectively. Thus, Equation 2 represents how much strain recovers in adjacent programming cycles. The values of R_f and R_r change in the first few cycles and then stay constant as the cycle number N increases. The variations of the first few R_f s and R_r s are attributed to the processing and energy storage history of the sample, and the polymer chains gradually align themselves in the deformation orientation during the shape memory programming process.¹⁰

1.1.3 SMPs with Noncovalent Interactions

Incorporating noncovalent interactions (e.g. hydrogen bonding, ionic bonding^{19,20}, π - π stacking²¹) into polymers provides a promising avenue for obtaining novel SMPs. This not only opens up possibilities to design materials that cater to various manufacturing conditions, but also allows other stimuli to trigger the shape memory behavior, such as thermal, pH, moisture and light.^{22–24} For this type of polymer, the reversible interactions serve as a molecular switch to isolate the temporary shape in its strained state. Taking the thermally triggered SMP with reversible binding groups as an example, heating the polymer above the physical-interaction transition temperature T_s results in the dissociation of the physical crosslinks. The noncovalent interactions reform

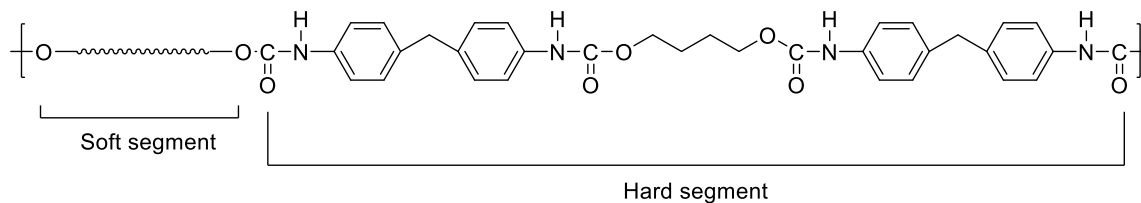
through cooling, and stabilize the temporary shape after tensile force retraction. Reheating above T_s promotes disassociation of the physical crosslinks to revert to the material's permanent state.

Hydrogen bonding is one of the most interesting categories among all the noncovalent interactions due to its dynamic and directional characteristics. Because of its thermal and solvent responsiveness, it imparts other properties such as self-assembly and self-healing to the SMP. This review discusses three types of hydrogen bonding functional groups (ureido-pyrimidinone (UPy), urethane, and vinyl-alcohol) that people utilize most commonly to design SMPs. In addition, it explains two main triggering strategies to induce shape memory behavior of hydrogen bonding containing SMPs. Finally, this review covers the role of hydrogen bonding in an emerging class of SMPs that possess two or more temporary shapes: multi-shape memory polymers (multi-SMPs).

1.2 Hydrogen Bonding Containing SMPs

1.2.1 Urethane Containing SMPs

The urethane group is the core component in a polyurethane (PU). The carbonyls and secondary amines in its structure are excellent hydrogen bond acceptors and donors respectively. Reacting a polyol with excess of a diisocyanate, followed by chain extension using a diol affords a segmented PU. The flexible polyol chain constitutes the soft segment of the PU, and the aromatic-containing diisocyanate acts as the hard segment (Scheme 1.1). PUs are chemically resistant, have good weatherability and sufficient mechanical properties to endure repeated operations,²⁵ making them



Scheme 1.1 Structure of PU.

suitable for SMPs. The semi-crystalline soft segment is usually the reversible phase, whereas the hydrogen bonding urethane linkage in the hard segment functions as physical crosslinks to stabilize the permanent shape. Recently, there were many studies investigating how hydrogen bonding in the PU determines the shape memory properties of polymers. Cao *et al.*²⁶ synthesized a PU using a polycaprolactone diol (PCL) and an aromatic diisocyanate, and added different amounts of nanoclay particles to fabricate shape memory nanocomposites. Although the nanocomposites demonstrated a higher mechanical integrity than the pristine PU above the melting temperature of the soft segment ($\sim 40^\circ\text{C}$), the R_r values of composites with 1%, 3% and 5% nanoclay incorporation were lower compared to that of pristine PU (Figure 1.3a). They found that this R_r drop correlated to the mixing of the PU's hard and soft phases promoted by the addition of nanoclay particles, which disturbed the formation of hydrogen bonding. Therefore, the hydrogen bonding netpoints lost some of the ability to hold the permanent shape during the recovery cycle. Moreover, phase mixing disrupted the formation of PCL crystalline regions, and the R_f decreased as a result of insufficient crystallinity to stabilize the temporary shape (Figure 1.3b).

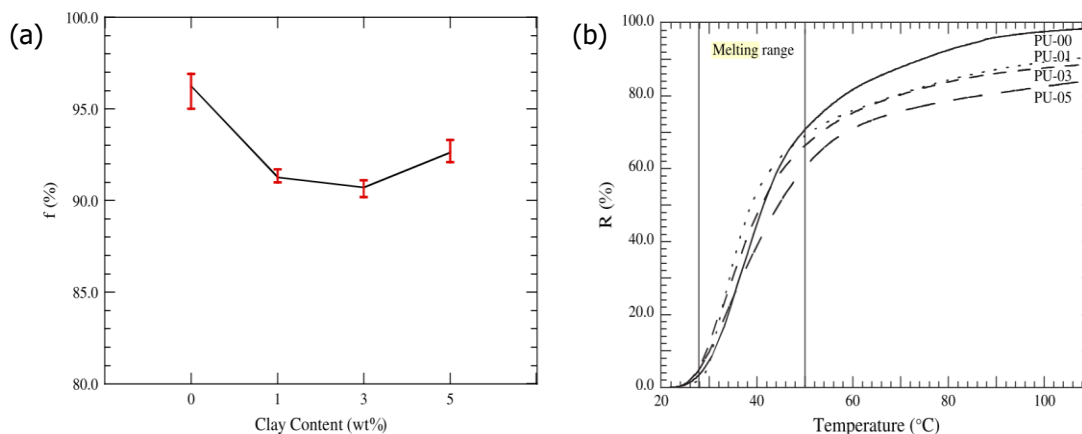


Figure 1.3 (a) Shape fixity of the polyurethane nanocomposites. Stretching rate was 20 mm/min; stretching ratio was 2.0. Shape recovery ratio of polyurethane and its nanocomposites under unconstrained condition during heating. Heating rate was 4 $^{\circ}\text{C}/\text{min}$. The images were reproduced from Reference 26.

Introducing other molecules that have hydrogen donor or acceptor groups to a PU also brings surprising properties to SMP. Chen *et al.*¹¹ blended a shape memory PU (SMPU30) with a liquid crystal compound, cholesteryl isonicotinate (INCh), which has a hydrogen bond donating nitrogen in its structure to generate shape memory supramolecular composites (Figure 1.4a). The electron rich pyridine nitrogen in INCh formed new hydrogen bonding pairs with the carboxylate groups in the PU, and restricted the mobility of polymer chains. This was indicated by a higher storage modulus in DMA (dynamic mechanical analysis) compared to the SMPU30 control, which

recovery through disrupting the hydrogen bonding formation in the structure. This study provides a facile method to obtain the PU with multiple switchable phases via introducing other hydrogen bond bearing molecules.

1.2.2 2-Ureido-4[1H]-pyrimidinone (UPy)-containing SMPs

Beijer *et al.* found that the 2-ureido-4[1H]-pyrimidinones (UPys) prepared from cytosine derivatives and isocyanates dimerized through self-complementary quadruple hydrogen bonding (QHB).²⁷ In most cases, UPy dimers form a stable DDAA (donor-donor-acceptor-acceptor) hydrogen bonding arrays (Figure 1.5) with a dimerization constant exceeding 10^6 M^{-1} in chloroform.

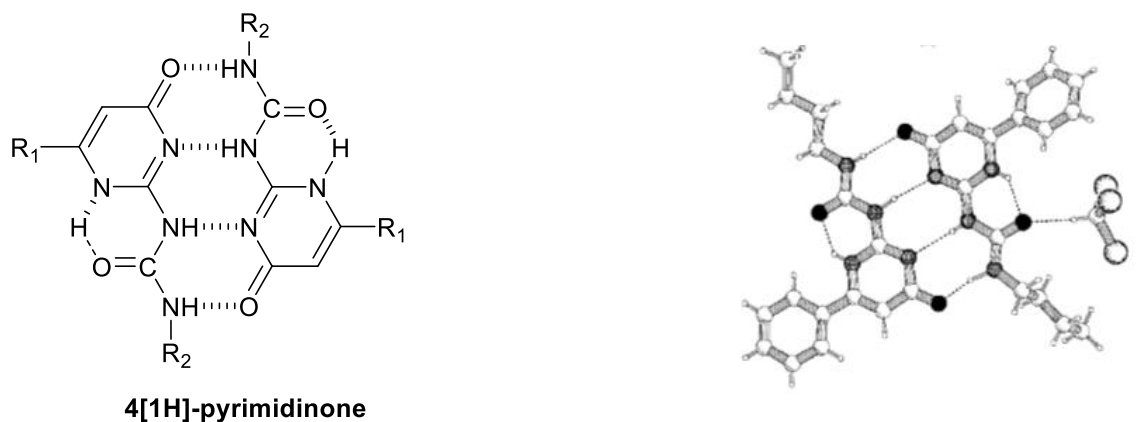


Figure 1.5. Structural representation of UPy dimers. Images were reproduced from Reference 14.²⁷

This exceptionally strong secondary interaction enables the formation of physical networks to isolate the temporary or permanent shape in SMPs. For example, a titin mimicking SMP utilized

the Upy hydrogen bonding motif in its structure.²⁸ Titin is a skeletal protein that has excellent mechanical and energy absorption properties due to the reversible breakage and formation of secondary interactions, and is able to recover to its original shape through refolding. The homopolymer **1** shown in Figure 1.6a consists of cyclic UPy modules in the backbone, and each monomer contains a pair of UPy groups that dimerize through QHB.

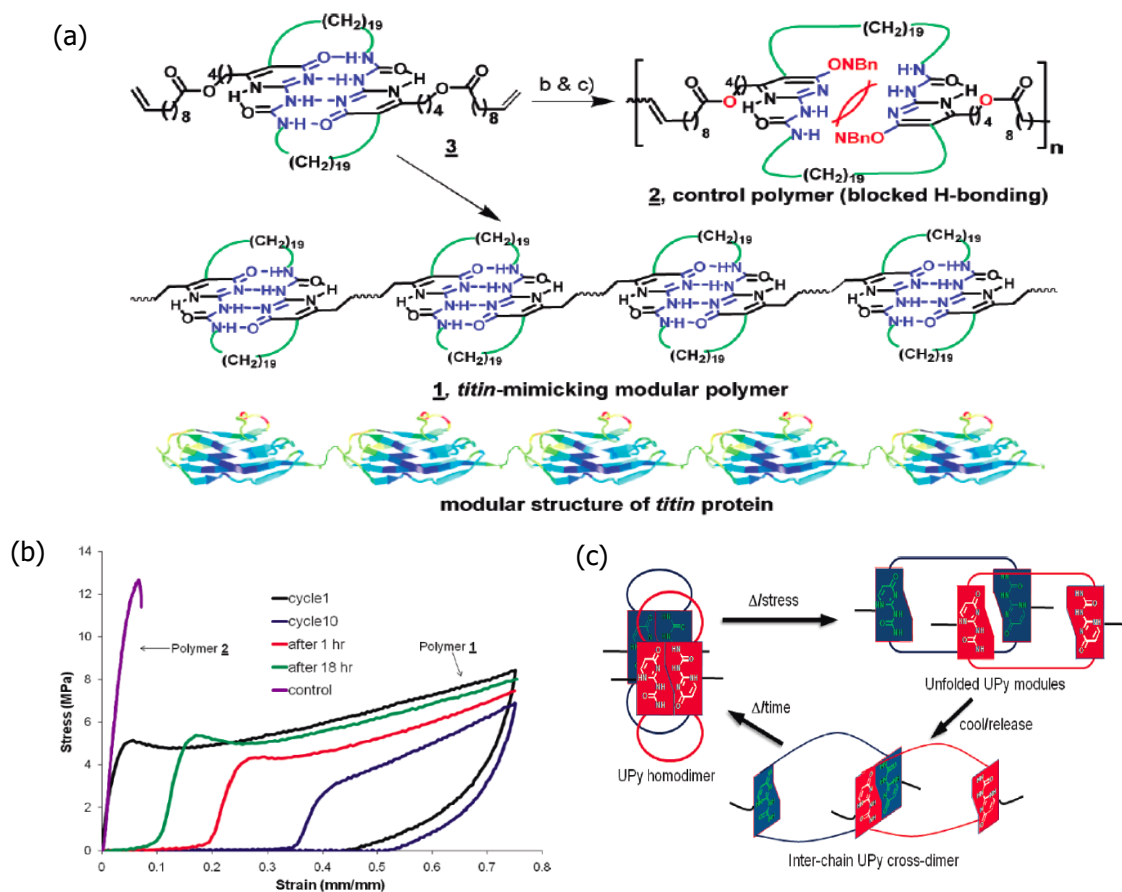


Figure 1.6. (a) Structure of titin-mimicking monomer, homopolymer 1 and control polymer 2. (b) Stress-strain curves for polymer 1 and 2. (c) Schematic representation of proposed shape memory behavior of polymer 1. The images were reproduced from Reference 28.

A synthesized control (homopolymer **2**) is structurally similar to **1** except that a bulky group lies in between the UPy dimers to screen the formation of QHB. Stress-strain study of homopolymers **1** and **2** revealed a dramatic difference in their mechanical properties. Homopolymer **2** was very brittle and failed immediately at only 7% strain, whereas the homopolymer **1** exhibited sufficient toughness, with the strain increased to up to 100% after yielding (Figure 1.6b). In addition, polymer **1** demonstrated excellent shape fixity and recovery, with the recovery rate inversely related to temperature. The interesting stress-strain behaviors and shape memory properties confirmed the critical role of hydrogen bonding. Stretching the polymer at higher temperatures resulted in chain unfolding and QHB homodimer dissociation. This released free UPy modules to form interchain cross-dimers, and established a temporary network structure (Figure 1.6c). Reheating brought the polymer back to its coiled, folded state; therefore, the UPy modules only form the homodimer with the other module in the same monomer, triggering shape recovery.

Moreover, many SMPs employ UPy as side groups. The flexible linker that bridges the UPy side group and the polymer backbone promotes molecular recognition and self-assembly of the polymer chains. Zhu *et al.* reported that introduction of UPy side groups into polyurethane soft segments contributed to the polymer's shape memory properties.²⁹ The QHB restricted the long-range segmental motion of the polymer chains and increased the T_g from 28.3 °C to 73.3 °C, which allowed fixation of the temporary shape at room temperature. Fast exchange of hydrogen bonding dynamics occurred when heating above 86 °C, facilitating polymer shape recovery. The resulting SMP demonstrated excellent immediate shape fixity ($R_f = 95.8\%$), however, due to low

incorporation of UPy in the polymer, the physical crosslinking density was insufficient to stabilize the temporary shape for an extended period of time.

1.2.3 Vinyl Alcohol Containing SMPs

The hydroxyl side groups in poly (vinyl alcohol) (PVA) provide locations for hydrogen bonding, making it a suitable material to absorb water and serve as a hydrogel. Due to their biocompatibility and good mechanical integrity,¹⁵ shape memory PVA hydrogels provide many opportunities for biomedical applications.

Li *et al.* synthesized an interpenetrating double network hydrogel comprising a PEG chemical network and a PVA physical network.¹² After being subjected to three cycles of freezing and thawing, the deformed PVA/PEG hydrogel acquired the ability to pin temporary shape through the formation of crystalline regions and a hydrogen-bonded physical network. Dissociation of hydrogen bonding and melting of crystalline regions at higher temperatures induced recovery to the permanent shape. The instant R_f of the hydrogel was reported to reach 90%, but the authors did not discuss the temporary fixation performance of the hydrogels at a longer time period. Moreover, they found that the hydrogel exhibited self-healing properties stemming from extensive interchain hydrogen bonding of the PVA side groups. The ruptured hydrogel regained 60 % of its original mechanical performance after putting the sides of the rupture into contact for 48 h, which was due to the hydrogen bonding interactions between the two fractured surfaces.

Chen *et al.*³⁰ discovered that hydrogen bonding plays an important role in defining both permanent and temporary shape of PVA hydrogels. Synthesis of the hydrogel involves blending PVA with tannic acid (TA) in water at 90 °C. TA formed strong hydrogen bonds as a result of its multiple-functionalities (Figure 1.7), while the hydroxyl side groups in PVA afforded weaker

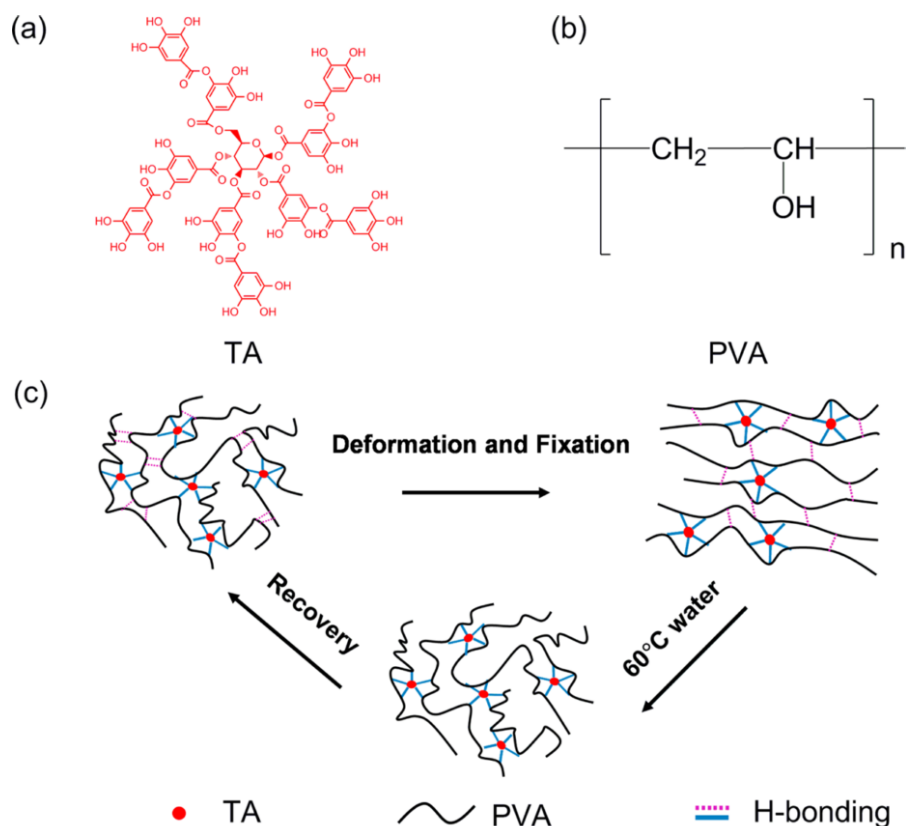


Figure 1.7. Molecular structure of TA (a) and PVA (b). Temperature-Responsive Shape Memory Mechanism of the PVA–TA Hydrogel (c). The images were reproduced from Reference 30.

interactions. The hydrogel displayed an excellent thermal-responsive shape memory performance originating from the breakage and formation of weaker hydrogen bonds from PVA chains. In addition, both the dried and wet hydrogel exhibited almost full recovery to the original shape at elevated temperatures with the recovery period ranging from several seconds to 2.5 min. However,

the authors still need more studies to investigate the connections between the hydrogel's water content and the shape recovery rates.

1.3 Responsive Stimuli of Hydrogen Bonding Containing SMPs

1.3.1 Thermal-induced SMPs

Thermal programming has turned out to be the most common strategy to trigger shape memory behavior of the hydrogen bond-containing SMPs. When hydrogen bonding functions as a molecular switch for temporary shapes,^{28,30} heating the polymer above the temperature at which the dynamic hydrogen bonds have fast exchange rates facilitates relaxation of the strained state. The exchange rate becomes slower at lower temperatures, allowing stabilization of the temporary shape. However, for those polymers that exploit hydrogen bonding interactions to define their permanent shapes,³⁰ shape recovery requires milder thermal application so as not to disrupt the materials' permanent structures.

Li and coworkers utilized a thermal trigger for their UPy-containing SMPs.³¹ They copolymerized 2 mol% ethyl methacrylate monomer containing pendent UPy side-groups with n-butyl acrylate and an acrylic trifunctional crosslinker to generate a polymer film (Figure. 1.8a). Thermo-mechanical study of the polymer demonstrated that UPy QHB effectively pinned the deformed shape after tensile stress removal (immediate R_f =90%). The strain relaxation was sluggish (shape recovered only 2-3% in an hour) at lower temperatures as a result of slow hydrogen

bonding exchange rate. Heating accelerated the exchange of dynamic bonding and dramatically weakened the physical network, triggering shape recovery.

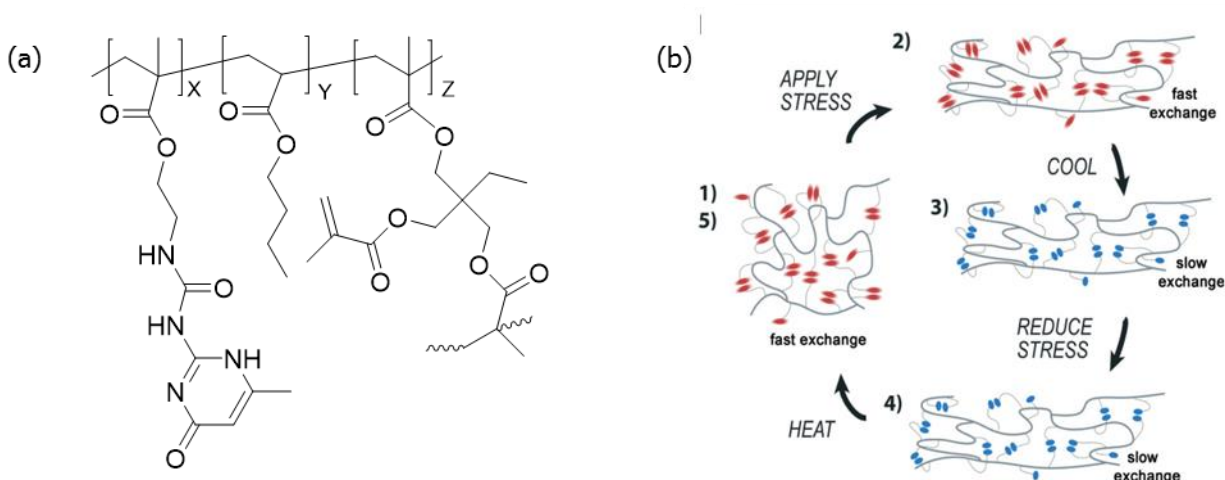


Figure 1.8. (a) Polymer structure. (b) Illustration of thermal-induced shape memory programming. The images were reproduced from Reference 31.

1.3.2 Moisture-induced SMPs

Exposure of hydrogen bond-containing polymers to water or other polar solvents facilitates the formation of hydrogen bonds between the polymer and the solvent, resulting in interesting shape memory effects. In addition, small solvent molecules promote chain mobility for shape recovery by acting as plasticizers to decrease polymer T_g . Because of its thermal energy-free nature, the moisture-triggering strategy is beneficial for application conditions where elevated temperature is undesirable.

Many reports identified moisture as an effective SMP stimulus. For example, Liu *et al.*³² explored the solvent effect on SMPs by immersing a styrene-based SMP in DMF for different amounts of time. The styrene-based SMP showed a decrease of storage modulus with the increasing soaking time. Moreover, both the DMA and DSC observed a decrease of T_g to up to 20 °C (soaked for 120 min) compared to that of the dry polymer with increasing time of solvent exposure (Figure 1.9a), demonstrating a loss of polymer mechanical integrity. FTIR (Figure 1.9b) revealed that DMF carbonyl stretching shifted to higher frequency with extended immersion time, which suggested that more and more DMF molecules were involved in hydrogen bonds with the polymer.

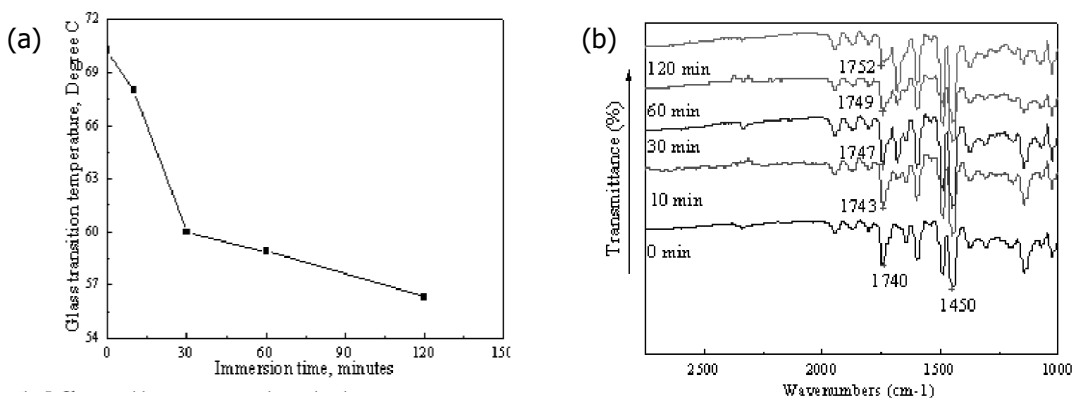


Figure 1.9. (a) Glass transition temperature vs. immersion time. (b) FTIR spectra of styrene-based SMP after different immersion hours for C=O stretching region. The images were reproduced from Reference 32.

Recently, Chen and coworkers³³ demonstrated that their polyurethane (PU), which had pyridine pendant groups, exhibited moisture-responsive shape memory behaviors. They placed elongated samples in a moisture chamber and measured the resulting strain at certain time intervals. As

expected, the samples experienced a strain recovery with the rate proportional to the chamber's relative humidity (RH) value and temperature. FTIR revealed that the preformed interchain hydrogen bonding between the pyridine nitrogen and N-H of the urethane (Py-N $\cdots$ NH) in the dry polymers became weaker after water exposure, which triggered shape recovery due to the reduced amount of physical crosslinking to restrict chain mobility. Thus, they proposed that water could either compete with urethane to hydrogen bond to pyridine (H-O-H $\cdots$ N-Py), or bridge two pyridine groups through hydrogen bonding (Py-N $\cdots$ H-O-H $\cdots$ N-Py).

Another important study pointed out that two types of water exist in PU, i.e. free and bound water.³⁴ Free water is lost easily at around 120 °C, while bound water associates tightly with the polymer through hydrogen bonding, and its complete removal happens only above polymer melting temperature (about 200 °C in this study).

1.4 Hydrogen Bonding in Multiple-SMPs

Multiple-SMPs are capable of storing two or more temporary phases, the number of which is directly associated with how many discrete phase transitions the polymers can go through.^{4,17} Shape programming of a triple-SMP (Figure 1.10) involves heating the polymer in shape 1 above the highest transition temperature T_D for deformation, and cooling down to an intermediate temperature to fix the temporary shape 2. Then the polymer is subjected to a further deformation followed by cooling below the lower transition temperature (T_g) to reach the temporary shape 3. During the recovery cycle, the polymer first relaxes to shape 2 before returning to the permanent

shape 1. In many multiple-SMPs, hydrogen bonding motifs promote the polymers' shape fixation and recovery processes.

