Structure Property Relationships for Polymers Bearing Reversibly Associating Side-groups

by

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Dedication

I dedicate this work to my wife Aimee and our two sons, Noah and Owen. Without your love, patience, and support this work would not be possible.
Biographical Sketch

Christopher Lloyd Lewis was born in Williamsport, PA on August 15, 1974. He attended the Pennsylvania College of Technology in Williamsport, PA from 1993-1997, completing his Bachelor of Science in Plastics and Polymer Engineering Technology in 1997. He began graduate studies at The University of Tennessee-Knoxville in Knoxville, TN in 1999, graduating with a Master of Science degree in Polymer Engineering in 2002. He spent several years in industry working in the areas of polymer processing and materials engineering for Tyco Incorporated, General Motors, and Delphi Corporation. Chris came to the University of Rochester in 2009 to pursue graduate studies in Chemical Engineering. He served as a teaching assistant for the Department of Chemical Engineering for the Spring and Fall 2010 semesters. He pursued the study of self-associating polymers and shape-memory materials under the direction of Professor Mitchell Anthamatten.

The following publications were a result of work conducted during doctoral study:

Publication A:


Publication B:

**Publication C:**


**Publication D:**


**Publication E:**

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And finally I would like to dedicate this work to my Lord and Savior, Jesus Christ, for whom all things are possible.
Abstract

The objective of this research is to establish structure-property relationships for macromolecules bearing reversibly associating side-groups. In previous studies we demonstrated shape-memory behavior for elastomer networks bearing strong ureido-pyrimidinone (UPy) hydrogen-bonding side-groups. However, relationships between the underlying viscoelastic behavior and side-group features such as hydrogen bond strength, structure, the presence of a permanent network and distance of the binding group from the macromolecular chain are not well established. Further, while numerous studies focus on the associative behavior of polymers in solution, few have examined their bulk behavior. To address this need, copolymers bearing weak ($\Delta H \sim 30\text{kJ/mol}$) or strong hydrogen ($\Delta H \sim 70\text{kJ/mol}$) bonding side-groups (HBSGs) were copolymerized with a low glass transition ($T_g$) polymer backbone into linear and network polymers. For polymers bearing weak HBSGs the temperature dependence of viscosity could be attributed to the elevation of $T_g$ alone whereas the rheological behavior of strong HBSG polymers could be attributed to side-group association. To explain our results, a “state-of-ease” model was developed that assumes continuous mechanical equilibrium between applied stress and the stresses arising from a permanent network and a second network that continuously reforms. The model is able to predict various rheological responses for UPy containing polymers such as dynamic mechanical and shape-memory behavior. The influence of micro-environment can also influence viscoelastic behavior. To assess the ability of a strong HBSG to dimerize within water swollen environments the swelling and
dynamic mechanical behavior of a hydrophilic polymer bearing UPy side-groups was studied. The presence of UPy reduced the rate of short-time swelling whereas long-time swelling increased with UPy concentration and was attributed to UPy disrupting the native polymer structure. While the presence of UPy dramatically increased the viscosity, it does not form a percolated network at low UPy concentrations, suggesting that UPy’s efficacy is reduced in the presence of water. In summary, by systematically studying several model polymers, this thesis exposes the degree to which reversibly binding side-groups can affect rheology, solid mechanics, and water sorption. The acquired knowledge can form a basis for materials design of future self-healing and shape-memory polymers, thermoplastic elastomers, and other field-responsive polymers.
Contributors and Funding Sources

This work was supervised by a dissertation committee consisting of Mitchell Anthamatten (advisor) and David Harding of the Department of Chemical Engineering and Professor Danielle Benoit of the Biomedical Engineering department.

Chapter 3 pertains to a study of the influence of reversible side chain bond strength on the viscoelastic behavior of polymer melts and crosslinked networks. I synthesized, characterized, and prepared all the sample materials. I performed all melt rheological characterizations, dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA). MacKenzie Hall and Ken Marshall, University of Rochester Laser Lab for Energetics (LLE), assisted with DMA measurements and Professor Harding and his research group at LLE assisted me with TMA measurements. Harry Stern, University of Rochester Center for Integrated Research Computing