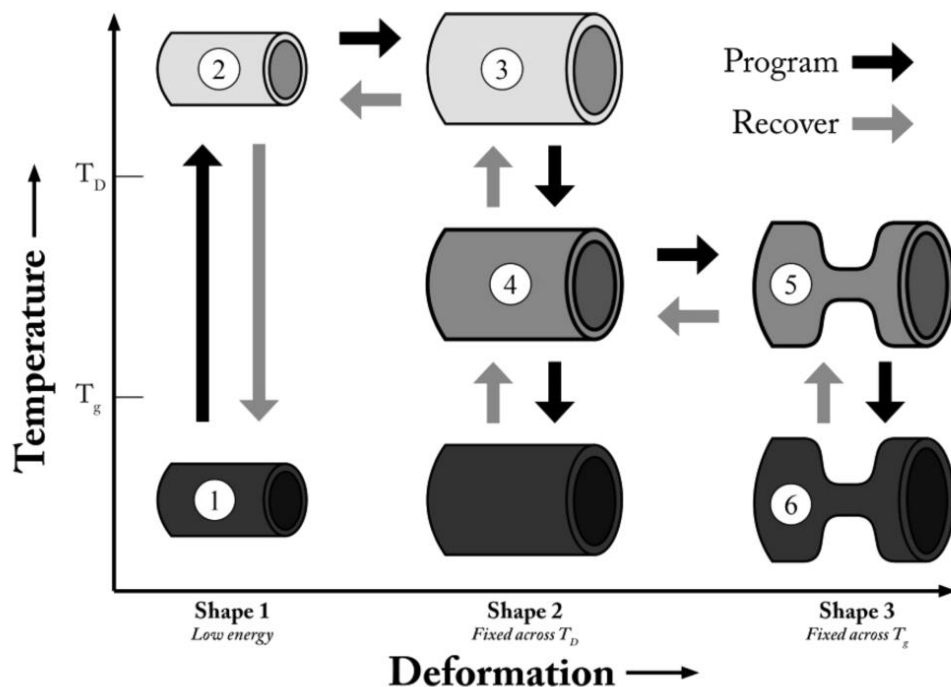


Figure 1.10. Schematic representation of the programming and recovery procedures of triple-SMP. The image is reproduced from Reference 35.

In one study, copolymerization of a UPy acrylate with an alkyl methacrylate and a crosslinker generated a polymer network consisting of chemical and physical crosslinks.³⁵ Both the glassy state of the polymer backbone and the UPy hydrogen bonding moiety function as the molecular switches to stabilize two temporary shapes, and the chemically-crosslinked network defines the permanent shape. Varying the concentration of each monomer or the alkyl length of methacrylate allowed the control of T_g and mechanical property of the polymer. This provides a facile method to fabricate tunable triple-SMPs catering to different applications.

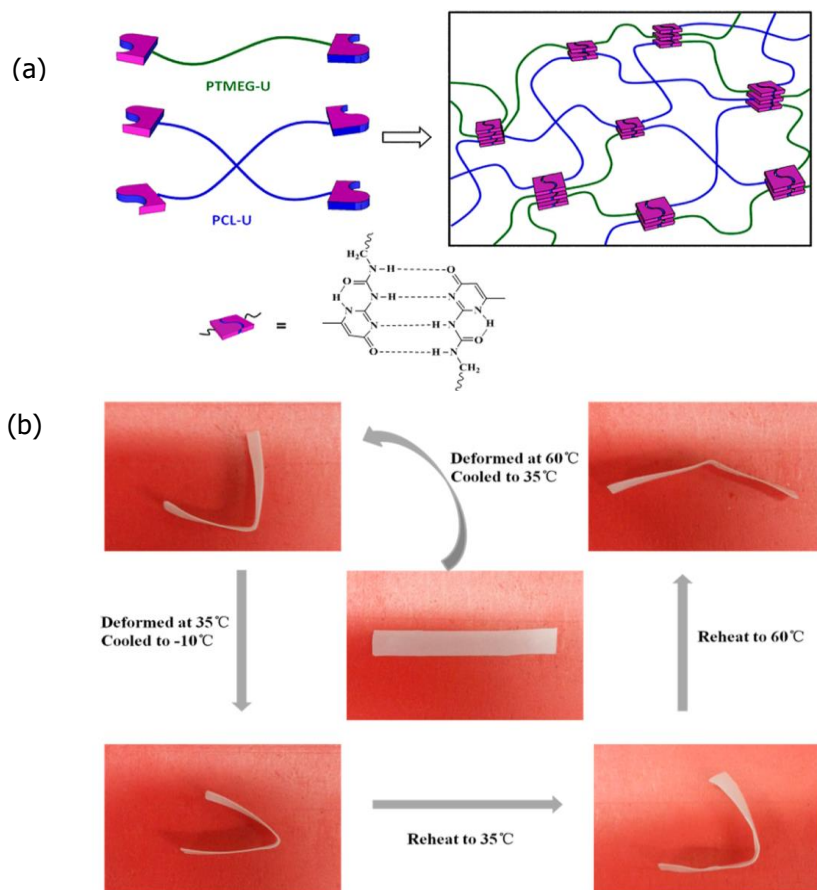


Figure 1.11. (a) Schematic representation of the PCL-PTMEG network. (b) Triple-shape memory effect of a strip sample of PCL₃₆-PTMEG₆₄. The images were reproduced from Reference 36.

In another study, Wei and coworkers employed quadruple hydrogen bonding (QHB) to combine two different crystalline phases into a network structure.³⁶ Linear poly(tetramethylene ether) glycol (PTMEG) and a four-armed PCL bearing UPy endgroups formed a physical network structure through complementary hydrogen bonding (Figure 1.11a). Figure 1.11b illustrates the shape memory process, in which the sample was first bent beyond the melting temperature of both the PCL and PTMEG phases (over 60 °C) followed by cooling to an intermediate temperature (35

°C) to fix at the temporary shape B. Further deformation and cooling to -10 °C allowed crystallization of the PEG phase to stabilize shape C. Reheating C back to the intermediate temperature enabled shape recovery to B first, and the full recovery was completed at 60 °C to return to the original shape A. The authors also investigated the correlation of PCL and PMEG ratio to the material's recovery performance. Surprisingly, they found that increasing the concentration of the four-armed PCL from 36% to 80% did not bring a remarkable improvement of recovery performance (only 4% increment). They suggested that reduced crosslinking density could be the reason, where the four-arm PCL might form weaker network structure compared to the linear PMEG. However, the free volume effect resulting from high incorporation of the bulky PCL could also be the reason for reduced crosslink density. Therefore, more investigations are necessary to explain such phenomena.

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Chapter 2. Cytosine and Ureido-cytosine Acrylic ABA Triblock Copolymers: Mechanical and Morphological Correlations

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2.1 Abstract

RAFT polymerization is a versatile and facile method for preparation of triblock copolymers with controlled molecular weight and low polydispersity. Poly(*n*-butyl acrylate) (PnBA) served as the central block, and chain extension with nucleobase-containing blocks, such as poly(cytosine acrylate), produced an ABA triblock architecture. The nucleobase external blocks and PnBA central block imparted structural integrity and flexibility. The flexible butylene linker in the cytosine acrylate segment facilitated intermolecular recognition and self-assembly. Moreover, hydrogen bonding between cytosine segments promoted physical crosslinking and enhanced mechanical performance. Post-functionalization with an isocyanate of cytosine-containing triblock copolymers afforded the corresponding ureido-cytosine block polymers with quadruple hydrogen bonding motifs, increasing the propensity for physical interactions. This thermally-reversible, noncovalent interaction also enabled melt processibility of ureido-cytosine polymers. Systematic comparison of the thermomechanical and morphological properties of cytosine and ureido-cytosine block copolymers revealed superior thermomechanical properties, extended modulus plateau regions, improved structural ordering, and excellent moisture resistance for the ureido-

cytosine polymers. This enhanced performance verified the quadruple hydrogen bonding-dominated physical behavior. Hence, structure-property-morphology relationships illustrated key characteristics for novel thermoplastic elastomers.

2.2 Introduction

Thermoplastic elastomers (TPEs) have received tremendous attention in recent decades due to their high mechanical strength while maintaining processability of materials, which facilitate impact in applications as automobile accessories, adhesives, electronic devices, and artificial tissues.^{1–5} Typically, TPEs are block or segmented copolymers that consist of soft and hard blocks. The soft block (low glass transition temperature (T_g)) contributes to flexibility, while the hard block (high T_g) imparts stiffness and mechanical integrity. Covalent linkages of chemically dissimilar blocks drive formation of microphase-separated morphologies, with the hard domains acting as physical crosslinks to afford elastomeric properties.

Integrating noncovalent interactions into block copolymers enables promising avenues for designing and fabricating stimuli-responsive and reversible functional materials.^{6–11} Among various noncovalent interactions, hydrogen bonding provides unique performance. Hydrogen bond strength lies between those of most covalent bonds and Van de Waals interactions, allowing for sufficient association between functional units. In addition, complementary hydrogen bonding promotes molecular recognition and directs self-assembly into ordered structures.¹² In particular, the nucleobase pairs in the DNA double helix structure are natural sources of hydrogen bond donors and acceptors, and adenine and thymine are widely incorporated into synthetic polymers

due to their biocompatibility and synthetic versatility.^{13–16} The self-association as well as the complementary association between nucleobases serve as physical crosslinks, which enhance physical properties of polymers and provide thermal or solvent reversibility.^{17,18} For example, Long *et al.* synthesized acrylic ABA triblock copolymers containing adenine or thymine pendent groups in the external blocks, and this work demonstrated that complementary hydrogen bonding enhanced thermomechanical properties and melt processability.⁹ Utilizing a similar approach, O'Reilly *et al.* fabricated thermally responsive mixed polymeric nanoparticles consisting of an adenine-functionalized diblock copolymer shell noncovalently bonded to a thymine-functionalized diblock copolymer core, indicating its potential application in targeted diagnosis and nanomedicine.¹⁹ However, the dimeric hydrogen bonding association between adenine and thymine remains insufficient to provide a highly crosslinked 3-D network structure.

Recently, Hails *et al.* reported that a ureido-functionalized cytosine is able to form strong self-complementary quadruple hydrogen bonding (QHB) with a dimerization constant ($K_a > 9 \times 10^6 \text{ M}^{-1}$ in deuterated benzene) near the previously reported ureido-pyrimidone (Upy) module.^{20,21} Reaction of a cytosine with an isocyanate allows the formation of an ureido-cytosine (UCyt), which dimerizes through a stable donor-donor-acceptor-acceptor (DDAA) hydrogen bonding array. Recently, UCyt is attracting increasing attention for the synthesis of supramolecular polymers, where the UCyt end groups serve as molecular stickers to join telechelic oligomers into polymers. Cheng and coworkers developed a polypropylene glycol (PPG) supermolecular polymer utilizing a low molecular weight UCyt-functionalized telechelic oligomer (PPG-UCyt).^{22,23} PPG-UCyt

exhibited polymer-like behavior and self-assembly occurred into a well-ordered lamellar structure in both solution and bulk. Recently, our group utilized a regioselective Michael-addition to synthesize novel cytosine and ureido-cytosine acrylate monomers and employed radical polymerization to achieve random copolymers containing cytosine or ureido-cytosine pendant groups. However, the random distribution of monomers in the copolymer chain hindered phase separation and self-assembly. As a result, incorporating UCyt pendant groups into block copolymers is essential to study the influence of QHB motifs on polymer mechanical and morphological properties, as well as self-assembly in the solid state. Despite significant interest, this area remains unexplored due to synthetic challenges and limited solubility of Cyt and UCyt containing block copolymers.

Herein, we describe a novel bioinspired triblock copolymers containing pendant ureido-cytosine QHB motifs, where the design is based on the hypothesis that QHB could promote intermolecular interaction through forming strong physical crosslinks, which would be possible to result in enhanced mechanical property and well-defined morphologies. Two-step RAFT polymerization enabled facile preparation of acrylic copolymers with a low T_g , poly(*n*-butyl acrylate) (PnBA) central block and a relatively high T_g , poly(cytosine acrylate) (PCyA) as external blocks. Post-functionalization of the CyA polymer precursors afforded the corresponding ureido-cytosine polymers (UCyA) with identical soft and hard block compositions. Systematic thermal, mechanical, and morphological comparisons between CyA and UCyA block copolymers with varied external chain lengths revealed the synergy of noncovalent interactions and block

copolymer self-assembly. Variable temperature FT-IR demonstrated the reversibility of the noncovalent network in response to thermal stimulus. The self-complementary QHB in the UCyA polymers increased the propensity and strength of physical crosslinks, which contributed to more ordered morphologies, enhanced thermomechanical properties, and improved processability of the copolymers.

2.3 Experimental Section

Materials

n-Butyl acrylate (nBA, 99+%) was purchased from Sigma-Aldrich and was passed through a basic alumina column before use. α,α' -Azobis(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized twice from methanol. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, Sigma-Aldrich, 98%), N,N'-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich, 99%), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, $\geq 99\%$), cytosine (Sigma-Aldrich, 99%), 2,6-di-tert-butyl-4-methylphenol (BHT, Sigma-Aldrich, 99%), potassium carbonate (K_2CO_3 , Acros, anhydrous, 99%), 1,4-butanediol diacrylate (Alfa Aesar, 99%), sodium sulfate (anhydrous, Spectrum, 99%), hexyl isocyanate (99%, TCI) were used as received. Toluene (HPLC grade), dimethyl sulfoxide (DMSO, HPLC grade), N,N-dimethylformamide (DMF, HPLC grade), dichloromethane (DCM, HPLC grade), acetone (HPLC grade), hexane (HPLC grade), methanol (HPLC grade) were purchased from Spectrum and used as received.

Analytical Methods

^1H NMR spectroscopy was performed using an Agilent U4-DD2 400 Hz spectrometer at 23 °C with polymers dissolved in CDCl_3 , or $\text{DMSO}-d_6$, or a mixture of both solvents (1:1, v/v). Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL/min at 30 °C on two Agilent PLgel 10 μm MIXED-B columns, which connected in series with a Wyatt Dawn Heleos 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. Thermal gravimetric analysis (TGA) of the CyA and UCyA block copolymers was conducted utilizing a TA Instruments TGA Q500 with a 10 °C/min heating ramp from ambient temperature to 600 °C under constant N_2 purge. The 5 wt % degradation temperature ($T_{d,5 \text{ wt}\%}$) corresponds to the temperature at which the polymer retains 95 % of its original weight. Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC Q2000 using a heat/cool/heat cycle at a heating and cooling rate of 10 °C/min from -90 °C to 150 °C under N_2 purge. The midpoint of the thermal transition step was used to determine the T_g of the CyA and UCyA polymers. Dynamic mechanical analysis (DMA) experiments on the annealed polymer films were achieved utilizing a TA Instruments Q800 in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 5 μm , a static force of 0.01N, and a force track of 125 %. The sample was cooled down to -80 °C and isothermed for 5 min, length measured, and ramped at a rate of 3 °C/min. The peak of the tan delta curve was utilized to determine the T_g values of the polymer. Variable temperature FTIR (VT-FTIR) was performed on a Varian 670-IR spectrometer equipped with a Pike Technologies variable

temperature GladiATRTM attachment (diamond crystal). The spectra were collected every 10 °C from 30 °C to 150 °C.

Small angle X-ray scattering (SAXS) experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu K α). The sample-to-detector distance was 1605 mm, and the 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 2 h. All SAXS data were analyzed using the SAXSGUI software package to obtain radially 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 X-ray wavelength. The graphs were overlaid and vertically shifted to facilitate comparison. Employing the equation $d=2\pi/q$ enabled the calculation of the domain spacing of each sample, where q represents the first-order scattering vector. A Veeco MultiMode scanning probe microscope allowed the analysis of surface morphology for the annealed CyA and UCyA polymer films. Phase images were acquired under tapping mode using the silicon tip with a spring constant of 42 N/m.

A TA Instruments Q5000 thermogravimetric sorption analyzer (TGA-SA) enabled the analysis of water sorption for the CyA and UCyA polymer films. During the experiment, the film first went through a 5 h pre-dry process and was then subjected to a series of humidity steps from 0%-95% relative humidity (RH) with a 5% increment, and water sorption was calculated based on the weight gain of the sample relative to its pre-dried weight. Each humidity step had a preset time of

120 min but was allowed to continue to the next step if the sample reached an equilibrium state (<0.01% of weight change within 10 min).

Synthesis of Difunctional Poly(nBA) Macro-CTA

A difunctional chain transfer agent (CTA) 1,6-bis(2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid)-hexane diamide (diDDMAT-NH₂) was synthesized according to a previous literature.²⁴ nBA (15 g, 117.03 mmol), diDDMAT-NH₂ (122.23 mg, 0.15 mmol), AIBN (2.48 mg, 0.015 mmol), and toluene (60 g, 20 wt% solution) were added into a 200-mL Schlenk flask with a magnetic stir bar (CTA/initiator=10:1). The flask was subjected to four freeze-pump-thaw cycles and subsequent back fill with argon. The reaction mixture was stirred at 70 °C for 5 h (58 % conversion), precipitated into 1000 mL cold MeOH/H₂O = 10:1 solution, and the resulting polymer was dried in vacuo at 40 °C for 24 h to afford a tacky, yellow solid. The molecular weight of the difunctional macro-CTA was measured by GPC in THF: M_n=40.7 kDa, PDI=1.18 (dn/dc=0.064 mL/g).

Synthesis of Poly(CyA-*b*-nBA-*b*-CyA) Triblock Copolymers

Cytosine acrylate monomer (CyA) was prepared according to our earlier procedure.²⁵ A 50-mL Schlenk flask was charged with difunctional macro-CTA (2g, 0.049 mmol), CyA (1.72 g, 5.56 mmol), AIBN (0.81mg, 0.0049 mmol), and DMF (14.88 g, 20 wt% solution). After four freeze-pump-thaw cycles and refilling with argon, the solution was stirred at 70 °C for 2-6 h to afford polymers with varied CyA outer block chain lengths (Scheme 1). Precipitation into cold

MeOH/H₂O=5:1 solution yielded a light yellow solid that was collected and dried in vacuo at 50 °C overnight. ¹H NMR in DMSO-*d*₆ revealed the molecular weight of two CyA external blocks after 6 h of reaction: M_n=20. 0 kDa, with 10 kDa in each external block assuming equal propagation rate on both chain ends, monomer conversion: 61%, CyA content: 17 mol%. (Figure S2.2 and S2.3)

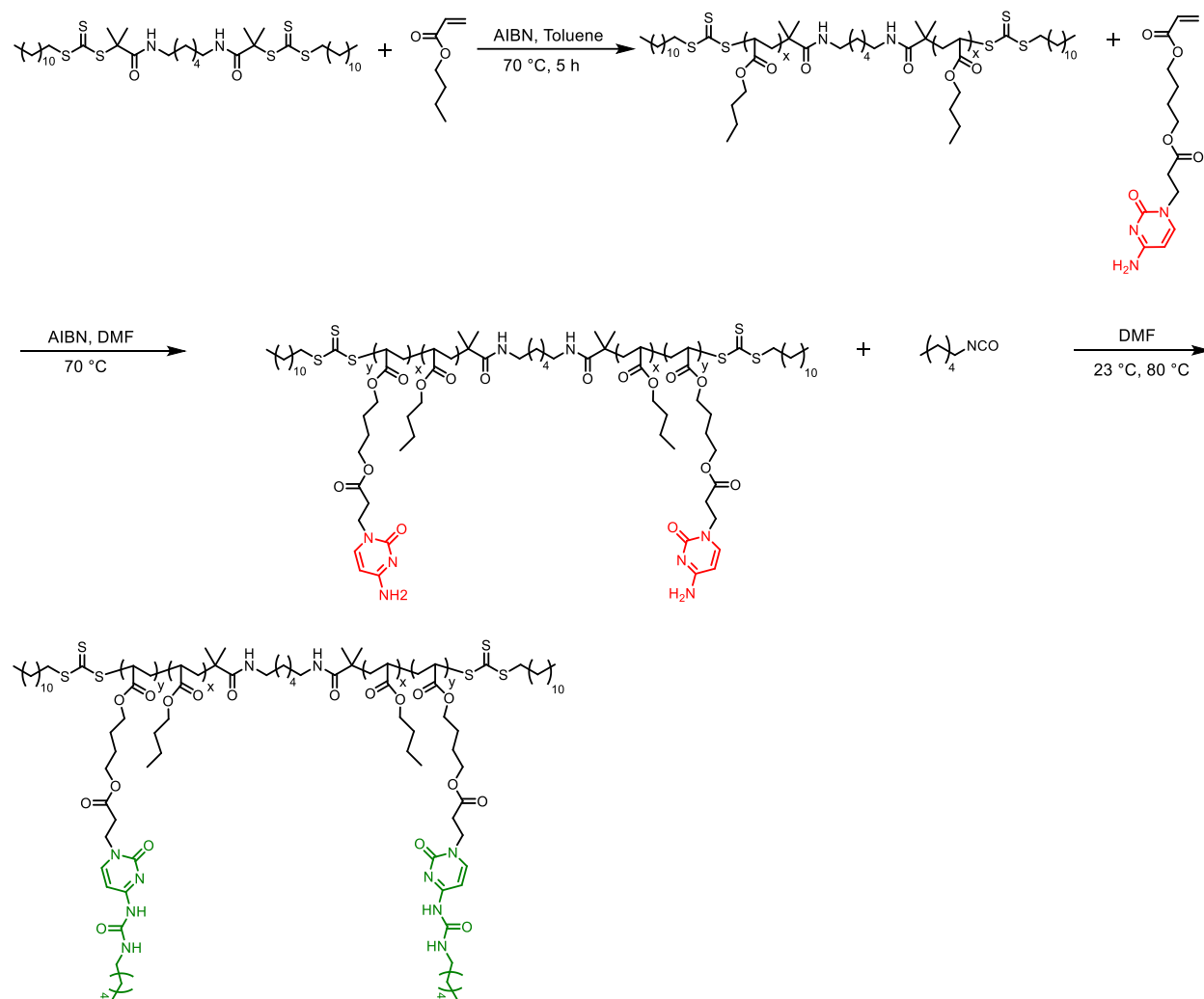
Synthesis of Poly(UCyA-*b*-nBA-*b*-UCyA) Triblock Copolymers

Poly(UCyA-*b*-nBA-*b*-UCyA)s with different lengths of external blocks were prepared through post-functionalization of the CyA containing triblock copolymers synthesized in the previous step (Scheme 1). Poly(CyA-*b*-nBA-*b*-CyA) (0.8 g, 1 eq) with 17 mol% of CyA content was dissolved in 10 mL dry DMF, and hexyl isocyanate (0.14 mL, 1.1 eq) was added dropwise into the solution. The content was reacted at 20 °C for 10 min, and then stirred at 80 °C for 16 h. Solution was precipitated into methanol, filtered, and dried under reduced pressure to generate a slightly yellow solid. ¹H NMR in DMSO-*d*₆ and CDCl₃ mixture confirmed the structure of the 17 mol% UCyA triblock copolymer product. (Figure S2.4)

Film Casting and Annealing Conditions

All CyA and UCyA triblock copolymers were dissolved 5 wt% in DMSO and DMF, respectively, and cast into PTFE molds to minimize deformation during film removal. The molds were covered with a glass petri dish and maintained at 50 °C for 3 d to allow slow evaporation of the solvent. The films were then placed under reduced pressure to dry for another 24 h, and annealed at 120 °C

for 12 h. A step-wise cooling approach was employed to slowly cool the film. The temperature was decreased by 30 °C each time and equilibrated for 3 h until room temperature. The resulting films were peeled from the molds and stored in desiccator prior to characterization.



Scheme 1. Synthesis of poly(CyA-*b*-nBA-*b*-CyA) and poly(CyA-*b*-nBA-*b*-CyA)

2.4 Results and Discussion

Synthesis of Cytosine Acrylate (CyA) and the Corresponding Ureido-cytosine Acrylate (UCyA) ABA triblock copolymers

Acrylates possess T_g s ≥ 100 °C lower than their methacrylate counterparts, due to the absence of the methyl substituent in the backbone. Utilizing the low T_g poly(n-butyl acrylate) (PnBA) as the central block offered flexibility to the block copolymers, while the aromatic content in the CyA external block contributed to chain stiffness (Scheme 1). Thus, adjusting the chain lengths of the soft and the hard blocks enabled tailoring polymer properties from rubbery to glassy. An alkyl spacer within the CyA monomer connects the cytosine module to the acrylate backbone, which tunes the T_g of the CyA outer block, and provides mobility for the cytosine module to self-assemble.²⁵

RAFT polymerization allowed for a facile and controlled propagation of the chain with a narrow polydispersity (PDI). Careful selection of CTA with a suitable reactivity of R- and Z- groups was crucial for successful RAFT polymerization. The tertiary carbon in the di-DDMAT R-group is a better homolytic leaving group compared to the acrylate radical, thereby ensuring efficient chain fragmentation and reinitiation.²⁶ A difunctional CTA (di-DDMAT) allowed divergent polymerization of the ABA triblock copolymer in two steps. In the first step, polymerization of the nBA afforded a difunctional PnBA-diCTA with an average molecular weight of 40.7 kDa and a PDI of 1.18 (Figure S2.1). An optimized CTA to initiator ratio (CTA/I=10) minimized the production of dead chains during the polymerization while maintaining a suitable polymerization

rate. The reaction remained homogeneous in toluene throughout the process with a conversion of 58% in 6 h. Precipitation into cold methanol/water solution afforded a >90% yield of the tacky yellow PnBA-diCTA. Subsequent drying in reduced pressure at an intermediate temperature (40 °C) for 24 h allowed complete removal of solvent and unreacted nBA monomer.

In the second step, chain extension of the CyA monomer using the macro-CTA afforded a CyA triblock copolymer. The reaction occurred in a homogeneous solution in DMF and became turbid within 10 min, indicating rapid conversion of monomer. As the reaction proceeded, the solution gradually turned completely opaque and light yellow, with the production of a less soluble polymer. Monomer conversion proceeded linearly and leveled after 6 h of reaction with a conversion of 62% (Figure S2.2). Therefore, targeting the reactions at different conversions within the linear region yielded ABA block copolymers with different CyA hard block contents. The CyA block copolymer was a light yellow solid due to the incorporation of the CyA monomer. ¹H NMR spectroscopy in DMSO-*d*₆ (Figure S2.3) provided an indirect measurement of the molecular weight of CyA external blocks since the block polymers are insoluble in typical GPC solvents. To calculate the molecular weight, resonances a-c at 5.5-7.7 ppm were attributed to chemical shifts of the four hydrogens in the cytosine aromatic ring and were normalized according to the GPC value of the PnBA central block (40.7 kDa, peak f). Averaging the value of peak a-c ((65.12+129.49+64.02)/4 = 64.66) afforded the number of CyA repeating units which was multiplied by the molar mass (309.3 g/mol) to determine a number-average molecular weight (*M*_n) of 20.0 kDa (6 h of

polymerization) with 10.0 kDa in each external block, assuming equal propagation rate on both sides.

Post-functionalization of poly(CyA-*b*-nBA-*b*-CyA) precursors using isocyanate enabled facile preparation of the corresponding poly(UCyA-*b*-nBA-*b*-UCyA) block copolymers with the identical soft and hard block composition, and allowed for direct comparison of physical properties between the CyA and UCyA polymer series. DMF was a suitable solvent due to solvation for both the reactant and product and allowing complete conversion to UCyA units, whereas DMSO was a poor solvent for the UCyA polymer. The aromatic isocyanate is less desirable for the reaction than the aliphatic isocyanate since the former is extremely reactive and leads a sterically hindered UCyA module, which prevented polymer from dissolving even in hot DMF. Polymers containing over 20 mol% of UCyA contents were unable to remain homogeneous in hot DMF, due to strong hydrogen bonding interactions. The reaction was completed after 12 h, and ¹H NMR spectroscopy revealed a clean product of the UCyA polymer (Figure S2.4). The resulting UCyA block copolymer was a slightly yellow solid that was softer than its CyA precursor, presumably due to the flexible hexylene in the side chain.

Thermal Analysis

TGA under N₂ revealed a step-wise weight loss profile for CyA and UCyA polymers (Figure 2.1). For CyA polymers, the first step weight loss represented the degradation of the spacer that connects the acrylic backbone and cytosine unit, and the second step comprised the degradation of acrylic backbone.²⁵ The $T_{d,5 \text{ wt\%}}$ of the CyA polymer decreased with increasing CyA content (Table 1), due to more thermally-unstable CyA pendent groups in the first degradation step. The UCyA polymers displayed a three-step weight loss profile, and the urea bond started to degrade at even lower temperatures (~ 160 °C). This agreed well with previous results on the urea-containing small

molecules and polymers, where the decomposition occurred between 150-200 °C.^{27,28} However, upon air exposure, the CyA polymers exhibited a lower thermal stability than the UCyA polymers at elevated temperatures with a dark orange color suggesting oxidation of the primary amine into a nitro group (Figure S2.4). Our research group also verified the susceptibility of poly(CyA-co-nBA)s to crosslinking at higher temperatures compared to poly(UCyA-co-nBA)s with the aid of isothermal rheological experiments.²⁵

Table 2.1. Summary of composition, thermal, and morphological properties of ABA block copolymers with varying CyA and UCyA contents

	CyA/UCyA in polymer (mol%)	CyA/UCyA in polymer (wt%)	Molecular weight (kDa)	$T_{d,5 \text{ wt}\%}$ (°C)	1 st T_g (°C)	2 nd T_g (°C)	Domain spacing (nm)
CyA	8	18	4.4-40.7-4.4	287	-46	93	39
UCyA		23	6.2-40.7-6.2	212	-45	N/A	36
CyA	10	21	5.4-40.7-5.4	280	-46	92	42
UCyA		27	7.6-40.7-7.6	210	-44	N/A	40
CyA	14	29	8.3-40.7-8.3	271	-45	94	52
UCyA		37	11.7-40.7-11.7	207	-44	N/A	41
CyA	17	33	10.0-40.7-10.0	266	-46	94	70
UCyA		41	14.1-40.7-14.1	208	-44	N/A	43

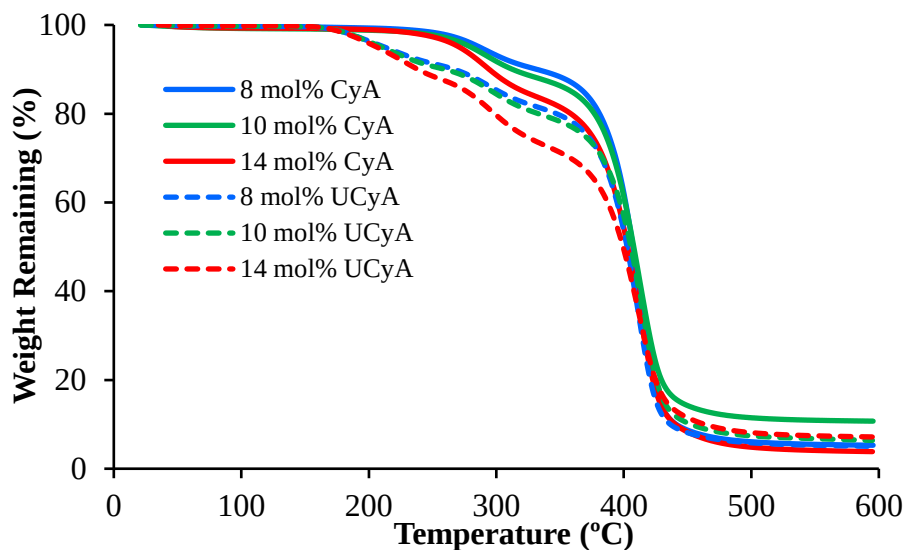


Figure 2.1. TGA thermograms of CyA and UCyA triblock copolymers with varying hard block incorporations. TGA was carried out from ambient to 600 °C, 10 °C/min under N₂.

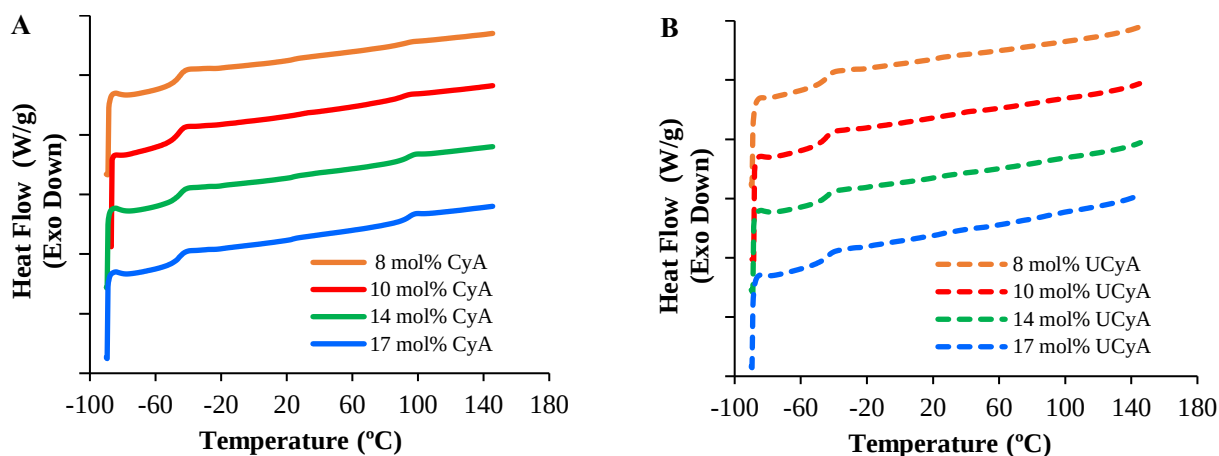


Figure 2.2. DSC traces of (A) CyA block copolymer and (B) UCyA block copolymer with varied amounts of CyA and UCyA, respectively. DSC was performed -90 °C-150 °C at 10 °C/min under N₂.

DSC thermograms (Figure 2.2A) displayed two thermal transitions for CyA polymers. The first transition at -45 °C (Table 2.1) represented the glass transition of the nBA soft block and agreed well with literature values.^{9,29} The second transition at 93 °C corresponded to the T_g of the CyA

hard block. The occurrence of two T_g s suggested a phase-separated morphology for the block polymers, where each block exhibited a separate T_g instead of a single T_g for random copolymers. The intensity of the first thermal transition remained constant as the second transition increased with increasing CyA content, confirming our assignment of T_g s. However, only the T_g of the nBA block appeared within the experimental temperature range (-90 °C to 150 °C) for the UCyA copolymers (Figure 2.2B). In order to study the thermal transition of the UCyA block, a second heat/cool/heat DSC experiment with an upper temperature of 200 °C (exceeds the thermal decomposition of the polymer) was performed (Figure S2.6). In the first heating cycle, the transition step at 148 °C-155 °C was attributed to the T_g of the UCyA block, which was closely followed by a large endothermic peak at 174 °C. The emergence of a new transition step at 82°C-95 °C in the second heating cycle accompanied a significant decrease of the endothermic intensities between 148 °C-180 °C relative to the first cycle, indicating the UCyt pendent group had already undergone a thermal degradation.

Thermomechanical Properties

All polymer samples with varied CyA or UCyA contents formed mechanically robust free-standing films utilizing a solution-cast method, while PnBA-CTA was an extremely soft and tacky solid that lacked mechanical integrity. Optical clarity throughout solvent casting and annealing suggested the absence of macrophase separation (Figure 2.3C and 2.3D). Selection of solvent is the key to the solution-cast method, since a suitable solvent will solvate the polymer and facilitate microphase separation. Both DMSO and DMF are excellent hydrogen bonding donors and

acceptors, which will disrupt the kinetically trapped intermolecular associations and enhance chain mobility for self-assembly. DMA confirmed a microphase-separated morphology for CyA and UCyA polymers (Figure 2.3A and 2.3B). At low temperatures, both the soft and hard phase were in the glassy state, displaying storage moduli over 1000 MPa. The first modulus drop occurred when the PnBA soft phase reached its glass transition temperature, with the first $\tan \delta$ maximum indicating the T_g of PnBA soft phase. A CyA random copolymer control, poly(CyA-*co*-nBA) (Figure 2.3A) exhibited a $\tan \delta$ peak approximately 30 °C higher than the CyA block copolymers, suggesting a phase-mixed morphology. Further increasing the temperature reached a plateau regime, where the rigid aromatic ring as well as the non-covalent interactions in the CyA/UCyA hard phase served to maintain the modulus. Owing to a lower degree of phase separation, the 9 mol% CyA random copolymer control displayed a much shorter and lower plateau modulus than the 8 mol% CyA block copolymer despite a similar hard phase content. The plateau moduli of the CyA polymers remained very high even at low incorporations of the hard phase (over 100 MPa for the 8 mol% CyA polymer), affording extremely brittle films that prohibited further mechanical testing. Interestingly, the UCyA polymers exhibited lower plateau moduli despite having higher crosslink density than the CyA precursors. It was presumed that the long hexylene-containing side chain played a key role in tempering the mechanical strength of UCyA polymers due to a plasticizing effect. This enhanced flexibility of UCyA polymers facilitated processing and enabled potential elastomers. The plateau region of the CyA polymer ended as temperature approached the T_g of the hard phase. For the 17 mol% CyA polymer, the increase of weak hydrogen bonding

crosslinking density accounted for its slightly prolonged plateau regime compared to the 8 mol% CyA polymer.

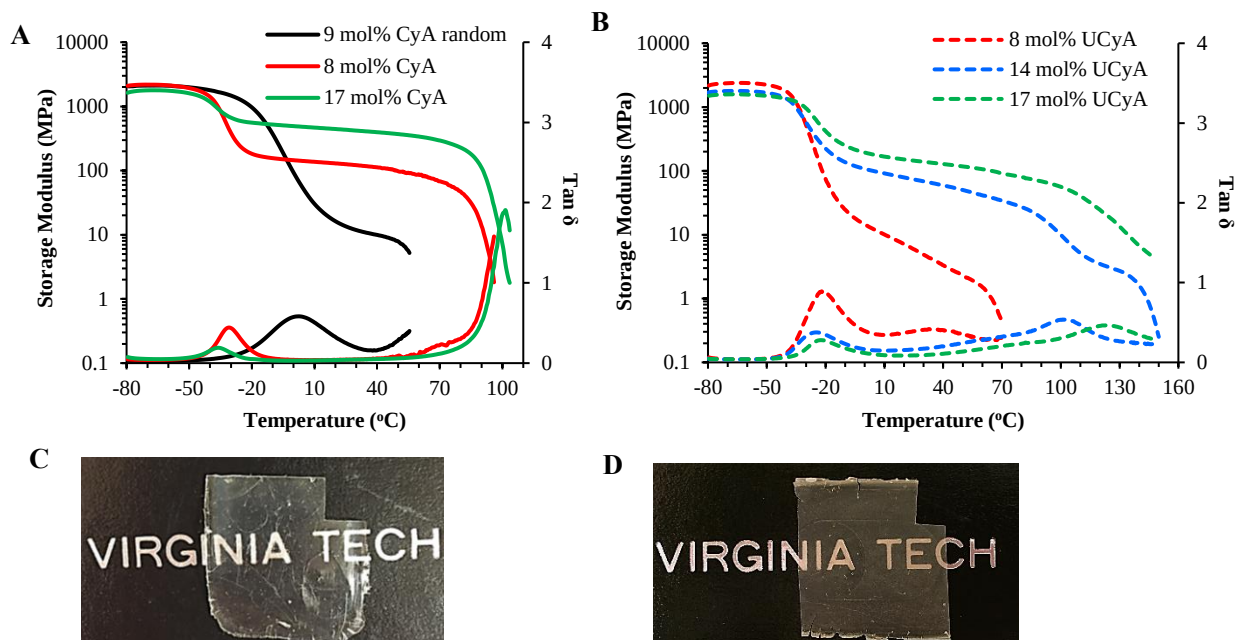


Figure 2.3. Dynamic mechanical comparison of storage modulus and $\tan \delta$ of the solution casted (A) CyA and (B) UCyA polymer films. Solution-cast 14 mol% CyA (C) and UCyA (D) block copolymer films. DMA was performed at 3 °C/min, oscillatory amplitude 5 μ m at 1Hz.

Figure 2.3B also depicts an enhanced thermomechanical performance of UCyA due to self-complementary hydrogen bonding. Doubling the hard phase content from 8 mol% to 17 mol% resulted in a dramatic increase of plateau moduli for UCyA polymer by two-orders of magnitude, whereas the plateau moduli of CyA polymers increased by only three times when the amount of hard phase was doubled. Interestingly, the UCyA polymers with a higher hard phase incorporation extended the plateau regime 20 °C higher than the CyA precursors. This significant enhancement of mechanical property correlated with self-complementary QHB in the UCyA polymers, where the hard phase served as strong physical crosslinks leading to formation of a mechanically robust

3-D network. Between 90 °C-110 °C, the 14 mol% UCyA polymer went through a small transition, which corresponded to the dissociation of the majority of hydrogen bonding. The synergy of UCyA hard block interactions as well as the remaining hydrogen bonding associations contributed to the secondary plateau region prior to terminal flow. Long *et al.* also observed a similar trend for the solution-casted adenine and thymine functionalized ABA block copolymers.⁹ A slight increase of the UCyA content to 17 mol% enabled a dramatic reinforcement of physical crosslinks, which further inhibited chain mobility and retarded flow. Hence, the QHB in the UCyA polymers played a crucial role in improving the thermos-mechanical strength due to the influence of stronger physical crosslinks.

Morphological Characterization

SAXS provided further insights into the phase ordering of the CyA and UCyA block copolymers (Figure 2.4). Table 2.1 presents the domain spacing of the polymers with varied CyA and UCyA contents, and both series exhibited an increase of domain spacing in tandem with molecular weight. In addition, the UCyA polymers possess smaller domain sizes than the corresponding CyA polymers, which was attributed to the enhanced physical crosslinking that facilitated denser packing of the polymer chain. The CyA polymers have less defined scattering peaks especially for the 14 and 17 mol% polymers, and extending the annealing time from 12 h to 24 h didn't improve the ordering. We correlated this less ordered morphology to an excess incorporation of the bulky cytosine group as well as the insufficient physical interactions, which contributed to a sterically hindered structure and a lower degree of packing. In contrast, the UCyA polymers exhibited more-

defined and higher-ordered scattering peaks even for the higher UCyA mol % polymers, demonstrating much ordered bulk morphologies. The strong propensity for the UCyt scaffold to dimerize and form QHB arrays promoted spatial recognition, whereas the self-association of the cytosine for the CyA polymers is too weak to drive self-assembly.

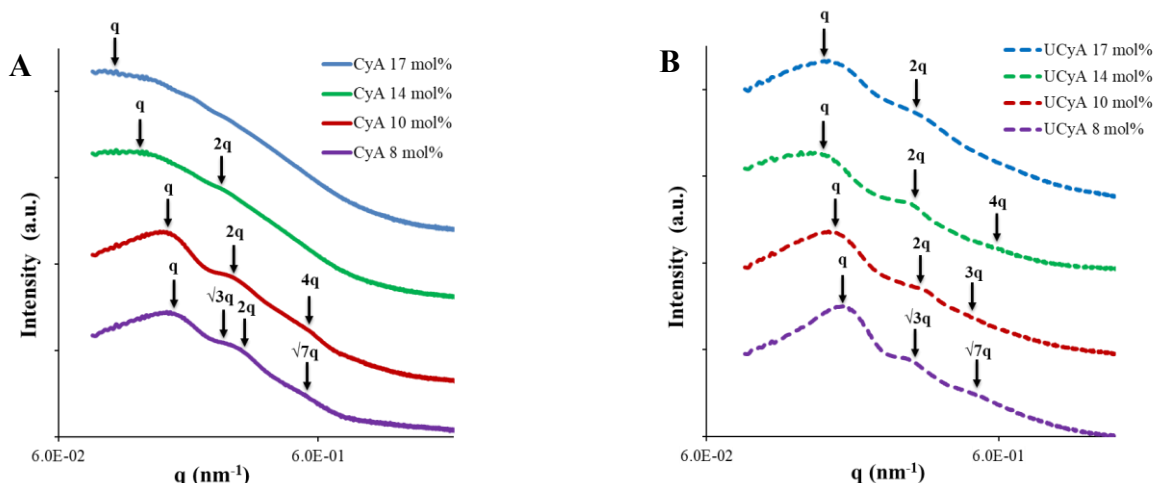


Figure 2.4. SAXS of solution casted (A) CyA and (B) UCyA polymer films with varying CyA and UCyA concentrations. Curves are shifted vertically for clarity.

SAXS also revealed a composition-dependent morphology for both the CyA and UCyA block copolymers. The 8 mol% CyA and UCyA polymers exhibited periodic peak maxima of $1q, \sqrt{3}q, 2q, \sqrt{7}q$ and $1q, \sqrt{3}q, \sqrt{7}q$, respectively, which are characteristic of the hexagonally packed cylinders. Increasing the hard block volume fraction caused a morphological transition from cylinder to lamellar for the 10 mol% CyA polymer as well as the 10 mol% and 14 mol% UCyA polymers. The characteristic scattering peaks for 17 mol% UCyA are $1q$ and $2q$, which are either lamellar or hexagonal cylinder structure or a mixture.

Atomic force microscopy (AFM) phase images confirmed the microphase-separated morphology for the CyA and UCyA block copolymers (Figure 2.5). The bright area indicates a higher elastic modulus and was attributed to the hard phase (CyA or UCyA block), while the dark area corresponds to the soft nBA block. Increasing the hard block volume fraction allowed the CyA polymers to evolve in the morphological sequence of cylinder-lamella-cylinder, and a less-defined phase image for the 17 mol% CyA polymer suggested a lack of ordering, which agreed well with SAXS results.

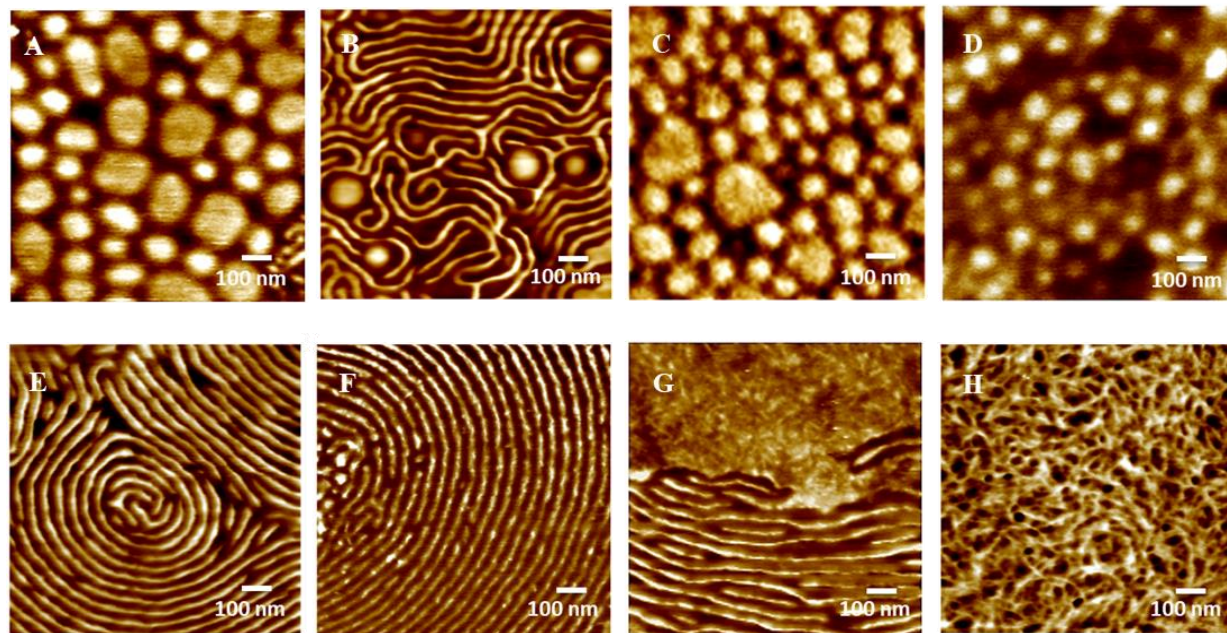


Figure 2.5. AFM phase images of solution-cast block copolymer films containing 8 mol% , 10 mol% , 14 mol%, and 17 mol% of CyA (A-D) and UCyA (E-H).

However, the AFM phase images of UCyA polymers showed less conformity to the SAXS predictions. The 8 mol% UCyA polymers exhibited the ordered lamellar morphology instead of the hexagonal cylinders revealed from the SAXS characterizations. This inconsistency is most likely attributed to the different affinity of UCyA block to the polymer-air interface, leading to a

different surface morphology from the bulk morphology. The 10 mol% UCyA and the 17 mol% UCyA are ordered lamella and bicontinuous gyroid, respectively, while the 14 mol% UCyA combined those two features. Both the AFM and SAXS revealed a more ordered morphology for the UCyA polymers compared to their CyA counterparts, and verified the QHB dominated self-assembly behavior.

Variable Temperature FT-IR

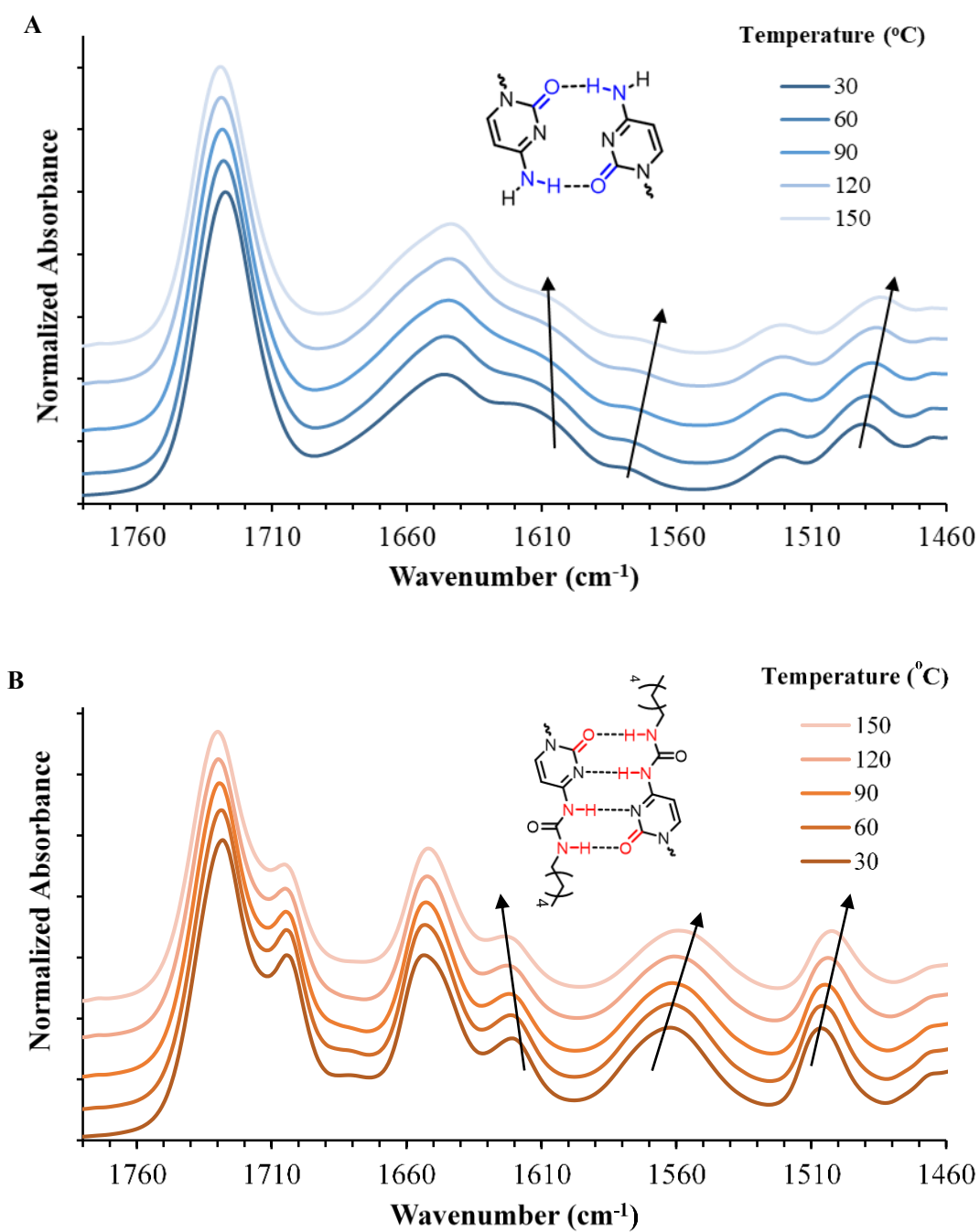


Figure 2.6. VT-FTIR spectra of (A) CyA and (B) UCyA triblock copolymers containing 17 mol% of CyA and UCyA, respectively in the 1400-1800 cm^{-1} region. Spectra were normalized according to the peak at 1730 cm^{-1} . VT-FTIR was performed from 30 °C-150 °C.

VT-FTIR spectroscopy elucidates the dynamics of hydrogen bonding association/dissociation in response to temperature. Figure 2.6A and B depict the infrared spectra of the 17 mol% CyA and 17 mol% UCyA triblock polymers in a temperature range of 30-150 °C, respectively. The band at 1610 cm^{-1} at 30 °C is indicative of the stretching vibration of the carbonyl group in the cytosine moiety (Figure 2.6A), which blue shifted to higher wavenumber at elevated temperatures. This was attributed to the dissociation of hydrogen bonding increasing the C=O bond strength in the cytosine units, resulting in an increase of vibration frequency at higher temperatures. In addition, the breakage of hydrogen bonds at elevated temperatures no longer restricted the bending motion of the N-H from the amine group, resulting in red shift of N-H bending vibration for the bands at 1577 cm^{-1} and 1492 cm^{-1} . The UCyA polymer shared similar trends for the shifting of the C=O stretching (1617 cm^{-1} , 30 °C) and N-H bending (1560 cm^{-1} and 1504 cm^{-1} , 30 °C) vibrations (Figure 2.6B). The absence of hydrogen bonding at elevated temperatures enabled an increase of the vibrational freedom for the molecule, resulting in band broadening and decrease of the absorption intensity for both the CyA and UCyA polymers.³⁰ The most significant shifting for the CyA polymer occurred between 60-90 °C, lower than the UCyA polymer (90-120 °C), which agreed well with the DMA results. The enhanced hydrogen bonding interactions in the UCyA polymer required much higher thermal energy to break apart compared to the weakly-associated CyA units. Thus, converting CyA to UCyA modules resulted in better thermal resistance and wider service windows for polymers.

Water Sorption

Figure 2.7 illustrates the equilibrium water uptake for CyA and UCyA polymers from 0 % to 95 % relative humidity. CyA polymers exhibited a significantly higher water sorption than their UCyA counterparts, and the amount of water absorbed increased with increasing CyA content. In contrast, the UCyA polymers followed an opposite relationship between water uptake and hard block content with the 17 mol% UCyA polymer absorbing less water than the 8 mol% UCyA polymer. It was presumed that the enhanced water resistance of the UCyA polymers was closely related to their chemical structure and morphology that differed greatly from the CyA precursor. The incorporation of hexyl and the urea functional group increased the hydrophobicity of UCyA polymer, resulting in a lower affinity to water. Furthermore, the QHB in UCyA polymers promoted a more ordered morphology and denser packing, which enabled an efficient insulation from moisture. On the contrary, the weakly self-associated CyA units generated a loosely packed structure, which created many channels for the access and storage of water. The excellent water repellence of UCyA triblock copolymers offers great promise for applications as biomaterials or other TPEs used in the humid environments, for water is usually a plasticizer which significantly weakens the mechanical properties.

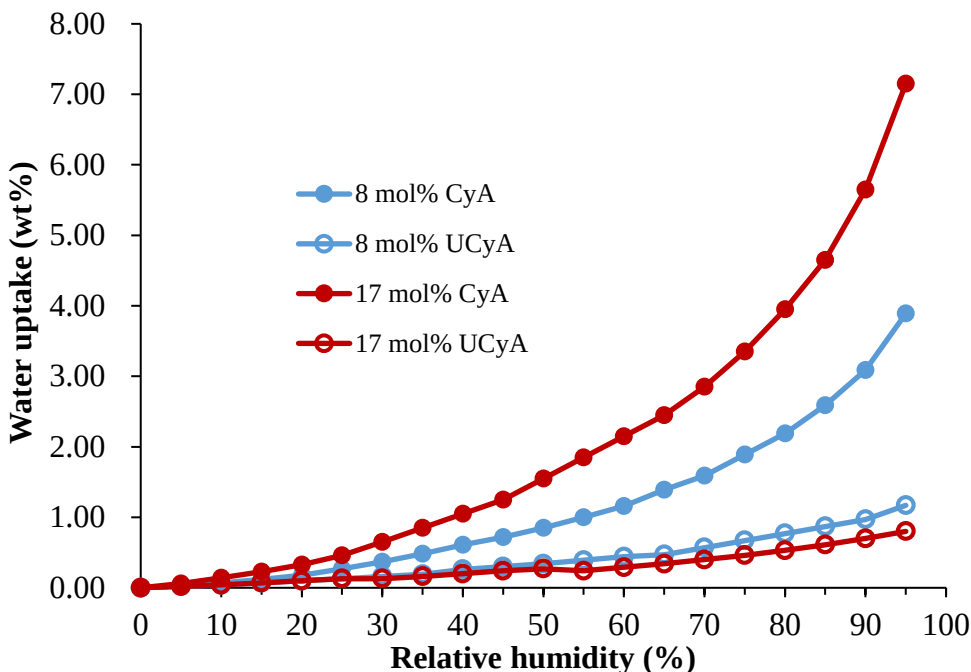


Figure 2.7. Equilibrium water sorption of poly(CyA-*b*-nBA-*b*-CyA)s and the corresponding poly(UCyA-*b*-nBA-*b*-UCyA)s in a step relative humidity ramp from 0% to 95% at a 5% interval.

2.5 Conclusions

This manuscript presents an unprecedented synthesis and characterization of ABA triblock copolymers functionalized with UCyt quadruple hydrogen bonding scaffolds. A two-step RAFT polymerization enabled CyA ABA triblock precursors with tunable molecular weight and different hard block contents varied from 8 mol% to 17 mol%. Post-functionalization of the polymers with an alkyl isocyanate afforded the corresponding UCyA triblock copolymers. Thermal, mechanical and morphological analysis of polymers allowed systematic comparisons of CyA and UCyA polymers with regard to their physical properties.

In general, converting CyA polymers to the corresponding UCyA polymers resulted in a lower $T_{d,5}$ wt% due to the incorporation of urea bonds. The reversible noncovalent interactions in the UCyA hard blocks served as strong physical crosslinks, which enhanced the thermal resistance of

mechanical strength while maintaining melt processability. In addition, the self-complementary QHB modules facilitated self-assembly, resulting in stronger microphase-separation and well-ordered morphologies. The denser packing of the UCyA polymer chain also prohibited the access of water, thus affording improved moisture resistance. Thus, Ucyt-functionalized ABA triblock polymers offer great promise as high performance TPEs for industrial and medical applications.

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2.7 Supporting Information

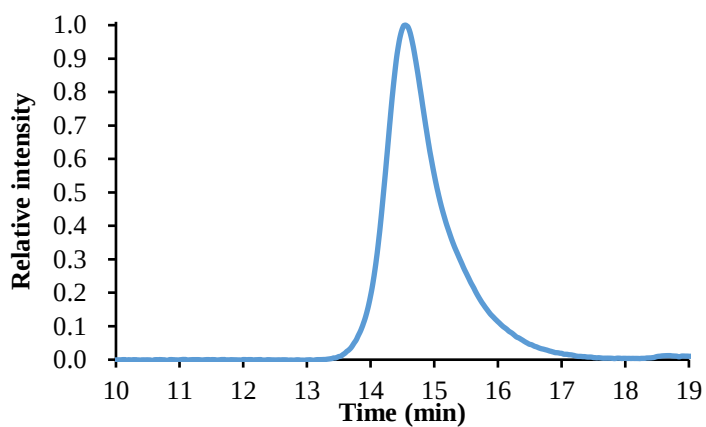


Figure S2.1. GPC trace of poly(n-butyl acrylate) difunctional macro-CTA

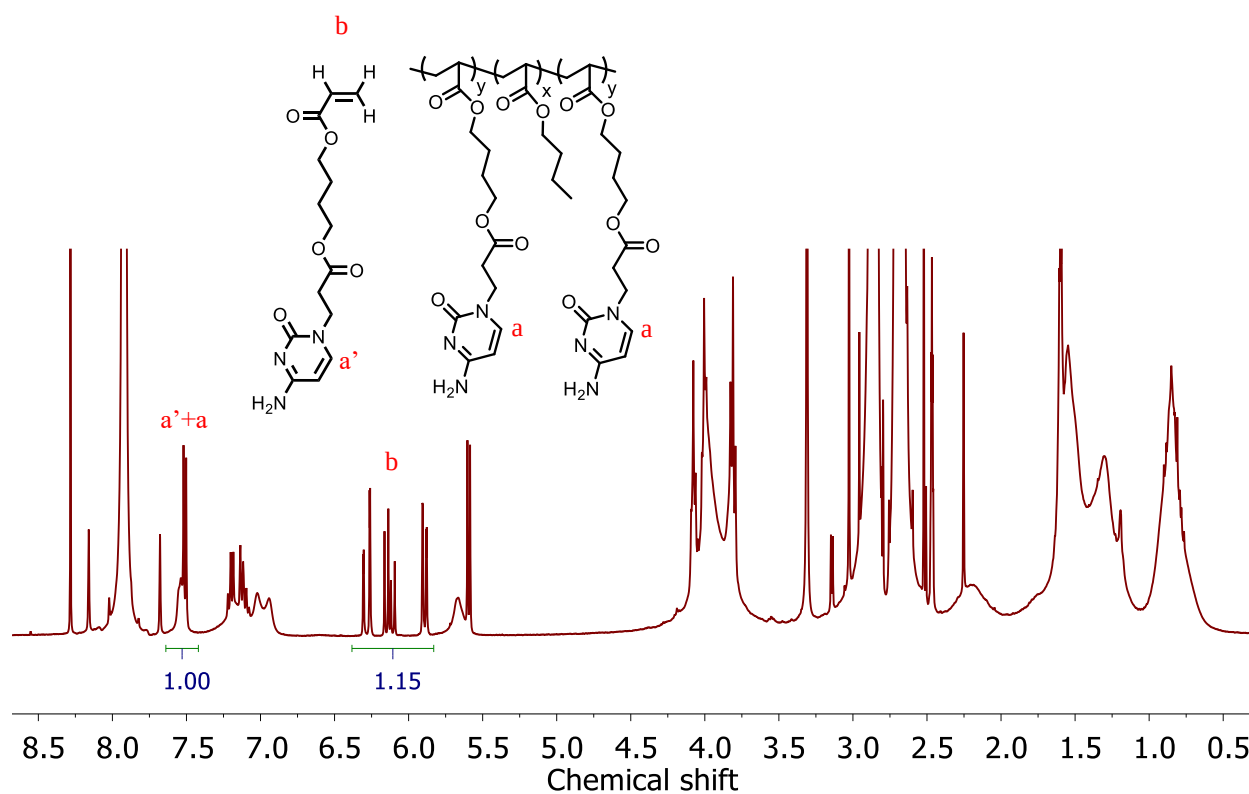


Figure S2.2. ¹H NMR spectrum of reaction mixture after 2nd RAFT polymerization step of cytosine block. The integrations of peak a, a', and b were used to calculate conversion

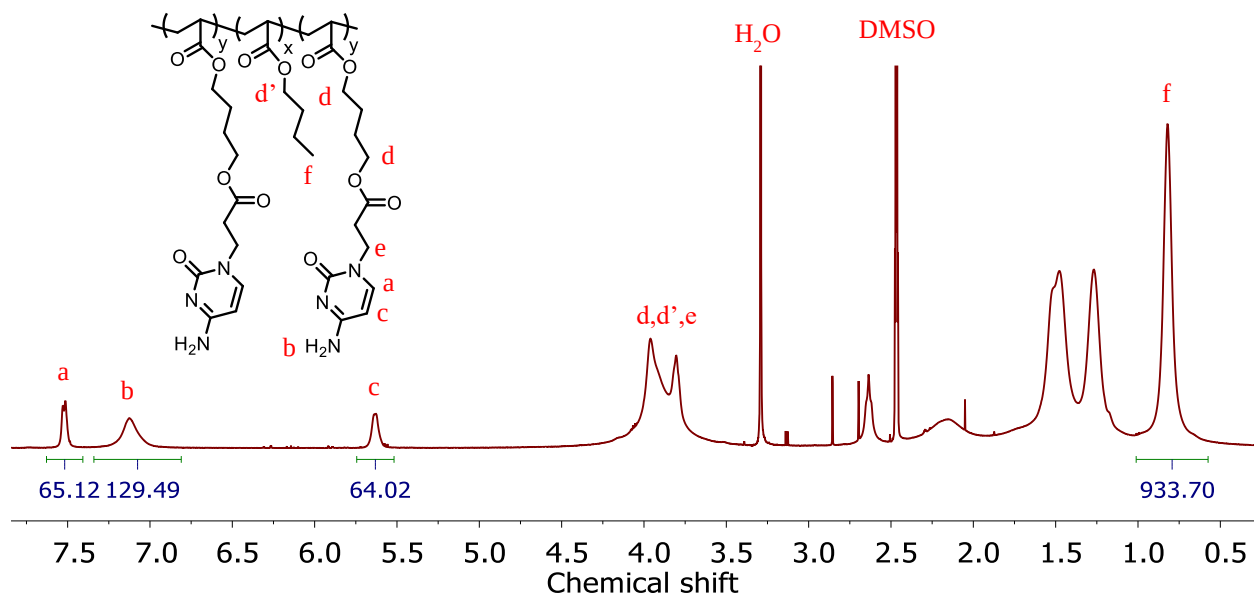


Figure S2.3. ^1H NMR spectrum of poly(CyA-*b*-nBA-*b*-CyA) with 17 mol% of CyA content.

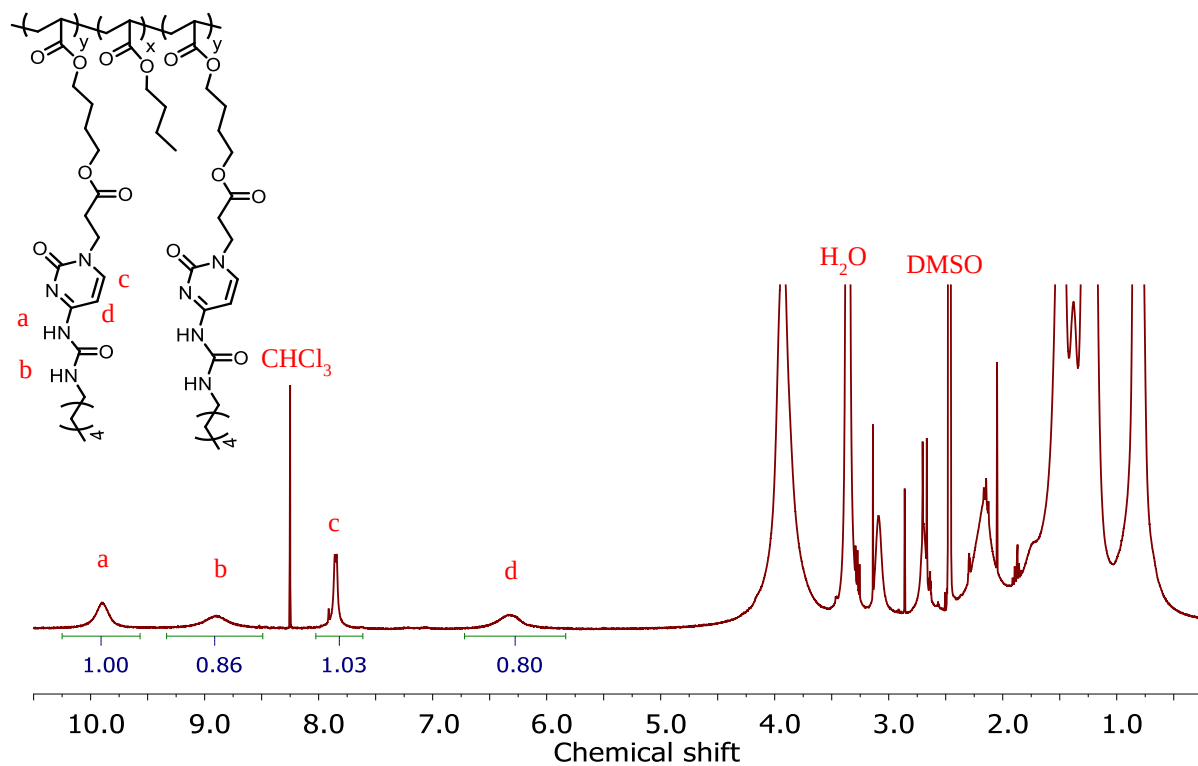


Figure S2.4. ^1H NMR spectrum of poly(UCyA-*b*-nBA-*b*-UCyA) with 17 mol% of UCyA content.

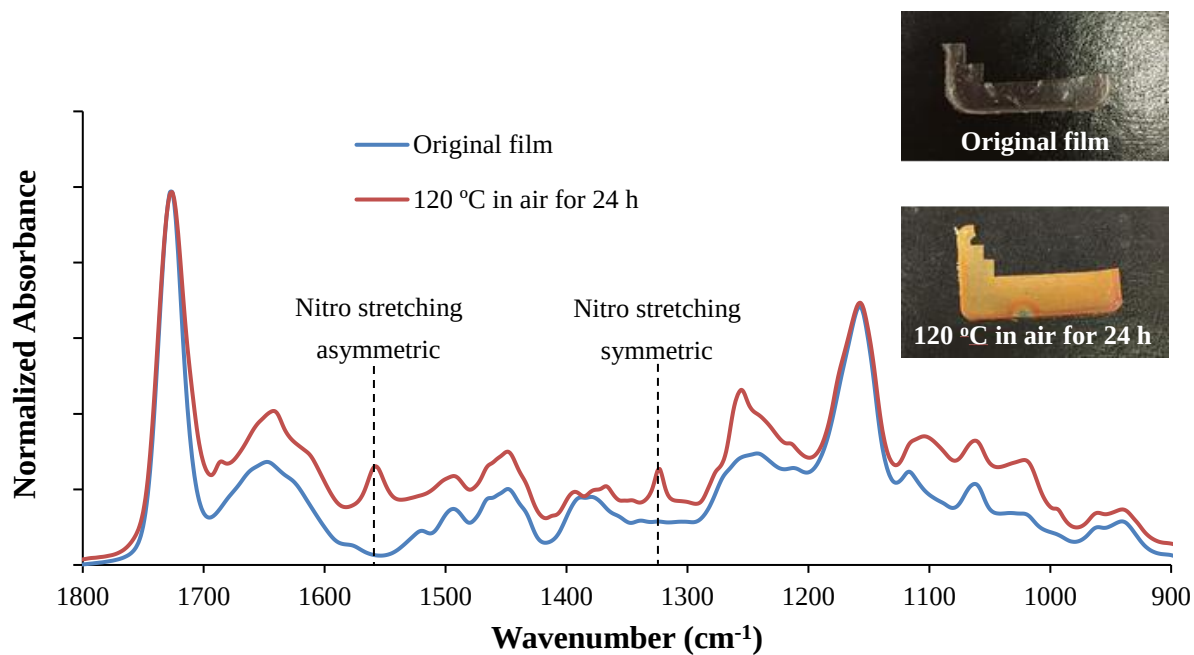


Figure S2.5. Attenuated total reflectance (ATR) spectra of the original 17 mol% CyA polymer film (blue) and the film exposed to air at 120 °C for 24 hours (red).

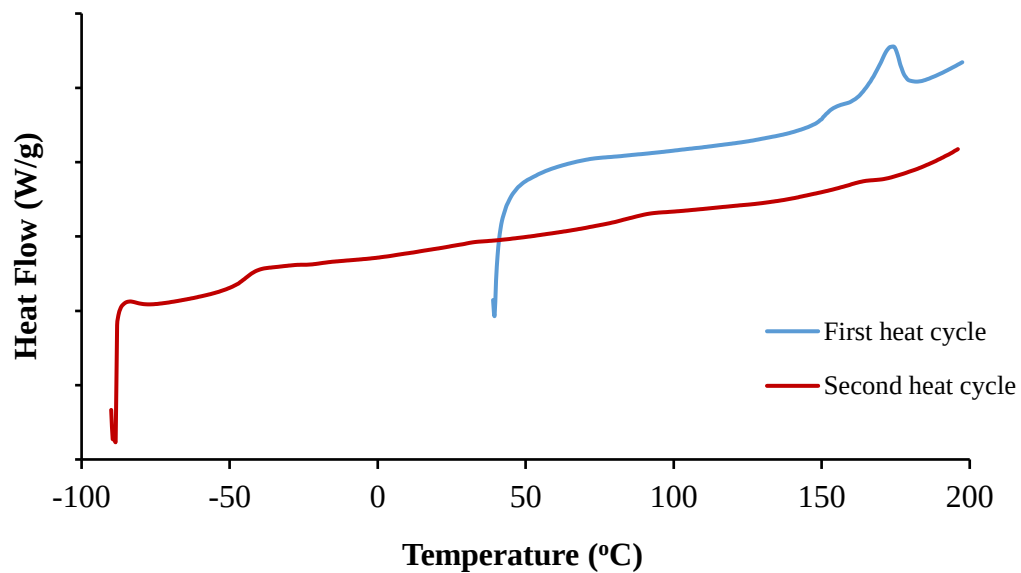


Figure S2.6. DSC traces of the 17 mol% UCyA polymer in the first and second heating cycle. TGA was performed from -90 °C to 200 °C, at 10 °C/min, N₂ purge.

Chapter 3. Doubly-charged Triblock Copolymers for Enhanced Physical Property and Self-assembly

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3.1 Abstract

Reversible addition-fragmentation chain-transfer polymerization (RAFT) afforded an unprecedented synthesis of doubly-charged DABCO salt-containing ABA triblock ionomers and the singly-charged analogs comprising a soft poly(n-butyl acrylate) (PnBA) center block and charged external hard blocks. Thermal analysis indicated the degradation of the DABCO salt-containing block copolymer followed closely to a reverse nucleophilic substitution pathway. Thermomechanical study revealed much stronger ionic interaction and an extended service temperature window of DABCO salt-containing block copolymers compared to their corresponding doubly-charged random copolymer and singly charged block copolymer controls, suggesting the formation of enhanced physical crosslinks for the DABCO block copolymers. Morphological characterizations confirmed that solution-cast DABCO block copolymers self-assembled into well-ordered lamellar microstructures. A unique three-phase morphology

elucidated the structure-property-morphology relationships of the novel doubly-charged ionic block copolymers.

3.2 Introduction

Ionomers represent a unique category of polymeric materials bearing <15 mol % of ionic units in the pendant groups. Non-directional Coulombic interactions induce the formation of ionic aggregates, resulting in significantly different physical properties compared to nonionic analogs.^{1–}

⁴ For example, strong dipole-dipole interaction promotes microphase separation, which enables polymer chains to self-assemble into interesting morphologies. Depending on the ionic content, the dipole-dipole interactions between ion pairs either result in small multiplets or large ionic clusters, both of which serve as physical crosslinks to restrict the mobility of polymer chains that are covalently bonded to the ionic groups, leading to enhanced mechanical performance and an extended plateau region.^{5,6} Furthermore, selection of different types of ions and counterions offers tunability of ion conductivity and thermal stability of polymers. The unique thermal, mechanical, and morphological properties facilitate impacts in many fields, including energy storage, biomedicine, water treatment, and food processing.^{7–10}

The successful launch of SurlynTM in the mid-1960s marked the production of the first commercial ionomers. The dynamic ionic bonding established strong physical networks, leading to significant improvement of stiffness while maintaining melt processability, which allows application as durable packaging materials.^{3,4,11} The extensive commercial impact spurred academic study on novel ion-containing polymers, especially ionic block copolymers, which offer a higher degree of phase separation and much-ordered microstructures. Living radical polymerization techniques afford polymers with defined molecular weights and architectures, and enable access to libraries

of ionic block copolymers due to its high tolerance of different monomers. Balsara *et al.* prepared polystyrene-block-polychloromethylstyrene (PS-*b*-PCMS) copolymers using nitroxide-mediated polymerization and modified the PCMS block with two different types of bonded cations. The resulting block copolymers exhibited highly-ordered lamellar morphology after annealing for 4 h.¹² Weiss *et al.* reported that the ionic associations of sulfonated poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene)(SEBS) resulted in an increase of T_g for the styrene block and a significant reinforcement of high-temperature tensile strength.^{1,13} Our group previously utilized RAFT polymerization to afford Li-ion containing poly (styrene-*b*-(styrene-Tf₂N-co-DEGMEMMA)-*b*-styrene) for energy storage applications and verified its enhanced mechanical robustness and ion transport property attributable to the phase separation of styrene hard block and ion-containing soft block.¹⁰ Despite the extensive studies in this field, most block copolymer ionomers only carry a single cation/anion with an electrostatically bonded counterion.

Ionomers containing doubly-charged monomers started to attract increasing academic interests in recent years. These doubly-charged ionomers displayed a better phase separation and enhanced physical properties compared to their singly-charged analogs, owing to their stronger ionic interaction. 1,4-Diazabicyclo-[2.2.2]-octane (DABCO)-based monomers are rigid, bicyclic structures bearing two quaternary ammonium charges, whose syntheses are enabled through quaternization of DABCO molecules using haloalkanes. Several studies highlighted the excellent antimicrobial performance of DABCO-based polyelectrolytes, which find applications as biomedical devices and additives for antifouling paints.^{7,14-16} Our group previously reported the synthesis of styrenic-DABCO monomers series VBDC_xBrCl to copolymerize with *n*-butyl acrylate to afford the DABCO salt-containing random copolymers.^{8,17} Systematic viscoelastic and tensile studies revealed significantly enhanced thermomechanical performance of the doubly-charged

DABCO copolymers compared to the singly-charged controls containing a similar charge density. Furthermore, the resulting DABCO copolymers exhibited a well-defined plateau region and a higher mechanical strength resulting from stronger physical crosslinks. However, these early studies only focused on homopolymers or random copolymers. While incorporating doubly-charged monomers into block copolymers could give rise to intriguing mechanical and morphological properties, this area remained unexplored due to synthetic challenges and complexity of the system.

This manuscript presents the first study of doubly-charged ABA triblock ionomers based on the hypothesis that interaction among multiple ionic units would result in the formation of ionic clusters, promoting intermolecular recognition and phase separation. An optimized, facile two-step RAFT polymerization enabled the synthesis of DABCO salt-containing triblock copolymers poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl)s and their block copolymer controls with defined molecular weights and low polydispersity. The PnBA center block possessed low glass transition temperature (T_g), which provided flexibility to the polymer, while the DABCO blocks imparted mechanical integrity. Solution-cast method facilitated the self-assembly behavior and provided optically-clear, free-standing films for all of the samples. Thermomechanical comparisons shed light on the influence of the doubly-charged units on viscoelastic property and elucidated the relationship between the polymer architectures and the formation of ionic clusters. SAXS and TEM characterized the solid-state morphology of the annealed DABCO block copolymers, which revealed well-defined lamellar microstructures and a unique three-phase morphology attributed to an enhanced phase separation.

3.3 Experimental Section

Materials

n-Butyl acrylate (nBA, 99+%) was purchased from Sigma-Aldrich and was passed through a basic alumina column before use. α,α' -Azobis(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized twice from methanol. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, Sigma-Aldrich, 98%), N,N'-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich, 99%), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, $\geq 99\%$), DABCO (Sigma-Aldrich, 99%), 1-bromooctadecane (Sigma-Aldrich, 99 %), 1-bromohexane (Sigma-Aldrich, 99 %), triethylamine (TEA, Sigma-Aldrich, $\geq 99.5\%$), 4-vinyl benzyl chloride (4VBCl, Sigma-Aldrich, 99%), and 2,6-di-tert-butyl-4-methylphenol (BHT, Sigma-Aldrich, 99%) were used without further purification. Toluene (HPLC grade), dimethyl sulfoxide (DMSO, HPLC grade), N,N-dimethylformamide (DMF, HPLC grade), dichloromethane (DCM, HPLC grade), acetone (HPLC grade), methanol (HPLC grade), and ethyl acetate (EtOAc, HPLC grade) were purchased from Spectrum and used as received.

Analytical Methods

^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were performed using an Agilent U4-DD2 400 Hz spectrometer at 23 °C. Monomers or polymers were dissolved in DMSO- d_6 , or the mixture of CD_3OD and CDCl_3 (1:1, v/v). Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL/min $^{-1}$ at 30 °C on two Agilent PLgel 10 μm MIXED-*b* columns,

which connected in series with a Wyatt Dawn Heleos 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. Thermal gravimetric analysis (TGA) of VBDC₁₈BrCl block copolymers was conducted utilizing a TA Instruments TGA Q50 with a 10 °C/min heating ramp from ambient temperature to 600 °C under constant N₂ purge. The 5 wt % degradation temperature ($T_{d,5 \text{ wt\%}}$) corresponds to the temperature at which the polymer retains 95 % of its original weight. Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC Q2000 using a heat/cool/heat cycle at a heating and cooling rate of 10 °C/min from -90 °C to 150 °C under N₂ purge. The midpoint of the thermal transition step was used to determine the T_g of the CyA and UCyA polymers. Dynamic mechanical analysis (DMA) experiments on the annealed polymer films were achieved utilizing a TA Instruments Q800 in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 μm , a static force of 0.01N, and a force track of 125 %. The sample was cooled down to -80 °C and isothermed for 5 min, length measured, and ramped at a rate of 3 °C/min. The peak of the tan delta curve was utilized to determine the T_g values of the polymer. Small angle X-ray scattering (SAXS) experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu K α). The sample-to-detector distance was 1605 mm, and the 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 2 h. All SAXS data were analyzed using the SAXSGUI software package to obtain radially 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 X-ray wavelength. The graphs were overlaid and vertically shifted to facilitate comparison. Employing the equation $d=2\pi/q$ enabled calculation of the domain spacing of each sample, where q represents the first-order scattering vector. A Veeco MultiMode scanning probe microscope allowed the analysis of surface morphology for annealed CyA and UCyA polymer films. Phase images were acquired under tapping mode using a silicon tip with a spring constant of 42 N/m.

Synthesis of DABCO Salt-containing Monomer VBDC₁₈BrCl

VBDC₁₈BrCl was prepared using a two-step procedure. DABCO (10.0 g, 89.2 mmol), 1-bromooctadecane (26.7 g, 80.2 mmol), and EtOAc (200 mL) were charged into a 500-mL, round-bottomed flask equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 24 h. White precipitates were filtered, washed with EtOAc, and dried in vacuum at room temperature overnight. The alkylated DABCO intermediate (24.8 g, 55.7 mmol), 4VBCl (9.4 g, 61.3 mmol) and BHT (120 mg) were dissolved in 100 mL CHCl₃ and stirred at room temperature for 12 h. White product was precipitated from solution, and was collected and washed with CHCl₃. The resulting solids were dried under reduced pressure at room temperature for 12 h to afford 25.6 g DABCO monomer (VBDC₁₈BrCl), yield 78 %. ¹H NMR (400 MHz, DMSO-*d*₆, Figure S3.1A): 7.62 (d, 1H, $J = 8.3$ Hz H_a), 7.54 (d, 1H, $J = 8.3$ Hz, H_b), 6.78 (dd, 1H, $J_1 = 11.0$ Hz, $J_2 = 17.7$ Hz, H_c), 5.94 (d, 1H, $J = 17.7$ Hz, H_d), 5.36 (d, 1H, $J = 10.8$ Hz, H_e), 4.92 (s, 2H, H_f), 3.89 (s, 12H, H_g), 3.47 (m, 2H, H_h), 1.61 (m, 2H, H_i), 1.21 (m, 30H, H_j), 0.81 (t, 3H, $J = 6.9$ Hz, H_k). ¹³C NMR (400 MHz, DMSO-*d*₆, Figure S3.1B): 139.75, 136.18, 133.82, 127.17, 126.41, 116.93, 66.05, 63.74,

50.73, 50.49, 31.73, 29.48, 29.44, 29.38, 29.21, 29.14, 28.89, 14.39. Mass spectrometry (ESI+): calculated $m/z = 598.1950$, found $m/z = 598.4351$.

Synthesis of Difunctional Poly(nBA) Macro-CTA

A difunctional chain transfer agent (CTA) 1,6-bis(2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid)-hexane diamide (diDDMAT-NH₂) was synthesized following an adapted literature procedure¹⁹. nBA (20 g, 156.0 mmol), di-DDMAT-NH₂ (163.0 mg, 0.20 mmol) and AIBN (3.3 mg, 0.020 mmol, CTA/I = 10) were dissolved in toluene (80 g, 20 wt% solids), and the reaction mixture was then added into a 250-mL single-necked Schlenk flask. The solution was degassed using four freeze-pump-thaw cycles and backfilled with Ar. The reaction mixture was then stirred at 70 °C for 6 h. ¹H NMR in DMSO-*d*₆ determined a monomer conversion of 54.5 %. Purification of polymer was enabled through precipitation into 1000 mL cold MeOH/H₂O = 10:1 mixture. The resulting polymer was dried in vacuum oven at 45 °C for 12 h to afford a tacky yellow solid. $M_n = 44.5$ kDa, PDI = 1.2 (GPC in THF, $dn/dc = 0.064$ mL/g)

Synthesis of Poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl) ABA Triblock Copolymers and the Corresponding Block Copolymer Controls.

Chain extension of the difunctional poly (nBA) Macro-CTA using the DABCO salt monomer (VBDC₁₈BrCl) enabled the synthesis of poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl)s. In a representative triblock copolymer synthesis, VBDC₁₈BrCl (1.34 g, 2.25 mmol), difunctional macro-CTA (1 g, 0.022 mmol), AIBN (0.37 mg, 0.0022 mmol, CTA/I = 10), and DMF/MeOH

solvent mixture (9.37 g, 1:1 wt/wt, 20 wt% solids) were charged into a 30-mL single-necked Schlenk flask. The reaction mixture was subjected to four cycles of freeze-pump-thaw and subsequent backfill with Ar. The reaction was allowed to react for 24 h at 70 °C and was purified through dialysis in MeOH/CHCl₃ mixture for 2 days. The resulting polymer was dried under vacuum at 50 °C overnight to afford a light yellow solid. ¹H NMR spectroscopy in CD₃OD/CDCl₃ (Figure S3.2) determined the M_n of the charged outer blocks = 32.4 kDa, with 16.2 kDa in each external block, assuming equal propagation rate on both chain ends. The ionic block content of the polymer was 14 mol%. Fabrication of poly(VBDC₆BrCl-*b*-nBA-*b*-VBDC₆BrCl) and the singly-charged poly(VBTEACl-*b*-nBA-*b*-VBTEACl) controls followed the same procedures utilizing PnBA macro-CTA with the identical molecular weight. ¹H NMR spectroscopy in CD₃OD+CDCl₃ calculated the mol% of the charged blocks, which were 14 mol% and 27 mol%, respectively (Figure S3.3-S3.4). VBDC₆BrCl and VBTEACl monomers were synthesized according to previous literature procedures.^{8,20}

Block Copolymers Film Casting and Annealing Procedures

All block copolymers were dissolved to 10 wt% solutions in a MeOH/CHCl₃ mixture (4:6, wt/wt) and were cast into rectangular Teflon molds. Each mold was covered with a glass petri dish to decrease solvent evaporation rate and allowed to evaporate at 20 °C overnight. The molds were further dried in a vacuum oven at room temperature for 24 h and annealed at 60 °C for another 24 h. After slowly cooling to room temperature, the films were peeled from the Teflon molds and stored in the desiccator prior to characterization.

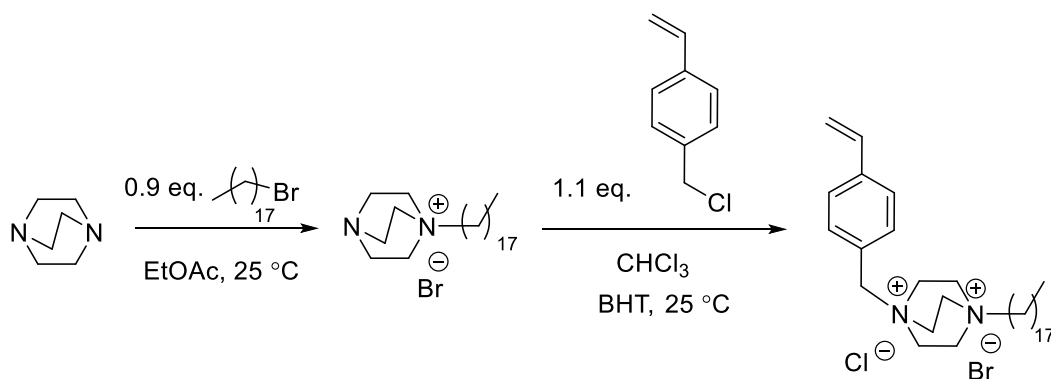
3.4 Results and Discussion

Monomer and Doubly-charged ABA Block Copolymer Synthesis

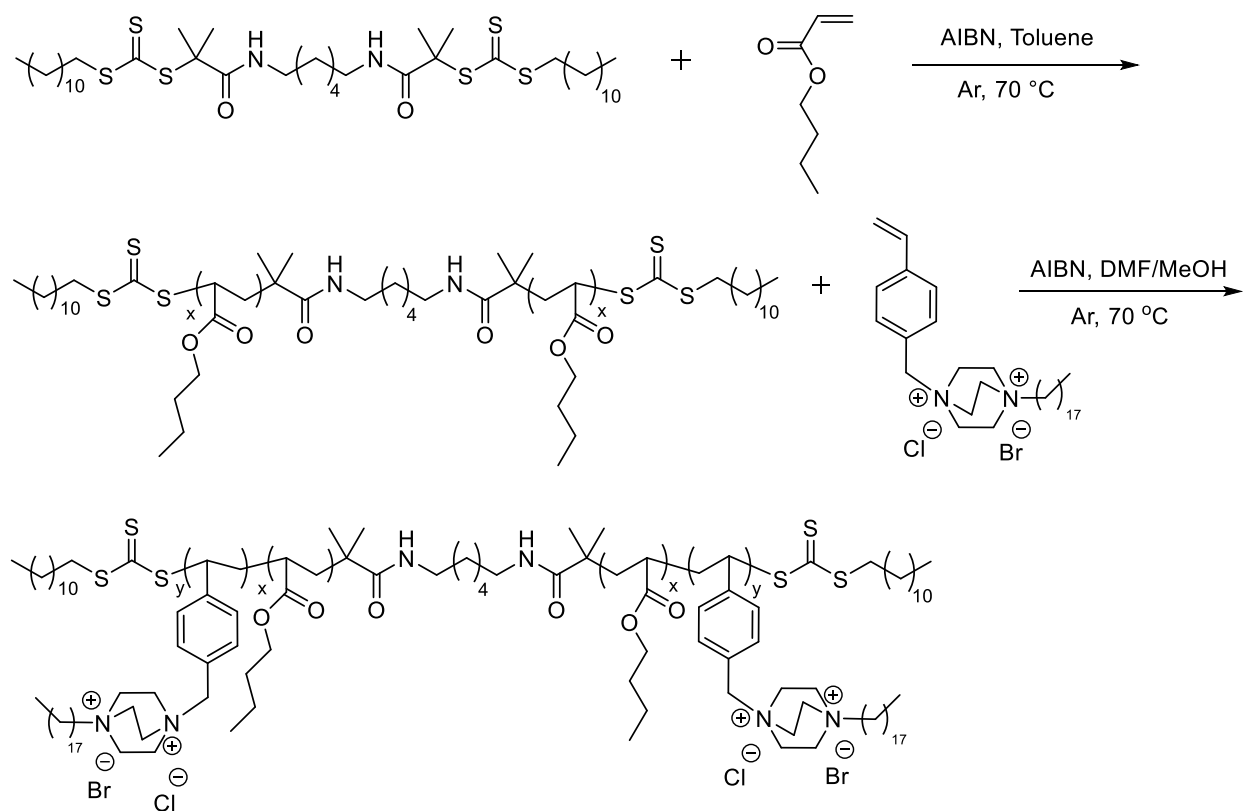
The synthesis of styrenic DABCO salt-containing monomer VBDC₁₈BrCl followed a facile two-step nucleophilic substitution reaction described in the early literature (Scheme 3.1).⁸ Careful selection of solvents allowed solvation of reactants while precipitating the charged product, which simplified the purification procedures with only filtration and washing required. Comparing to the previously synthesized VBDC_xBrCl monomers with shorter alkyl chains ($x = 2-6$), VBDC₁₈BrCl was more hydrophobic due to the incorporation of an octadecyl side chain. The increase in hydrophobicity helped to boost the monomer yield, since the alkylated-DABCO intermediates with a shorter chain (DABCO-C_x, $x=2-6$) were extremely hygroscopic, resulting in a significant loss of product during filtration.

RAFT polymerization facilitated the synthesis of poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl) ABA triblock copolymers utilizing a difunctional CTA with sufficient reactivity of Z- and R-groups relative to the corresponding monomers (Scheme 3.2). An optimal CTA/I ratio minimized the production of dead chains in the early stage of polymerization while maintaining a suitable polymerization rate.^{21,22} The first step afforded difunctional poly (nBA) macro-CTA with 55 % monomer conversion in 6 h, and GPC in THF determined the $M_n = 44.5$ kDa and PDI of 1.2. Precipitation into cold MeOH/H₂O solvent and subsequent drying in a vacuum oven at 40 °C ensured the complete removal of solvent and unreacted nBA monomer.

Utilizing the difunctional PnBA macro-CTA rendered a divergent chain extension of VBDC₁₈BrCl monomer. A mixture of DMF and MeOH helped to solvate the reactants and maintained the solution in a homogeneous state throughout the reaction. Precipitation into different organic solvents failed to purify the resulting block copolymer, with heavy emulsions and bubbles being produced in the process. The hydrophilic charged head and the hydrophobic long alkyl tail contributed to an amphiphilic character of VBDC₁₈BrCl monomer, which served as a surfactant to trap the final polymer within the monomer micelles. Dialysis of the reaction solution in MeOH/CHCl₃ enabled effective purification and minimal loss of polymer. The resulting product was a light yellow, elastic solid that has a different texture from the tacky PnBA macro-CTA. Insolubility of the polymer in common GPC solvents prohibited GPC molecular weight measurement. ¹H NMR spectroscopy in CD₃OD+CDCl₃ (Figure S3.2) served as the primary tool for molecular weight calculation, wherein we utilized the ratio between the integral of the methylene protons from the DABCO blocks at 3.63 ppm (peak c) and the terminal methyl protons from both the PnBA and the DABCO blocks located at 1.04-0.74 ppm (peak d+d').



Scheme 3.1. Synthesis of DABCO salt-containing monomer VBDC₁₈BrCl



Scheme 3.2. Synthesis of poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl) ABA triblock copolymers

The polymerization of VBDC₁₈BrCl blocks proceeded at a relatively slower rate with 56% monomer conversion in 24 h, compared to 63% conversion for the VBC₆BrCl triblock copolymer control (poly(VBDC₆BrCl-*b*-nBA-*b*-VBDC₆BrCl)) in 6 h. We correlated this slower polymerization kinetics to the alkyl chain length difference between VBDC₁₈BrCl and VBDC₆BrCl, since longer alkyl chains usually lead to a lower critical micelle concentration (CMC) and a higher micelle association number N .^{23,24} Thus, the propensity of VBDC₁₈BrCl to aggregate into larger micelles significantly decreased the concentration of the free monomer in proximity to the PnBA macro-CTA and reduced the rate of chain propagation and monomer consumption. Using PnBA macro-CTA with identical molecular weight (44.5 kDa), chain extension with different

amounts of VBDC₁₈BrCl monomers to target at a certain conversion (56 % conversion in 24 h), afforded VBDC₁₈BrCl block copolymers with varied external block contents (9,11, and 14 mol%, respectively).

Table 3.1. Summary of composition, thermal, and morphological properties of VBDC₁₈BrCl ABA block copolymers with varying charge contents

VBDC ₁₈ BrCl in polymer (mol%)	VBDC ₁₈ BrCl in polymer (wt%)	Molecular weight (kDa)	$T_{d,5\text{ wt\%}}$ (°C)	1 st T_g (°C) DSC	1 st T_g (°C) DMA	2 nd T_g (°C) DSC	2 nd T_g (°C) DMA
9	32	10.3-44.5-10.3	215	-46	-27	N/A	56
11	37	12.9-44.5-12.9	210	-45	-28	N/A	58
14	42	16.2-44.5-16.2	208	-45	-30	N/A	57

Thermal Analysis

Thermogravimetric analysis (TGA) revealed variation of thermal properties of DABCO salt-containing block copolymers with ionic content. The polymers exhibited relatively low thermal stability, with degradation occurring around 190 °C (Figure 3.1). This thermal behavior is typical of ammonium polyelectrolytes, which usually dequaternize below 200 °C via two possible pathways: Hoffmann elimination and Reverse Menshutkin (nucleophilic substitution) degradation. Our group has previously reported that the experimental weight loss closely followed the nucleophilic substitution mechanisms for both the trialkylammonium polyelectrolytes and

DABCO salt-containing random copolymers,^{8,25} where substitution occurred when nucleophilic counterions attacked the α -carbon of an amine group, converting the substituent to a tertiary amine. Figure 3.1 also displays a 3-step weight loss profile of all of the ionic block copolymers. The first two steps corresponded to the dequaternization of the alkylic and benzylic ammonium, respectively. The 3rd step was attributed to the degradation of more thermally stable acrylic backbone. Scheme 3.3 illustrates the 1st and 2nd degradation mechanisms of the polymers followed the nucleophilic substitution pathway, and Table 3.2 summarizes the theoretical and experimental values of the polymers weight loss. The calculated 1st step weight loss from the alkylic ammonium dequaternization agreed well with the experimental measurements, however, the experimental weight loss for the 2nd degradation is higher than the theoretical weight loss based on the

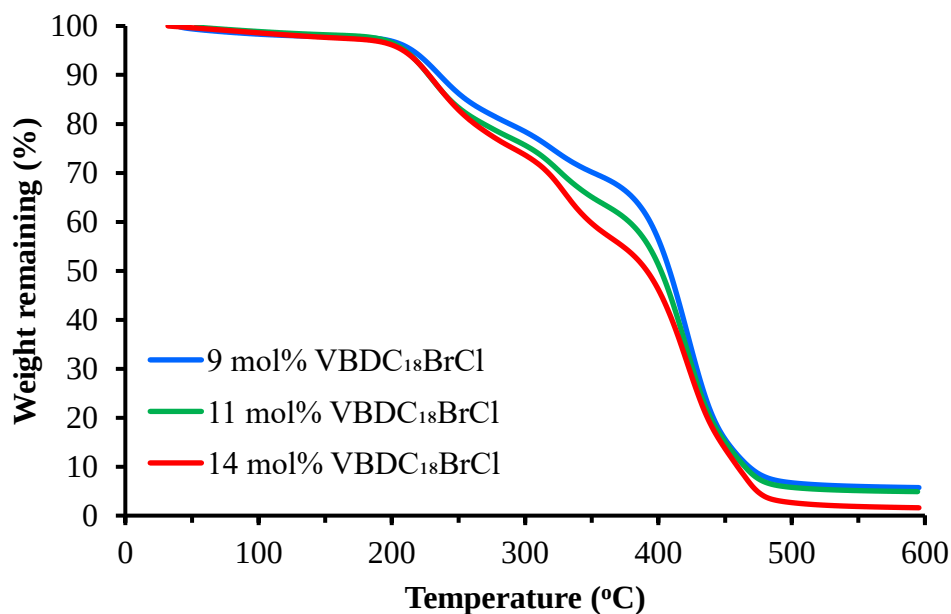
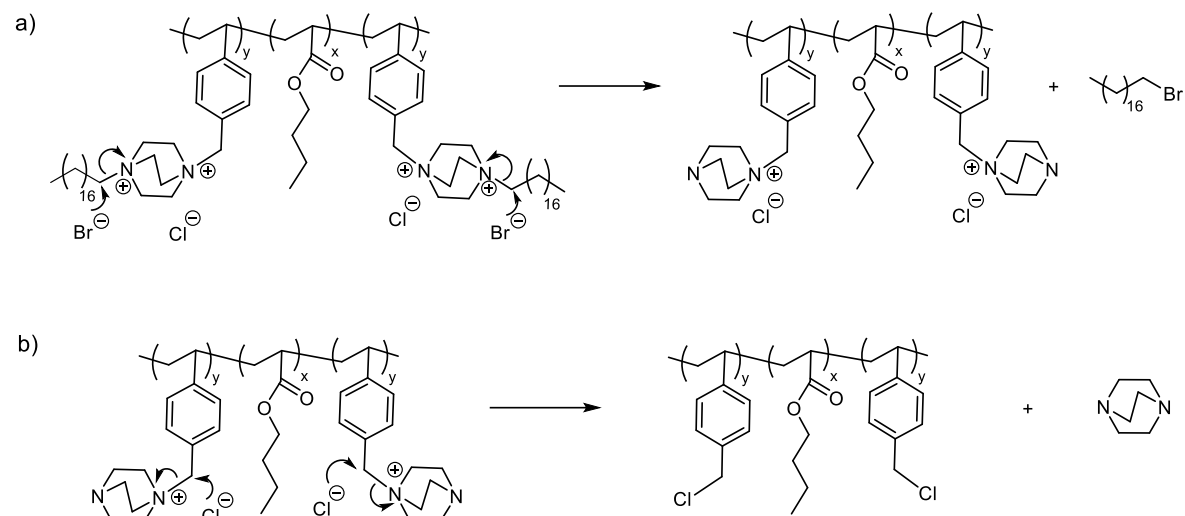


Figure 3.1. TGA thermograms of VBDC₁₈BrCl triblock copolymers with varying hard block incorporations. TGA was carried out from ambient to 600 °C, 10 °C/min under N₂.



Scheme 3.3. 1st (a) and 2nd (b) step of thermal degradation of quaternary ammonium through nucleophilic substitution.

Table 3.2. Correlation of the 1st and 2nd weight loss of VBDC₁₈BrCl block copolymers to nucleophilic substitution pathway

VBDC ₁₈ BrCl in polymer (mol%)	VBDC ₁₈ BrCl in polymer (wt%)	Experimental 1 st step weight loss (wt %)	Theoretical 1 st step weight loss nuc. (wt %)	Experimental 2 nd step weight loss (wt %)	Theoretical 2 nd step weight loss nuc. (wt %)
9	32	21	18	33	24
11	37	22	21	38	28
14	42	22	24	41	32

benzylic ammonium dequaternization, possibility resulting from the concurrence of the decomposition of the styrenic backbone that normally takes place around 300 °C.²⁶ Furthermore, the $T_{d,5 \text{ wt\%}}$ of the block copolymer decreased with increasing hard block composition, due to more incorporation of the thermally-labile charged block.

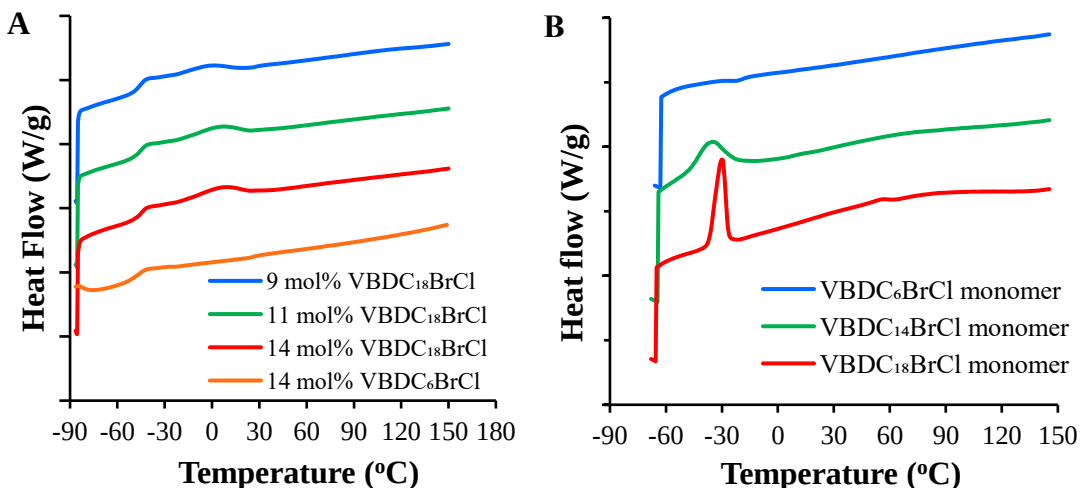


Figure 3.2. DSC traces of (A) VBDC₁₈BrCl and VBDC₆BrCl and block copolymers and (B) different VBDC_xBrCl monomers (x=6,14,18). DSC was performed at 10 °C/min under N₂.

DSC investigated thermal transitions for the block copolymers with varied ionic contents (Figure 3.2A). All of the polymers shared a constant thermal transition step at -45 °C, which matched well with literature values for the glass transition temperature of PnBA.^{27,28} DSC failed to detect the T_g of the ionic block. Long *et al.* also reported the absence of thermal transition steps in the DSC traces for DABCO salt-containing random copolymers with over 25 mol% ionic content.⁸ Interestingly, VBDC₁₈BrCl block copolymers exhibited a broad thermal transition between -18 °C – 20 °C, which was not observed for the VBDC₆BrCl block copolymer analog. This suggested that the broad thermal transitions for VBDC₁₈BrCl polymers might be associated with their longer alkyl tail compared to the VBDC₆BrCl polymers. Figure 3.2B presents DSC traces of DABCO salt-containing monomers with different alkyl chain lengths varying from 6 to 18 carbons. The C₆-monomer barely exhibited any melting transition below its degradation temperature, while a broad melting endotherm started to emerge for C₁₄-monomer and evolved into a sharp endotherm at -30

°C for the C₁₈-monomer. The melting endotherms of the VBDC₁₈BrCl block copolymers appeared broader and shifted to higher temperatures than the C₁₈-monomer. It was presumed that the strong ionic interactions restricted the mobility and limited the packing of the octadecylene chain. Several studies also reported the destabilization of the octadecylene side chain crystallites and shifting of the crystal melting points when copolymerizing octadecyl (meth)acrylate with other monomers.^{29–}

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Thermomechanical Properties

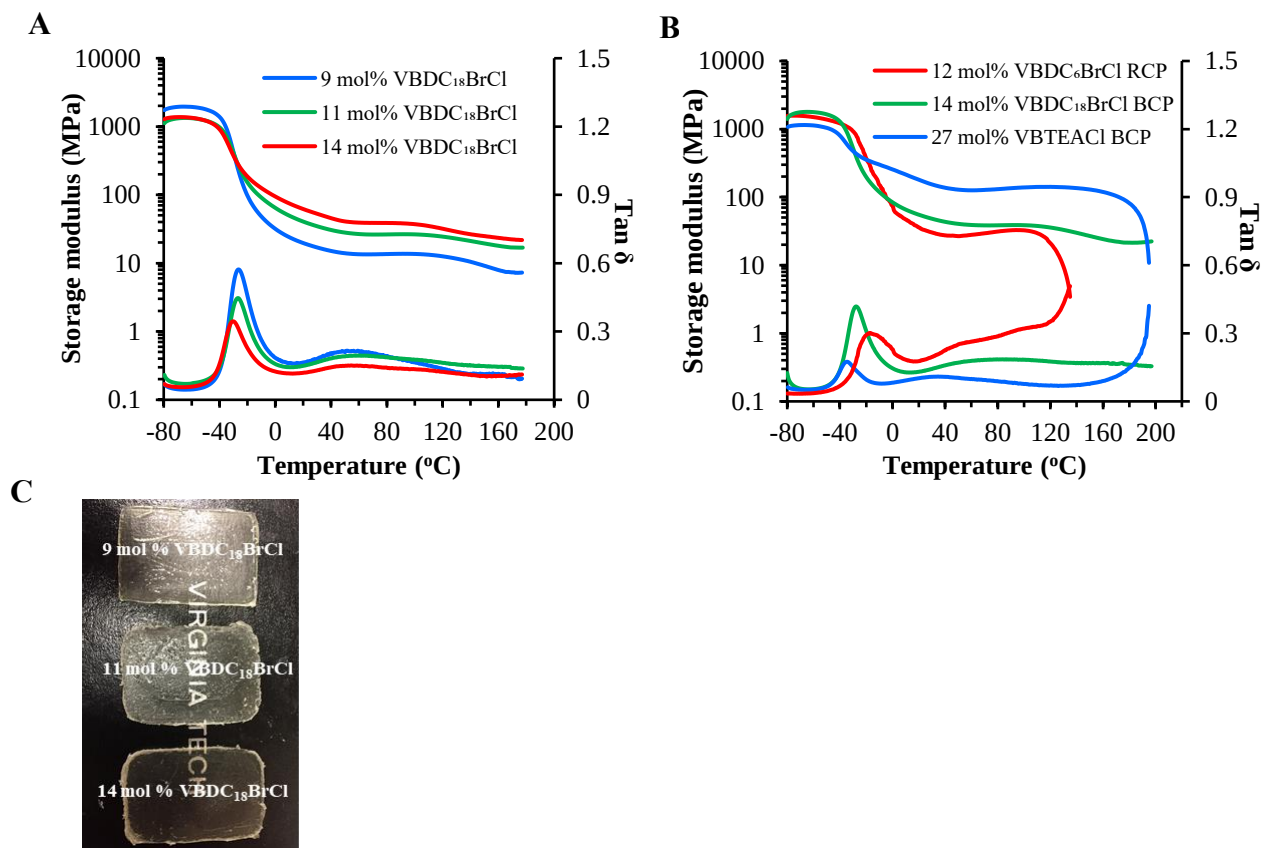


Figure 3.3. Dynamic mechanical comparison of storage modulus and tan δ of the solution-cast (A) VBDC₁₈BrCl block copolymers with varied charged block contents (B) 14 mol% VBDC₁₈BrCl block copolymer and its controls with similar ionic density. DMA was performed at 3 °C/min, oscillatory amplitude 15 μ m at 1 Hz. (C) Solution-cast VBDC₁₈BrCl block copolymer films.

Utilizing solution-casting method, all VBDC₁₈BrCl block copolymers formed free-standing and mechanically robust films. Solution-casting is more desirable for controlling the morphologies of block copolymers, as it not only enhances polymer chain mobility, but also aids formation of equilibrium morphologies through slow solvent evaporation. Whereas melt-pressing techniques usually result in kinetically-trapped morphologies.^{1,28} Selection of solvent is the key to generating films with isotropic properties. Optical clarity of all the block copolymer films in MeOH/CHCl₃ mixture throughout the drying process suggested the absence of macrophase separation (Figure 3.3C). Dynamic mechanical analysis (DMA) confirmed microphase-separated morphologies for VBDC₁₈BrCl block copolymers. The storage modulus decreased when the PnBA block acquired enough energy for long-range segmental motion, which corresponded to a maximum in $\tan \delta$ around -27 °C indicating the T_g of the PnBA soft matrix. The higher T_g of PnBA obtained from DMA compared to DSC was due to frequency dependence of molecular relaxation. In addition, the T_g of the PnBA block decreased ~3 °C when increasing the ionic composition from 9 to 14 mol%, which was correlated to an enhanced phase separation of polymer with a higher ionic content. Continuing to raise the temperature triggered relaxation of the ionic block. The $\tan \delta$ curve revealed a second T_g at 56 °C corresponding to the glass transition temperature of the hard domain, which remained constant for all of the VBDC₁₈BrCl block copolymers. Sen *et al.* and Chisholm *et al.* also reported a similar T_g for the sulfonated styrenic block copolymers.^{1,32} Increasing the ionic block composition from 9 to 14 mol% broadened the second $\tan \delta$ peak, suggesting further restriction of hard phase mobility and slower chain relaxation due to increasing ionic interactions.

The plateau moduli increased with increasing ionic block incorporation, which was attributed to an increased physical crosslink density.

Figure 3.3B displayed the influence of polymer architecture on thermomechanical property for DABCO salt-containing polymers. The doubly-charged random copolymer analog (12 mol% VBDC₆BrCl RCP)⁸ exhibited a terminal flow around 110 °C, where the dissociation of ionic crosslinks started to occur. In contrast, the doubly-charged block copolymer with a similar ionic composition (14 mol% VBDC₁₈BrCl BCP) displayed an extended plateau region, which persisted even above the degradation temperature of the polymer (around 190 °C). This enhanced mechanical property of the block copolymer resulted from phase separation of the hard and soft phases, permitting formation of ionic clusters to establish a highly-crosslinked 3-D network. In contrast, the ionic aggregates in the random copolymer were fewer and more dispersed due to its phase-mixed morphology. Figure 3.3B also highlights the improved mechanical integrity at elevated temperatures for the doubly-charged block copolymer compared to the singly-charged block copolymer counterpart. The dissociation of the ionic aggregates of the singly-charged block copolymer control (27 mol% VBTEACl BCP) occurred around 160 °C despite possessing a similar charge density as the 14 mol% VBDC₁₈BrCl block copolymer, which indicated a much stronger ionic interaction for each DABCO salt unit relative to two triethylammonium groups.

Morphological Characterization

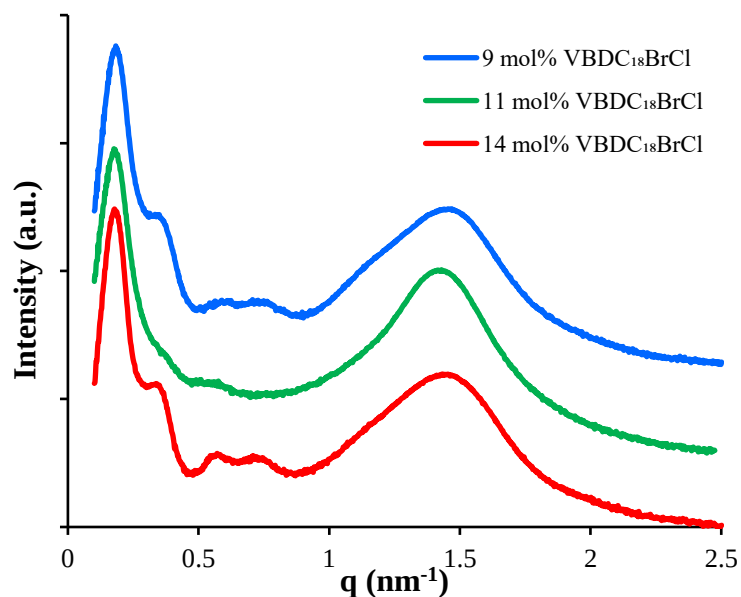


Figure 3.4. SAXS of solution-cast VBDC₁₈BrCl polymer films with varying charge concentrations. Curves are shifted vertically for clarity

SAXS profiles in Figure 3.4 verified a multiphase-morphology of the annealed DABCO-salt containing block copolymer. All curves exhibited a broad peak around $q \sim 1.4 \text{ nm}^{-1}$, located within the region that most investigators have reported for ionic aggregates (between 1.2 and 1.8 nm^{-1}).^{13,33} In addition, each curve showed at least three scattering maxima between $q=0$ -1 nm^{-1} , suggesting a long-range ordered microstructure due to phase separation of the soft and hard blocks. All of the block copolymers revealed scattering maxima at $1q$, $2q$, $3q$, ($4q$), which were characteristic of lamellar morphology. The first order periodic scattering peak $1q$ was correlated with the periodicity(d) of the microdomain, and using $d=2\pi/q$ determined an average distance $d=36$ nm for each lamellar period. Thus, the solution-cast ionic block copolymers revealed a unique

three-phase structure that consisted of highly ordered, lamellar forming PnBA soft phase and DABCO salt hard phase, as well as an ionic aggregate phase located within the hard domain.

TEM cross-section micrographs in Figure 3.5 provides further insight into the microstructures of the DABCO salt-containing block copolymers, whereas the surface morphology under AFM failed to reflect the bulk structure due to a higher affinity of the ionic block to the film-air interphase (Figure S3.5), although AFM confirmed microphase separation of the polymers. The TEM results agreed well with the SAXS measurement, with all three samples exhibiting a well-ordered lamellar morphology. The light region was attributed to the PnBA soft phase, while the dark region indicated a higher electron density and therefore corresponded to the ion-containing hard phase.

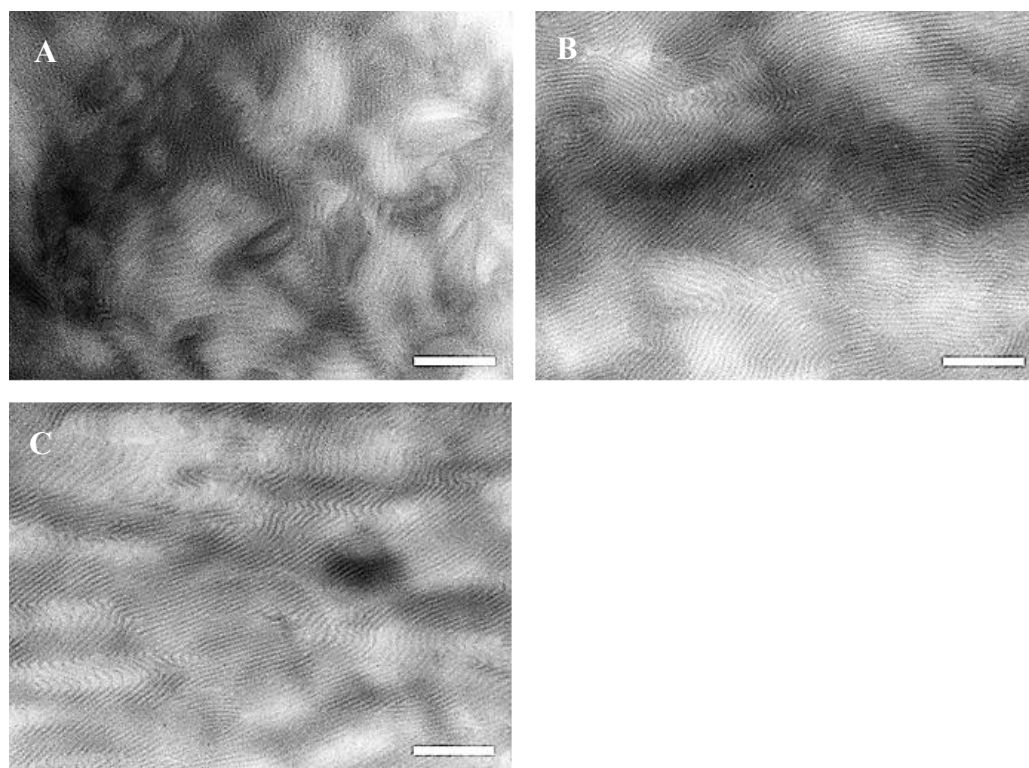


Figure 3.5. TEM revealed a well-defined lamellar morphology for solution-cast VBDC₁₈BrCl polymer films with varying charge concentrations (A) 9 mol% (B) 11 mol% (C) 14 mol% . Scale bars represent 500nm for all images.

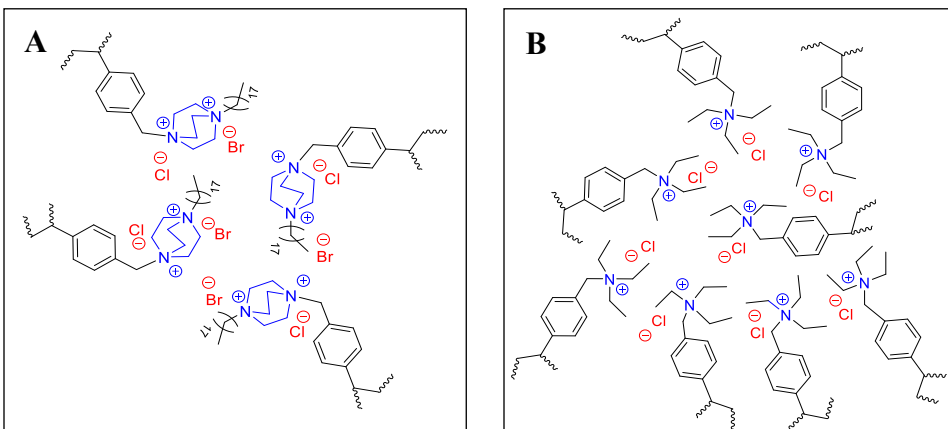


Figure 3.6. Schematic representations of dipole-dipole interaction of DABCO salt-containing polymer (A) and the VBTEACl-containing polymer with the identical charge density (B).

Figure 3.6A and B depict the dipole-dipole interactions for DABCO salt-containing polymer and its singly-charged polymer control, respectively. According to the well-agreed theoretical model proposed by Eisenberg *et al.*, two counteracting forces, i.e. electrostatic force and elastic force, determine the formation of ionic clusters. The electrostatic interactions between charge units favor ionic aggregation, while the elastic forces tend to pull apart the association due to local chain extension, thereby opposing the formation of ionic clusters.¹⁵ For the singly-charged polymer (Figure 3.6B), the number of chains involved in generating an ionic aggregate is a double compared to that of the doubly-charged analog (Figure 3.6A) with the identical charge density, thereby increasing the entropic penalty to afford ionic clusters. In contrast, the formation of ionic clusters for the doubly-charged polymer is more energetically favorable owing to a much smaller elastic forces for the electrostatic attractions to overcome, which promotes phase separation and self-assembly into well-ordered morphologies.

3.5 Conclusions

We report an unprecedented synthesis of VBDC₁₈BrCl block copolymers with varied charged block lengths (9 mol% to 14 mol%) and a series of charged copolymer controls utilizing RAFT polymerization. Chain extension with VBDC₁₈BrCl monomer exhibited a slower propagation rate than the VBDC₆BrCl monomer due to the amphiphilic character of VBDC₁₈BrCl, which more easily formed larger micelles during the reaction, reducing the concentration of the free monomer. TGA revealed a three-step weight loss profile and agreed well with the theoretical value calculated using the nucleophilic substitution degradation pathway. The VBDC₁₈BrCl polymers also exhibited a destabilized side-chain crystallization in DSC, in which the strong ionic interactions prohibited the packing of the octadecylene side chain. DMA showed an enhanced mechanical properties for the doubly-charged block copolymer, with a prolonged plateau region extending beyond the polymer degradation temperature, whereas the singly-charged analog displayed an earlier terminal flow despite having a similar charge density. DMA also provided evidence for the influence of ionomer architecture on the mechanical property, and demonstrated the formation of stronger physical crosslinks for block copolymers due to a better phase separation compared to the corresponding random copolymers. SAXS and TEM confirmed a well-ordered lamellar microstructure and a unique three-phase morphology of VBDC₁₈BrCl block copolymers. Hence, the enhanced dipole-dipole interaction between the DABCO salt units showed great promise in promoting interchain recognition, facilitating self-assembly, and improving mechanical property, which provides new avenues for designing novel energy devices and biomedical materials.

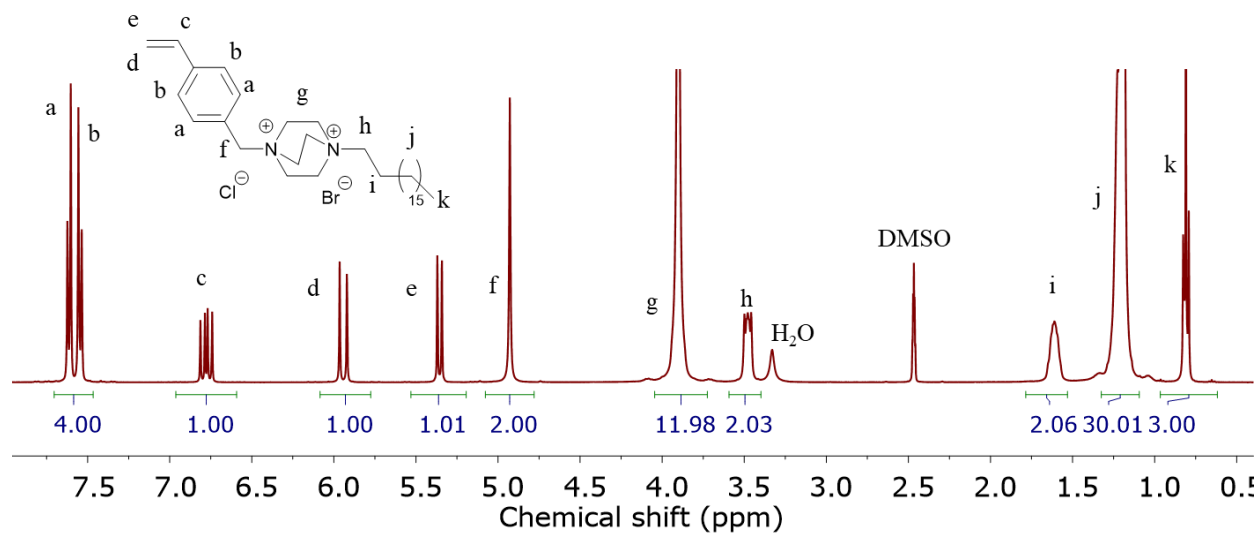
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3.7 Supporting Information

A



B

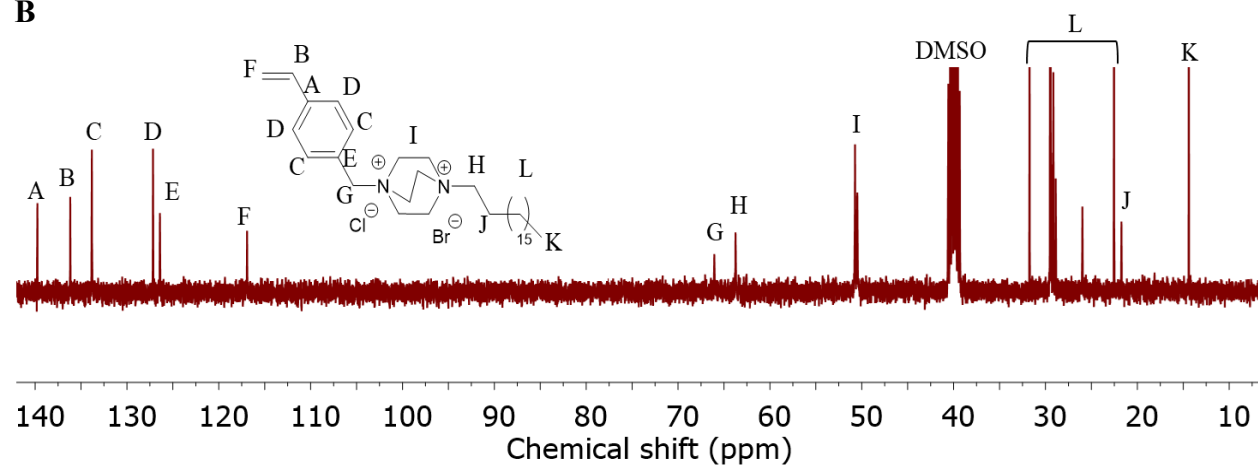


Figure S3.1. (A) ¹H and (B) ¹³C NMR spectra of VBDC₁₈BrCl monomer.

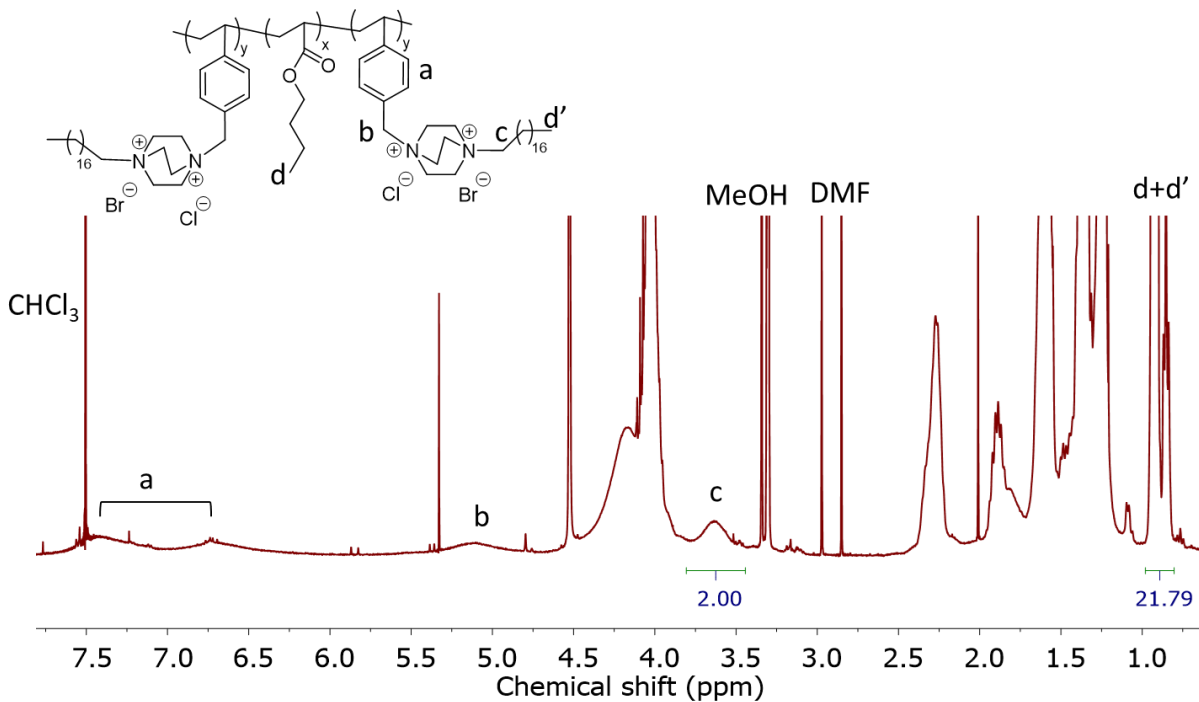


Figure S3.2. ^1H NMR spectrum of poly(VBDC₁₈BrCl-*b*-nBA-*b*-VBDC₁₈BrCl) with 14 mol% of VBDC₁₈BrCl content.

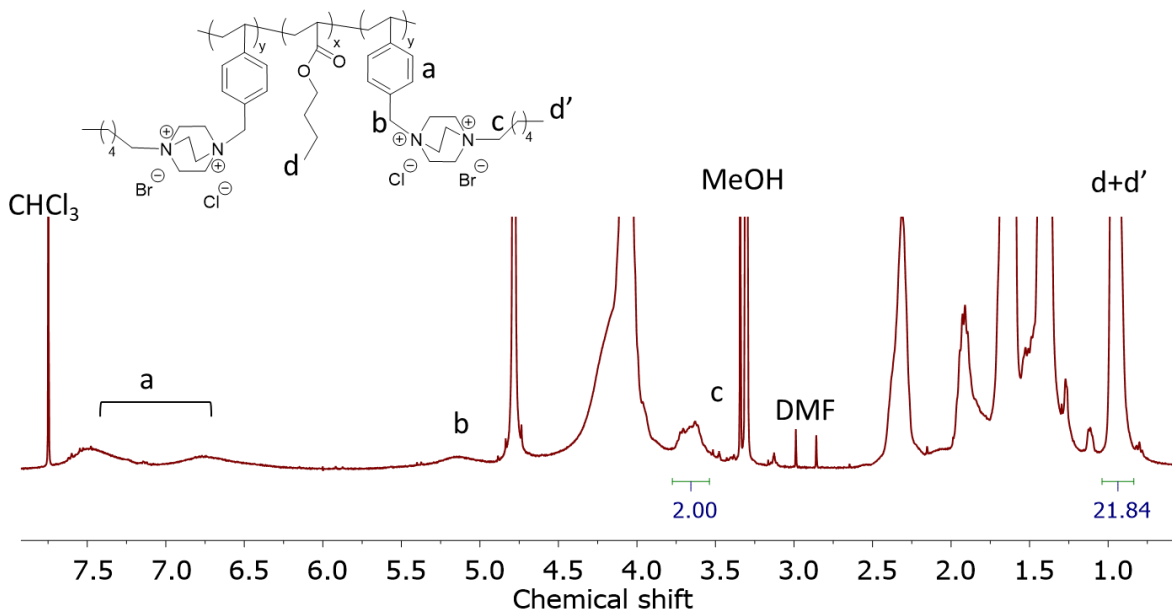


Figure S3.3. ^1H NMR spectrum of poly(VBDC₆BrCl-*b*-nBA-*b*-VBDC₆BrCl) with 14 mol% of VBDC₁₈BrCl content.

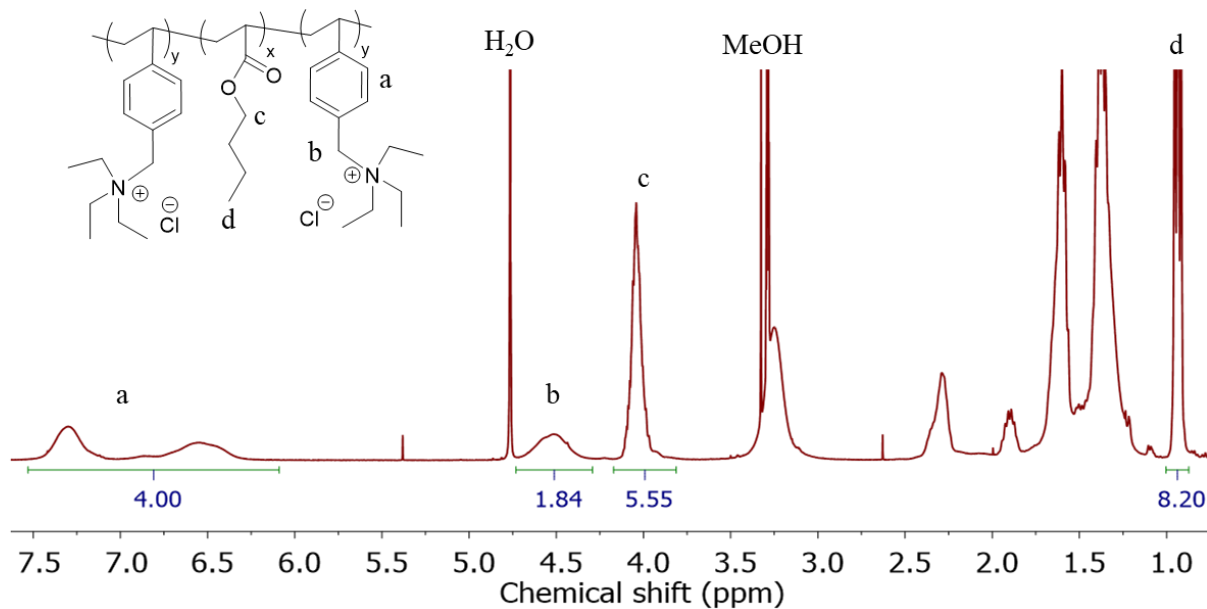


Figure S3.4. ^1H NMR spectrum of poly(VBTEACl-*b*-nBA-*b*-VBTEACl) with 27 mol% of VBTEACl content.

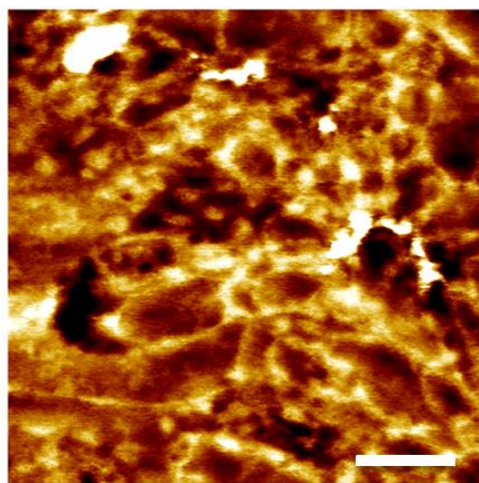


Figure S3.5. AFM phase image of solution-cast VBDC₁₈BrCl block copolymer films containing 11 mol% of VBDC₁₈BrCl. Scale bar represents 500 nm.

Chapter 4. 3D-Printing Hydrogen Bonding Network: Reactive Urea Monomers

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4.1 Abstract

Incorporation of hydrogen bond functionalities into 3-D printable acrylate resins offers promising avenues for improving the inter-layer adhesion of printed objects. The multiple hydrogen bonding helps to form physical crosslinks between layers, which ensures the isotropic performance of objects fabricated using layer-by-layer mask projection micro-stereolithography (MP μ SL). In addition, the thermally-reversible feature of hydrogen bonding maintains the melt processability of the acrylic resins. Within the designed photo-crosslinkable system, a novel acrylate monomer served as a plasticizer in the diacrylate polymer matrix. Varying the resin compositions offered a high degree of tunability of the crosslinking density, leading to different mechanical properties. The intermolecular hydrogen bonds functioned as physical crosslinks, which not only contributed to polymer elastomeric property, but also assisted in preventing stress-relaxation of the networks. This chapter will assess the efficacy of hydrogen bonding in 3D printable urea networks.

4.2 Introduction

Additive manufacturing, often referred to as 3D printing, allows unprecedented control of object complexity. Materials science and engineering represent two different approaches to gain access to tunable and functional 3D printed matrices. In contrast, structural engineering explores mechanical property control through physical structure design.¹⁻³ Novel functional resins demonstrate even more promising advantages, not only in mechanical properties, but also in conductivity,⁴ molecule transportation,⁵ and biological applications.^{6,7} Mask projection micro-stereolithography (MP μ SL) is a modified stereolithography (SL), where an entire cross-section layer is photo-cured through digitally patterned, dynamic mask. MP μ SL improves the resolution from 100 μ m (SL) to 10 μ m and reduces the overall printing time. However, the inherent anisotropic performance of the layer-by-layer structure is problematic for various applications. Thus, efforts have been made to improve inter-layer adhesion, and hydrogen bonding is one of the promising candidate technologies.

Hydrogen bonding provides unique secondary interactions due to its directionality and thermal-reversibility. Although hydrogen bonds are relatively weak compared to covalent bonds, the accumulation of multiple hydrogen bonds can introduce physical crosslinks that are as strong as chemical crosslinks. Previous studies have focused on the potential of hydrogen bonding in supramolecular assembly,⁸ thermoplastic elastomers,⁹ and micro-phase separated morphology.¹⁰⁻¹² Therefore, the dynamic nature and strong interaction of hydrogen bonding in polymers exhibit great potential in additive manufacturing as a way to bridge layers.

Herein, we hypothesize that incorporation of multiple hydrogen bonding motifs into photocrosslinkable resin would improve interlayer adhesion of the 3-D printed object by forming physical crosslinks. Based on this hypothesis, we designed a hydrogen bond network system composed of a novel urea monoacrylate monomer and a diacrylate polymer suitable for MP μ SL. A facile three-step synthesis produced a urea monoacrylate resin with high yields and at large scale, which formed a mechanically robust network with a diacrylate upon UV exposure. Varying the composition of the urea monoacrylate offered a high degree of tunability of mechanical properties. The urea moieties associated with each other through multiple hydrogen bonds, establishing reversible physical crosslinks to strengthen the interlayer adhesion. Furthermore, the synergy of the chemical and physical crosslinks minimized the stress-relaxation both in air and in water. Systematic thermal, mechanical studies illustrated the structure-property relationship of urea network system.

4.3 Experimental Section

Materials

1,1'-Carbonyldiimidazole (CDI, 99 %), hexylamine (98%), trimethylamine (99+%), 6-amino-1-hexanol (97%), poly (ethylene glycol) diacrylate (PEG-DA, Mw=575), acryloyl chloride (99%+), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 99%) were purchased from Sigma-Aldrich and used without further purification. Krasol (Mw=2000) was purchased from Cray Valley and was used as received. Methoxyphenol (MEHQ, 98+%) was purchased from Alfa Aesar. Hexanes

(Fisher Scientific, HPLC grade), chloroform (THF; Fisher Scientific, HPLC grade), N,N-dimethylformamide (DMF, HPLC grade), and anhydrous dichloromethane (DCM; Sigma-Aldrich, HPLC grade, anhydrous) were used as received.

Analytical Methods

^1H NMR spectroscopy was performed on an Agilent U4-DD2 400 Hz spectrometer at 23 °C in CDCl_3 or $\text{DMSO}-d_6$. Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC Q2000 using a heat/cool/heat cycle at a heating/cooling rate of 10 °C/min from -90 °C to 130 °C under N_2 purge. Glass transition temperatures (T_g) were determined using the midpoint of the thermal transition step. Stress-relaxation experiments on the photo-crosslinked films were employed utilizing a TA Instruments Q800 dynamic mechanical analyzer in tension mode at a frequency of 1 Hz and 0.5% strain. The film was equilibrated at 35 °C, isotherm for 5 min, length measured, and displaced for 60 min. Submersion stress-relaxation tests in water were performed using a submersible clamp. Samples were presoaked in water at 23 °C for 48 h before the experiment. An Instron 5500R universal testing instrument characterized the tensile property of the urea networks at a crosshead speed of 50 mm/min. Tensile test results were based on an average of five measurements.

Synthesis of N-hexyl-1H-imidazole-1-carboxamide (Scheme 4.1)

To a 500-mL round bottomed flask, CDI (48.1 g, 0.30 mol) and 200 mL chloroform were added. Hexylamine (20.0 g, 0.20 mol) were slowly injected into the suspension solution. The solution

turned clear immediately, generating a large amount of heat in the process. The reaction mixture was stirred at room temperature for another 12 hours, and was washed twice with water to get rid of the unreacted CDI and then washed once with brine. Rotary evaporation the solvent at 60 °C afforded a colorless oil intermediate. The structure and purity of the intermediate were confirmed using ^1H NMR spectrometry (400 MHz, CDCl_3) (Figure S4.1): 8.47 (t, 1H, $J=5.6$ Hz), 8.20 (s, 1H), 7.56 (s, 1H), 6.90 (s, 1H), 3.28 (q, 2H, $J=6.7$ Hz), 1.50 (m, 2H, $J=7.3$ Hz), 1.28-1.32 (m, 6H), 0.77 (t, 3H, $J=7.0$ Hz)

Synthesis of N-hexyl-N'-(6-hydroxyhexyl)urea (Scheme 4.1)

N-Hexyl-1H-imidazole-1-carboxamide (22.4 g, 0.11 mol), 1-amino-6-hexanol (13.5 g, 0.11 mol), and 150-mL chloroform were charged into a 200-mL round bottomed flask equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 24 h. The solution was washed twice with water and once with brine. Removal of the solvent under reduced pressure afforded white solids that were dried under vacuum at 50 °C overnight. Yield 95 %. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (Figure S4.2): 5.69 (t, 2H, $J=5.7$ Hz), 4.32 (t, 1H, $J=5.18$ Hz), 3.35 (q, 2H, $J=5.2$ Hz), 2.92 (q, 4H, $J=6.5$ Hz), 1.43-1.14 (m, 16H), 0.84 (t, 3H, $J=7.2$ Hz). Mass spectrometry (ES+): m/z calculated for $[\text{M}^+]$: found 244.2071 g/mol, calculated: 244.2152 g/mol.

Synthesis of 6-(3-hexylureido)hexyl Acrylate Monomer (Scheme 4.1)

N-hexyl-N'-(6-hydroxyhexyl)urea (32.2 g, 0.13 mol), TEA (20.0 g, 0.20 mol), and anhydrous DCM were added into a 500-mL round bottomed flask equipped with a magnetic stir bar. The

suspension solution was cooled in ice bath, and acryloyl chloride (17.9 g, 16.0 mL, 0.20 mol) was added dropwise into the solution. The reaction was kept at 0 °C for 30 min, and slowly warmed to room temperature to react for 12 h. The reaction mixture was poured into 100 mL 1N HCl aqueous solution to neutralize excess TEA, and the organic layer was washed twice with water, once with saturated NaHCO₃, and finally once with brine. The solution was dried over MgSO₄ overnight and the solvent was removed by rotary evaporation to afford orange solids that were purified using a silica plug with CHCl₃/EtOAc = 2:1. Evaporation of the eluent produced a white solid (20.2 g, yield: 53%). ¹H NMR in DMSO-*d*₆ confirmed the structure and purity of the urea monoacrylate monomer (Figure S4.3): 6.31 (dd, 1H, *J*₁=1.7 Hz, *J*₂=17.3 Hz), 6.2 (dd, 1H, *J*₁=10.3 Hz, *J*₂=17.3 Hz), 5.93 (dd, 1H, *J*₁=1.6 Hz, *J*₂=10.3 Hz), 5.71 (m, 2H), 4.09 (t, 2H, *J*=6.7 Hz), 2.94 (q, 4H, *J*=7.0 Hz), 1.60 (quin, 2H, *J*=7.0 Hz), 1.39-1.18 (m, 14H), 0.85 (t, 3H, *J*=6.9 Hz). Mass spectrometry (ES⁺): *m/z* calculated for [M⁺]: found 298.2157 g/mol, calculated g/mol : 298.2239 g/mol. Melting point: 70 °C.

Synthesis of Urea Monoacrylate Homopolymer (Scheme 4.2)

Urea monomer (2 g, 6.71 mmol), AIBN (1.1 mg, 0.00671 mmol), and DMF (6 g) were charged into a 25-mL round bottomed flask equipped with a magnetic stir bar. The solution was sparged with Ar for 20 min and was reacted at 65 °C for 24 h. The polymer was precipitated from MeOH/H₂O= 2:1 and dried under vacuum overnight to afford a tacky colorless solid. ¹H NMR spectroscopy confirmed the chemical structure of the urea homopolymer (Figure S4.4)

Photo-polymerization Procedures (Scheme 4.3)

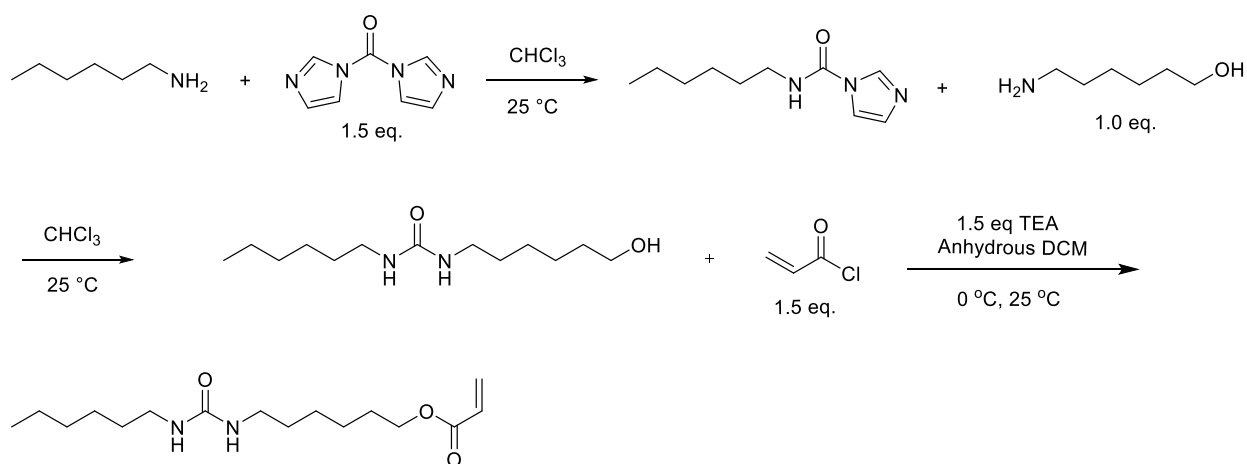
In a representative urea matrix synthesis: urea monoacrylate monomer (0.5 g), PEGDA or KrasolDA (0.5 g, urea/DA=50/50, w/w), MEHQ (5 mg, 0.5 wt), and TPO (10 mg, 1 wt%) were added to a rectangular PTFE mold. The mold was heated on a hot plate at 70 °C until all of the urea monomer reached the molten state, and the liquid resin was blended thoroughly using a spatula. Then, the mold was immediately cured utilizing the UV Fusion at a speed of 6 fpm and the curing process was repeated three times. The resulting gels were soaked in ethanol to remove any unreacted resin, and dried under vacuum at room temperature overnight.

4.4 Results and Discussion

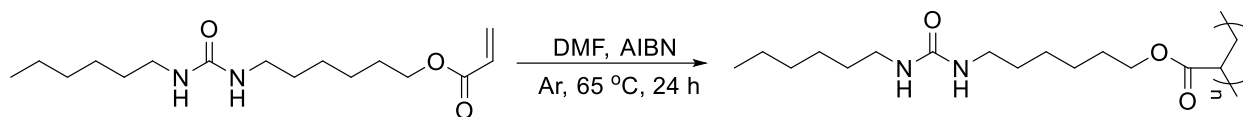
Preparation of Urea Monomers and Photo-crosslinked Matrix.

The synthesis of the urea monoacrylate was achieved through a facile three-step reaction (Scheme 4.1). CDI is more beneficial for urea preparation, since it is much safer to handle than isocyanates and is less sensitive to reaction conditions, which make it more suitable for large-scale synthesis. In the first step, an excess of CDI ensured a single-side functionalization of hexylamine and avoided the production of the doubly functionalized byproduct. The CDI suspension in chloroform turned clear immediately upon adding hexylamine, accompanied by a large amount of heat, indicating the reaction had occurred. Pouring the reaction mixture into deionized water removed the excess CDI, with many bubbles generating due to the decomposition of CDI in water.

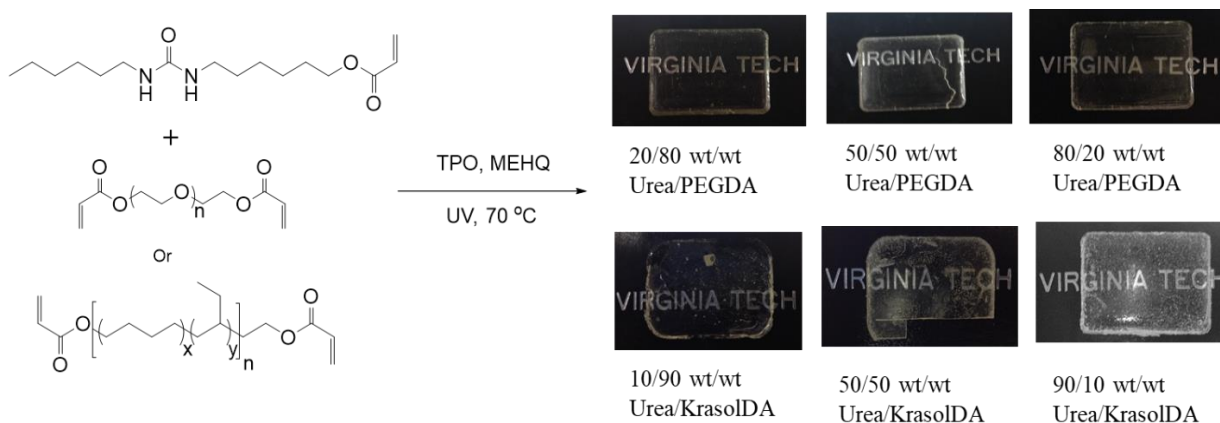
Evaporation of chloroform after the workup procedure afforded a viscous oil intermediate that was directly applied to the next step. Functionalization of the other side of CDI in the 2nd step also took place in chloroform. The solution remained homogeneous throughout the reaction, and TLC enabled quantitative monitoring of the reaction progress. The resulting urea alcohol was a white crystalline material, obtained in over 95 % yield. In the third step, reaction of the urea alcohol with acryloyl chloride afforded urea monoacrylate monomer. TEA removed the hydrochloric acid produced during the process, which served as a base and a catalyst to move the reaction forward. The reaction mixture became orange upon adding the acryloyl chloride, which was attributed to the complex that formed between TEA and acryloyl chloride.¹³ The reaction was complete within 12 h, with the white TEA·HCl salt precipitating from solution. An acid wash in the workup neutralized the excess TEA and removed the TEA·HCl salt. Then, the organic layer was subjected to twice of water wash and a final base wash to adjust the pH. Evaporating the solvent afforded an orange solids, and a silica plug enabled the removal of the orange complex and yielded the white urea monomer product with a melting point of 70 °C.



Scheme 4.1. Synthesis of 6-(3-hexylureido)hexyl acrylate (urea monomer).



Scheme 4.2. Synthesis of urea homopolymer.



Scheme 4.3. Photopolymerization of urea monoacrylate with diacrylates into chemically-crosslinked gel.

Photopolymerization under UV light provided crosslinked films for thermal and mechanical characterization. Preparation of resin above the melting temperature of urea monomer generated a homogenous liquid for printing and avoided the addition of solvents, which prevented film warpage and shrinkage. A small amount (0.5 wt%) of inhibitor MEHQ prevented crosslinking during resin preparation. Exposure to UV light induced TPO to produce reactive radicals and triggered polymerization of urea monoacrylate and diacrylate to generate a chemically-crosslinked network. All of the resulting gels are mechanically-robust and optically-clear. A preliminary 3-D printed object in Figure S4.6 revealed well-defined structures and details, proving the suitability of the resin for 3-D printing. Varying the monoacrylate and the diacrylate compositions enabled

tunability of mechanical property, with more incorporation of the diacrylate leading to an increase of brittleness for the urea network due to high density of chemical crosslinks.

Thermal Analysis

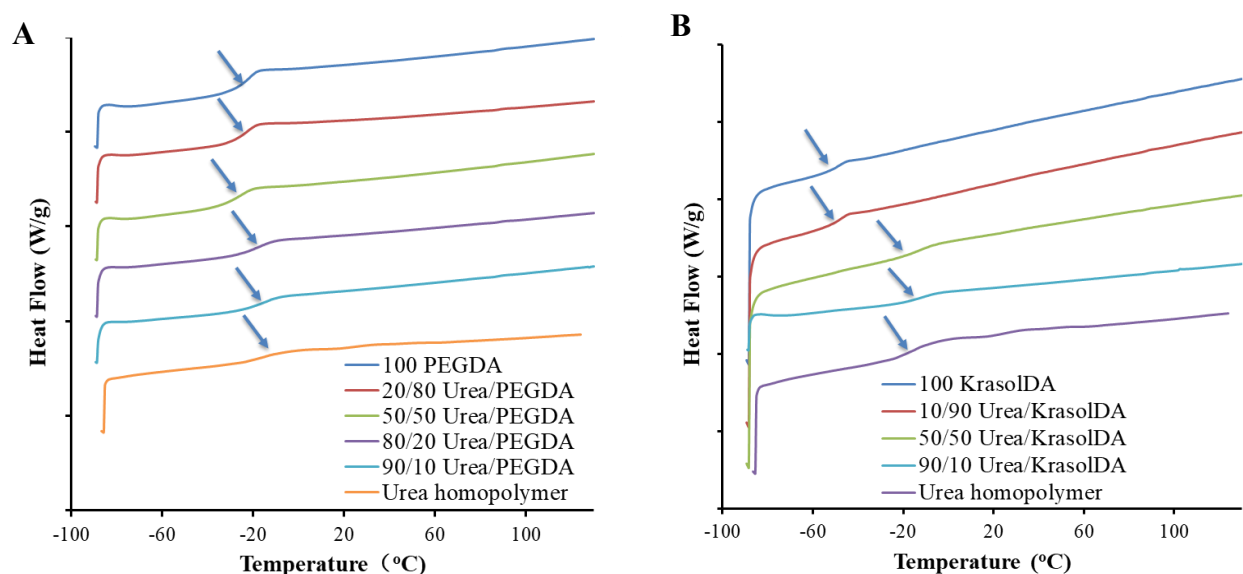


Figure 4.1. DSC traces of urea/PEGDA (A) and urea/krasolDA (B) network system with varied compositions. DSC was performed -90 °C-150 °C at 10 °C/min under N₂.

Table 4.1. Summary of T_g s of urea networks with varied urea/PEGDA (U/P) or urea/KrasolDA (U/K) compositions.

Composition	100 P	20/80 U/P	50/50 U/P	80/20 U/P	90/10 U/P	100 K	10/90 U/K	50/50 U/K	90/10 U/K	100U
T_g (°C)	-23	-23	-27	-17	-15	-49	-48	-14	-11	-14

Figure 4.1 displays the T_g values for both the urea/PEGDA and urea/KrasolDA network systems, and Table 4.1 summarizes the T_g values for all compositions. For urea/KrasolDA networks (Figure 4.1B), incorporation of the urea monomer raised the T_g of the pure KrasolDA network by approximately 40 °C. The higher T_g for 90/10 urea/KrasolDA than the urea homopolymer was

attributed to chemical crosslinks, which further restricted molecular segmental motion. For urea/PEGDA system, however, increasing the urea content led to an initial decrease of T_g , which probably resulted from a dramatic reduction of chemical crosslinks in the system. The deviation of T_g for both the network systems from values predicted by the Fox equation was due to the chemically-crosslinked structures, which followed a more complicated relationship. The T_g values of both the urea/PEGDA and urea/KrasolDA systems were still relatively low ($<-10\text{ }^{\circ}\text{C}$) for application as retainers. We will address this issue in a forthcoming publication using urea monomer and diacrylate that possess a more rigid structure.

Stress-Relaxation

Figure 4.2A-B shows the stress-relaxation properties of urea/PEGDA and urea/KrasolDA under air, respectively. The urea/PEGDA system exhibited constant stress-relaxation moduli during the experiment. The synergy of physical and chemical crosslinks prevented the slippage and stretching of the polymer chains during the stress application process, enabling an excellent capability to retain stress. Urea/KrasolDA networks also revealed no stress-relaxation within 60 min. The 90/10 urea/KrasolDA failed the test, as the film was too soft to load on the clamps. In addition, urea/PEGDA networks displayed much higher relaxation moduli than the corresponding urea/KrasolDA networks, resulting from its lower molecular weight between the chemical crosslinks. Varying the proportion of the monoacrylate and diacrylate allowed for the tailoring of relaxation moduli. The relaxation modulus first increased with increasing urea content and achieved a maximum value at 50/50 composition. However, further increasing the amount of urea

monomer resulted in decrease of relaxation moduli. This trend reflected the influence of crosslink density on the relaxation modulus of the network, which was a trade-off between chemical and physical crosslinks. At low urea composition, the diacrylate comprised the majority of the resin and chemical crosslinks dominated the network. Whereas for systems with high urea concentration, the network was formed primarily via physical crosslinks. Incorporation of more urea monomer led to an increase of physical crosslinks at the expense of chemical crosslinks. The overall crosslink density reached a maximum at intermediate urea incorporation, where both the chemical and physical interactions acted cooperatively to reinforce the mechanical property.

Submersion DMA in water facilitated the measurement of stress-relaxation performance of the urea networks under a working environment similar to that of retainers in the human mouth (Figure 4.6). Both urea/PEGDA and urea/KrasolDA networks displayed constant stress-moduli in 60 min. Figure 4.3 also compared the stress-relaxation of the urea networks under dry and hydrated states. In general, the hydrated networks exhibited lower stress-relaxation moduli than the dried counterparts, which was attributed to the water uptake for both systems as evidenced from TGA-SA measurements shown in Figure S4.5. The water molecules served as plasticizers to increase the flexibility of the polymer chain. In addition, water molecules are excellent hydrogen bonding donors and acceptors, which will break apart the physical crosslinks of the network through competing with the urea moiety to form hydrogen bonds, resulting in decrease of relaxation moduli. The 90/10 urea/PEGDA film demonstrated a similar stress-relaxation modulus in water as the corresponding urea/KrasolDA film, whereas the dried urea/PEGDA films possessed much higher

moduli than their urea/KrasolDA analogs. This lower susceptibility of urea/KrasolDA system resulted from a more hydrophobic chemical structure of KrasolDA compared to PEGDA, with 90/10 urea/KrasolDA only taking up approximately half the amount of water as the corresponding urea/PEGDA network according to Figure S4.5. Thus, the resistance of both the urea network systems to stress-relaxation in water and air offered great promises in dental applications.

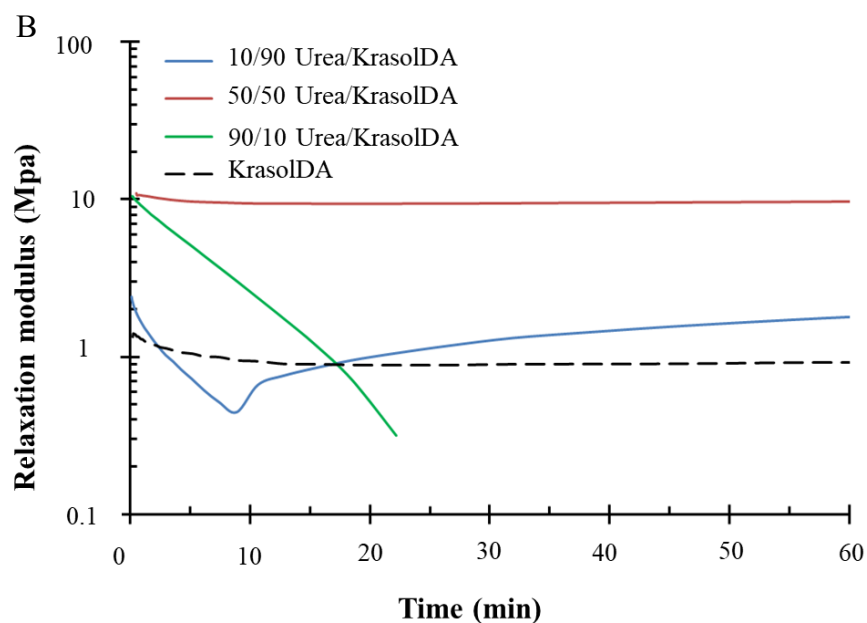
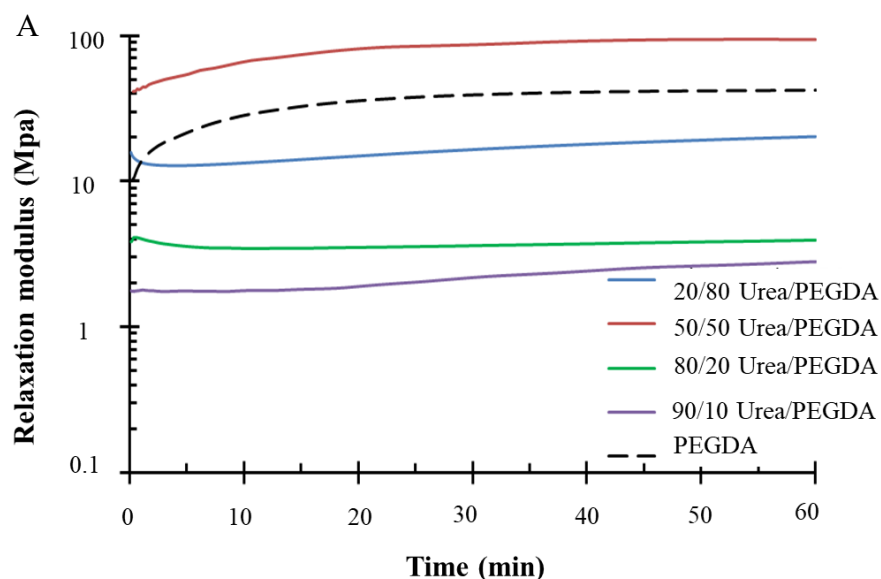


Figure 4.2. Stress-relaxation experiments of urea/PEGDA (A) and urea/krasolDA (B) network system with varied compositions. Experiments were carried out at 35 °C, 1Hz, under 0.5% strain.

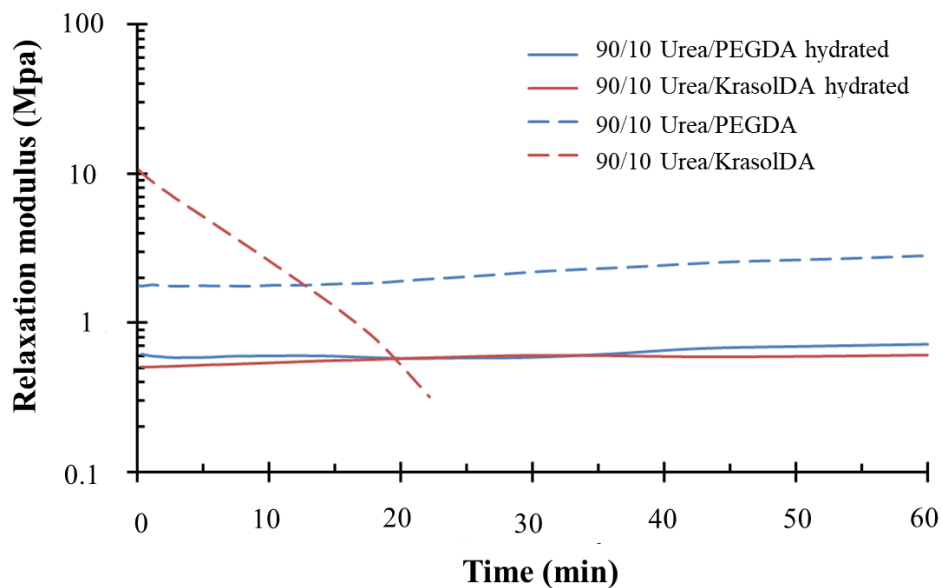
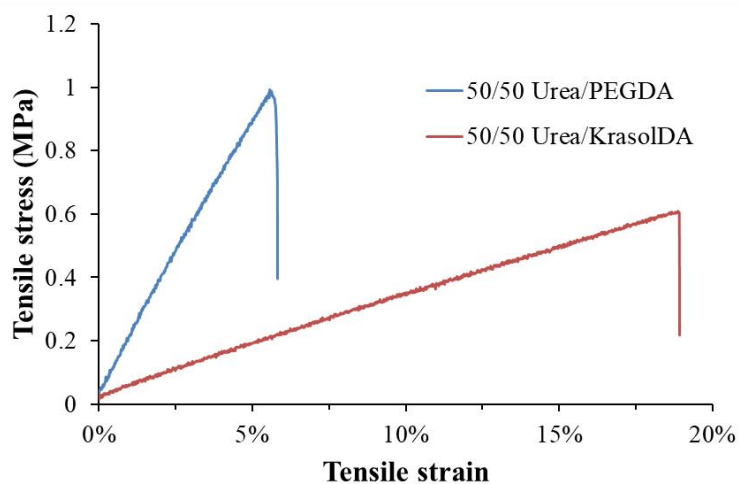


Figure 4.3. Stress-relaxation comparisons of urea/PEGDA and urea/KrasolDA network systems under hydrated and dry conditions.

Tensile Property



50/50 Urea/PEGDA



50/50 Urea/KrasolDA

Figure 4.4. Stress-strain comparisons of 50/50 urea/PEGDA and 50/50 urea/KrasolDA network.

Figure 4.4 presents stress-strain relationships of urea/PEGDA and urea/KrasolDA network. An optimal composition 50/50 was selected for both systems based on the stress-relaxation results. 50/50 urea/PEGDA exhibited 5.6 % tensile strain at break with Young's modulus of 14.7 MPa, whereas 50/50 urea/KrasolDA system displayed 15.3 % tensile strain at break with Young's modulus of 3.4 MPa. The tensile results agreed well with the stress-relaxation tests, which indicated a lower mechanical strength and higher flexibility of the urea/KrasolDA compared to the urea/PEGDA analogs. However, the Young's moduli for both systems were still too low to serve as retainers (~ 1 GPa). Our future work will target improving the mechanical strength while retaining the flexibility of the urea network.

4.5 Conclusions

We designed photo-crosslinkable acrylate resins consisting of a novel urea monoacrylate and a diacrylate for MP μ SL. Utilizing CDI instead of isocyanates offered a facile and a safer approach to synthesize the urea monomer on large scale. Photopolymerization of resins above the melting temperature of urea monoacrylate enabled the fabrication of the urea network in the absence of solvent, which prevented dimensional shrinkage of the object. The diacrylate generated a chemically-crosslinked network upon exposure UV light, whereas the urea moiety formed reversible physical crosslinks via hydrogen bonding. Adjusting the composition of the urea monoacrylates and diacrylates allowed us to tailor the mechanical property through varying the crosslinking density of the network. The resulting urea networks displayed constant moduli during

the stress-relaxation experiments, demonstrating no stress-relaxation in both air and water. The resin showed great promise for fabricating an optically-clear and stress-relation free object using 3-D printing but the modulus of the network still needs improving for dental applications. Our future works will focus on addressing the modulus and T_g issues through optimizing the urea monomer and diacrylate structures.

4.6 References

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4.7 Supporting Information

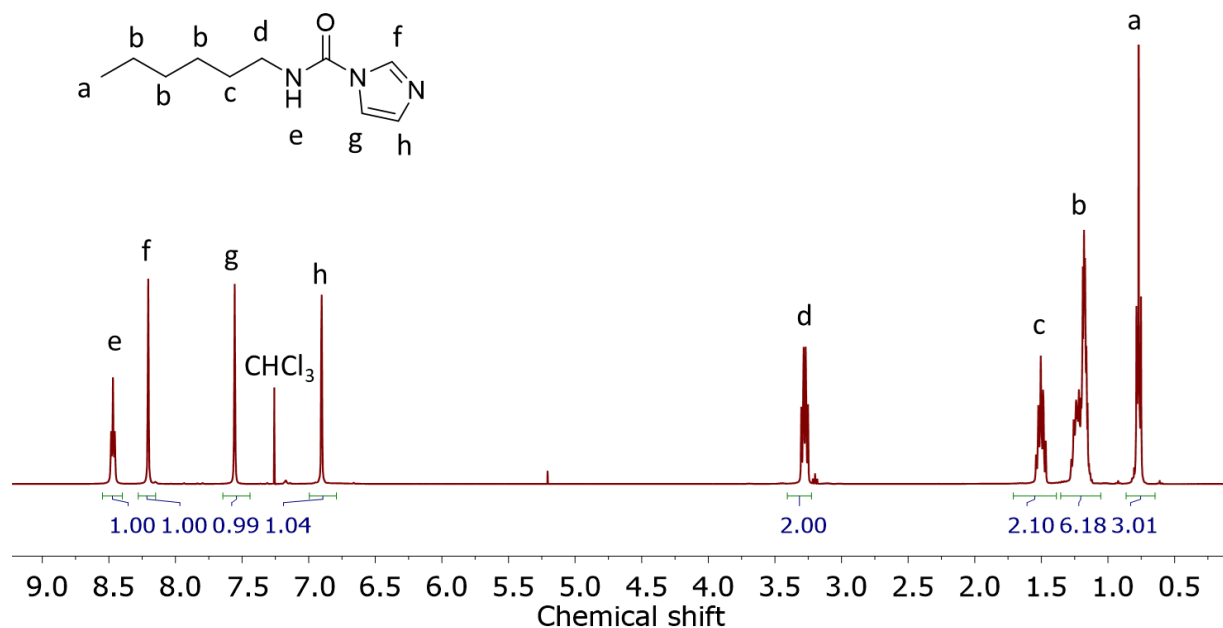


Figure S4.1. ¹H NMR spectroscopy of N-hexyl-1H-imidazole-1-carboxamide.

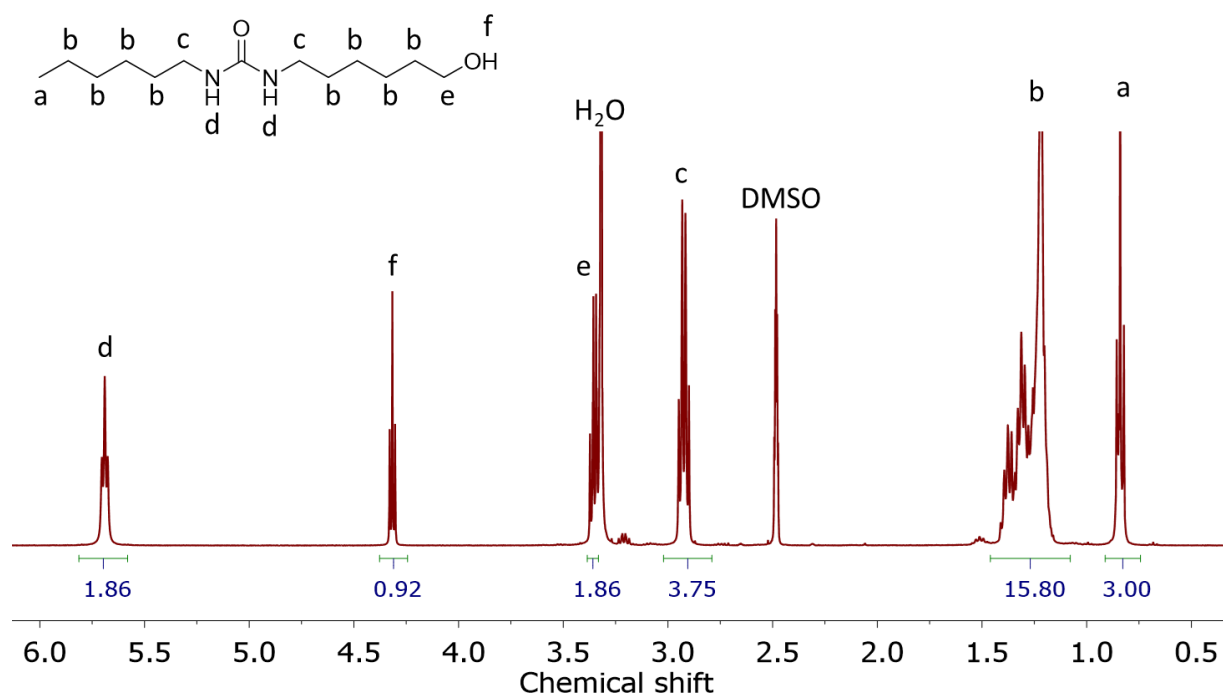


Figure S4.2. ¹H NMR spectroscopy of N-hexyl-N'-(6-hydroxyhexyl)urea.

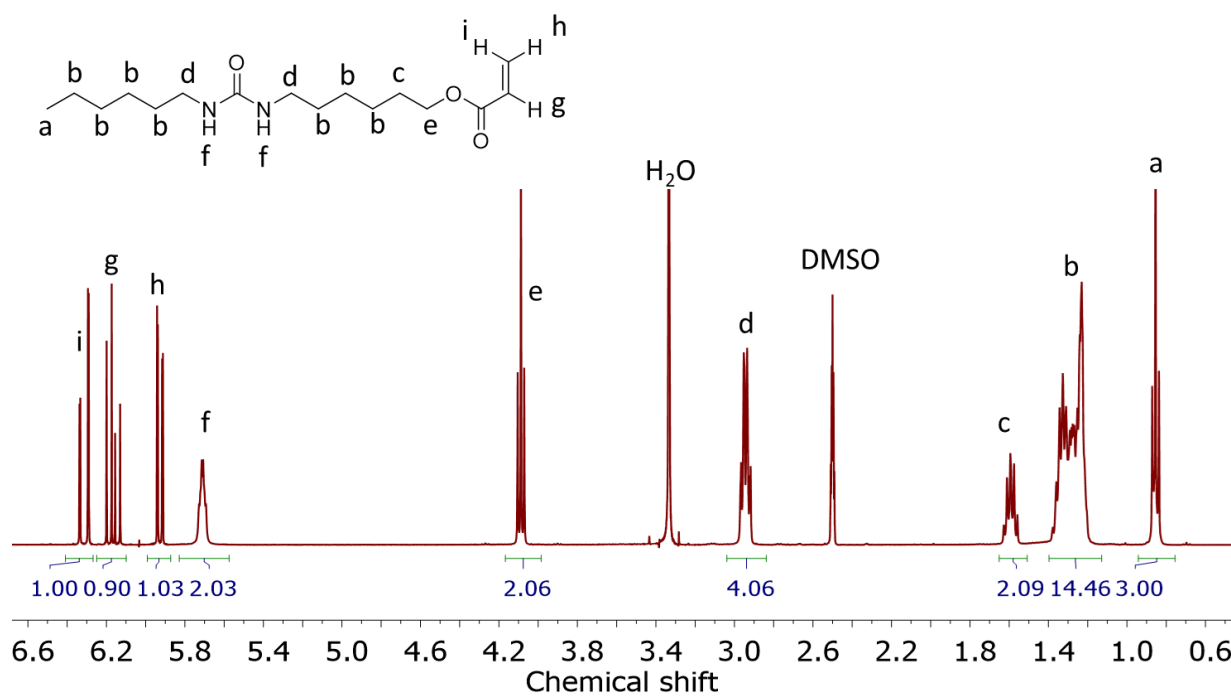


Figure S4.3. ¹H NMR spectroscopy of 6-(3-hexylureido)hexyl acrylate monomer.

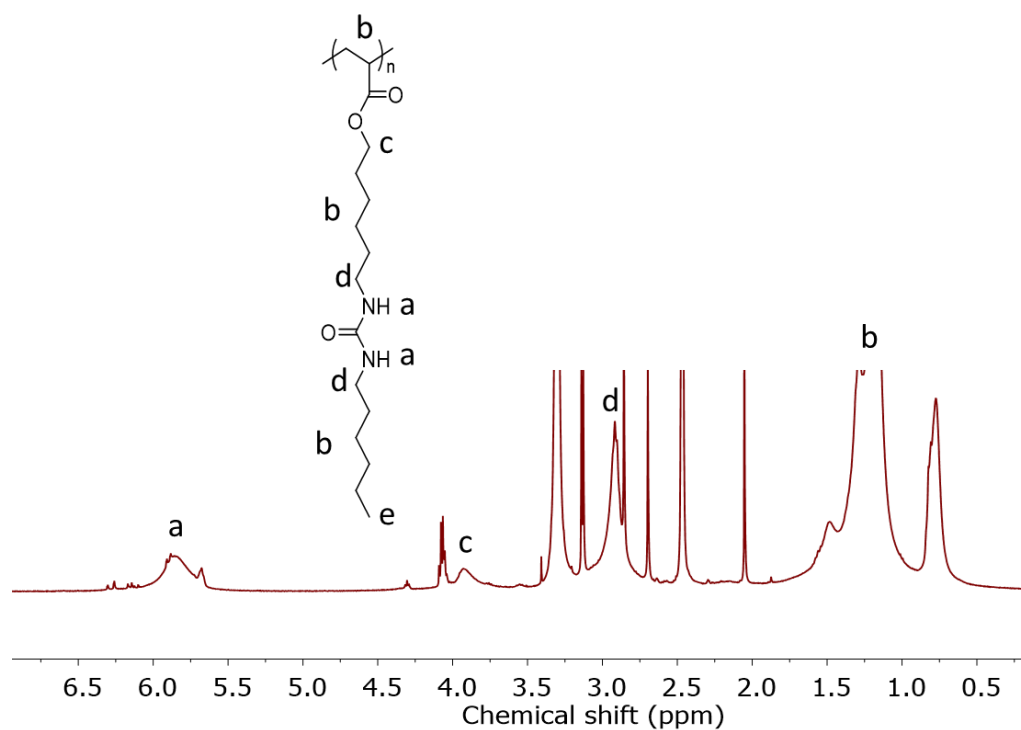


Figure S4.4. ^1H NMR spectroscopy of urea acrylate homopolymer.

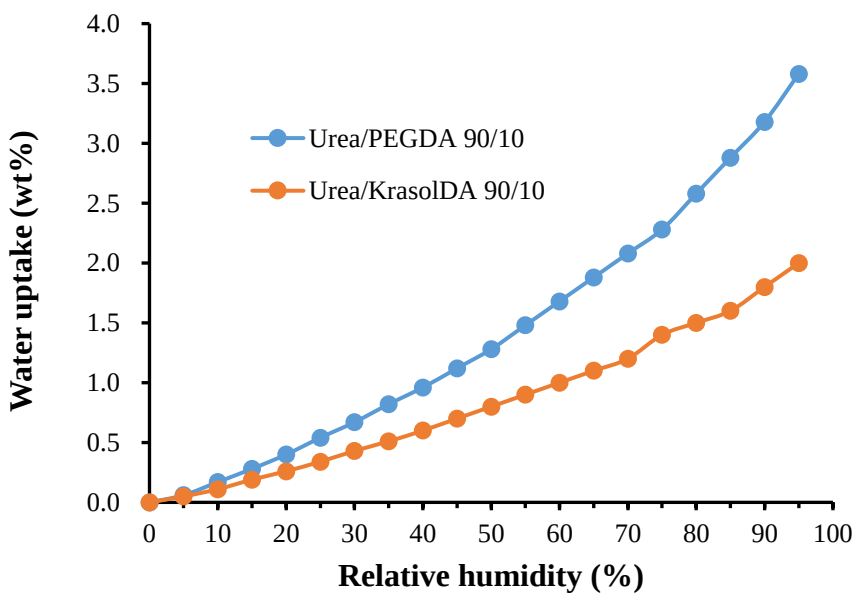


Figure S4.5. Equilibrium water sorption of urea/PEGDA 90/10 and urea/krasolDA 90/10 in a step relative humidity ramp from 0% to 95% at a 5% interval.

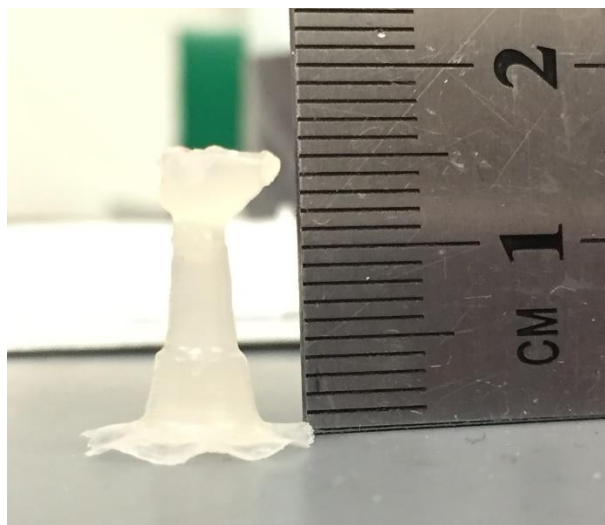
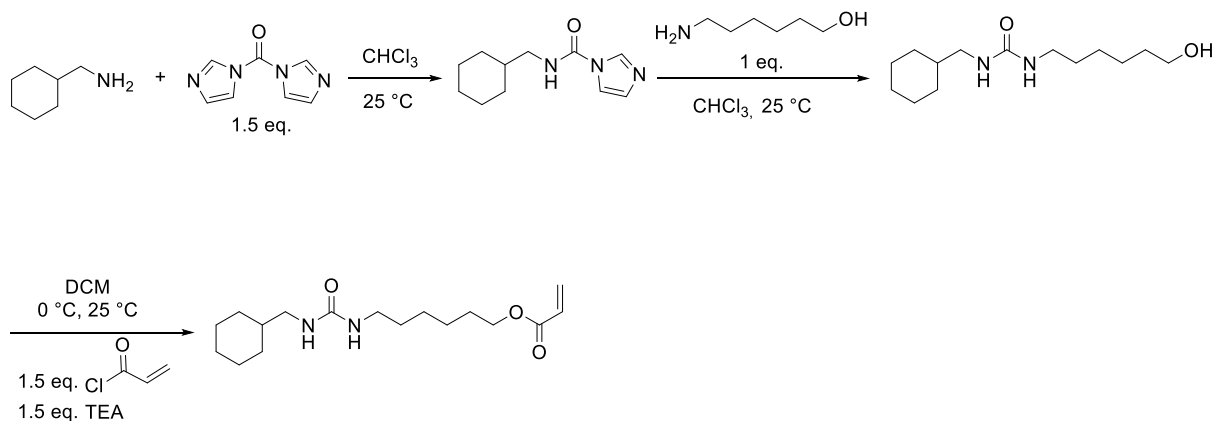


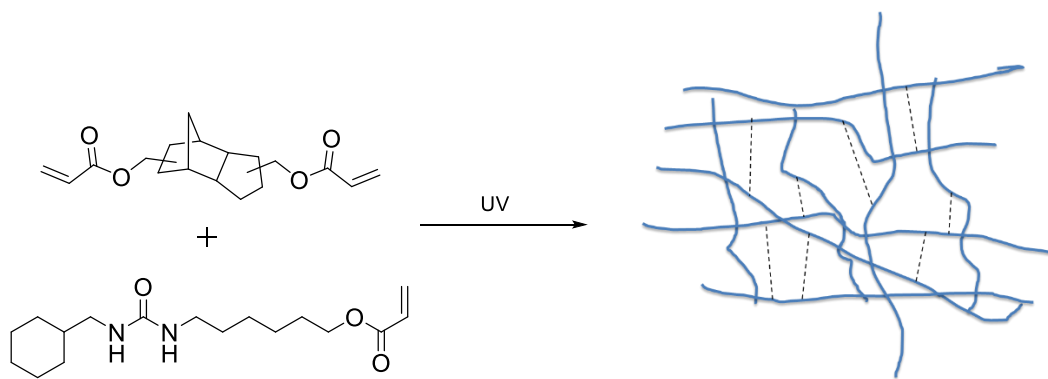
Figure S4.6. A preliminary 3-D printed object using 50/50 urea/PEGDA combination.

Chapter 5. Future work

5.1 3-D Printable Urea-containing Resin with Enhanced Glass Transition Temperature and Mechanical Property for Dental Applications.

Our previous work on urea-containing systems for 3-D printing exhibited relatively low T_g s and moduli for application as retainers. Future work will focus on designing novel urea networks with enhanced mechanical integrity. Incorporation of a cyclic group into the urea structure via reacting CDI with cyclohexylmethylamine will elevate the structural rigidity while maintaining its crystallizability for hot melt printing (Scheme 5.1). Tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate is a colorless and nonvolatile liquid that possesses high structural rigidity. Therefore, 3-D printing the novel urea and tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate blends should yield a network with reinforced mechanical strength and with no stress-relaxation. A systematic thermal, mechanical and printing study will assess the efficacy of the novel urea network for dental applications.

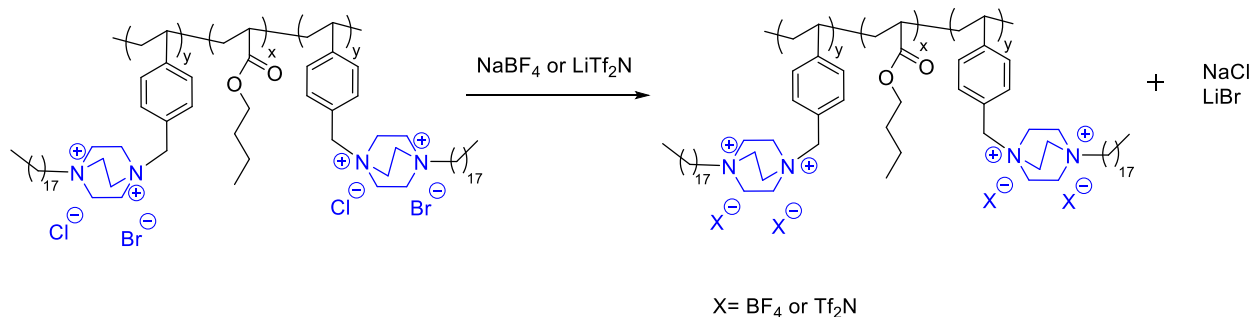




Scheme 5.1. Synthesis of the urea monomer and photopolymerization process.

5.2 Influence of Counter Anions on Self-assembly Behavior of DABCO Block Copolymers

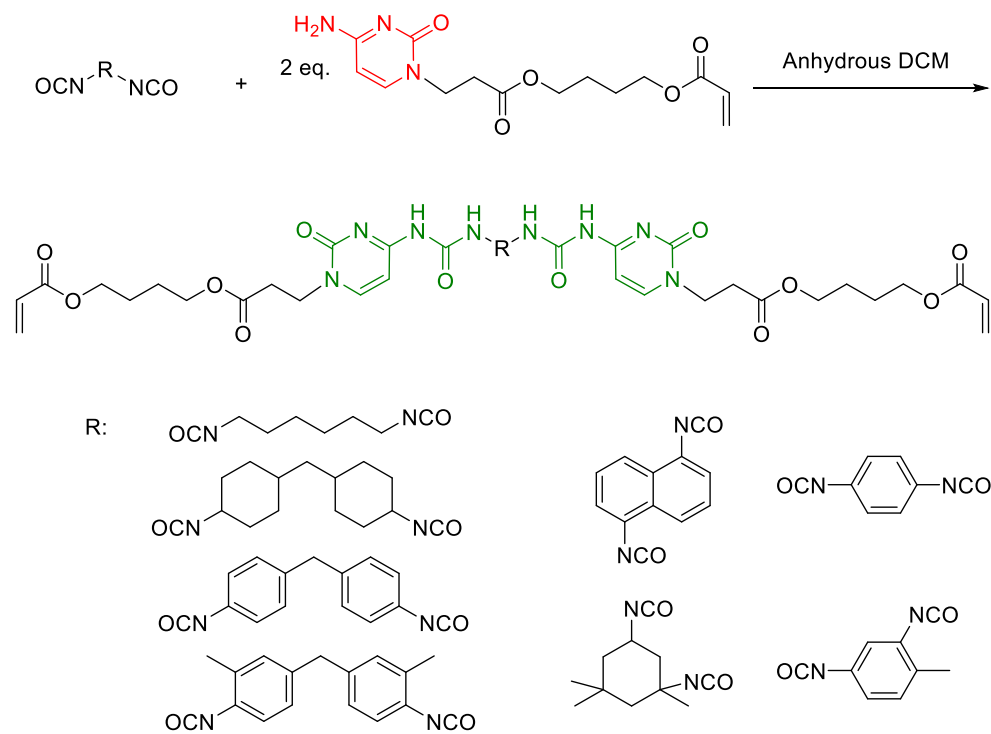
Previous work in Chapter 3 studied the physical property and morphological behavior of DABCO ABA block copolymers containing halogen counter anions. The dipole-dipole interactions between ion pairs induce self-assembly, resulting in complex hierarchical microstructures that correlate closely with the types of the counterions. Systematic comparisons of the mechanical property and morphology of DABCO salt-containing block copolymers with different counter anions (BF_4 , Tf_2N) (Scheme 5.2) would provide an answer to this question. Probing the bulk morphology of the polymers will give information on the size and interparticle distance of the ionic aggregates, as well as how they affect the block copolymer microstructures. DMA analysis will provide insights into the structure-property-morphology relationships for those polymers.



Scheme 5.2. Synthesis of DABCO salt containing block copolymers with different counterions through anion-exchange process.

5.3 Quadruple Hydrogen Bonding-containing Resin for Enhancing Interlayer Adhesion of 3-D Printed Objects

Previous work confirmed the enhanced adhesion property of ureido-cytosine group compared to the cytosine group due to its extremely strong quadruple hydrogen bonding. Future work involves incorporating quadruple hydrogen bonding into photo-crosslinkable resin via synthesizing ureido-cytosine functionalized diacrylates. Reaction of one equivalent of a di-isocyanate with two equivalents of cytosine acrylate should afford a bis(ureido-cytosine) diacrylate (Scheme 5.3), which will generate a chemically-crosslinked network upon exposure to UV light. In addition, the bisureido-cytosine units will dimerize to form enhanced physical crosslinks via DDAA hydrogen bonding arrays, which helps to reinforce the adhesion between different printed layers. Selection of a suitable linker between the isocyanate moieties will not only optimize the bisureido-cytosine adhesion, but will also tailor the mechanical property of the network. Hence, comparison of the tensile and thermomechanical property of bis(ureido-cytosine)s employing different diisocyanates functionalizations will illustrate key characteristics for novel hydrogen bonding containing resins.



Scheme 5.3 Synthesis of bis(ureido-cytosine) diacrylate.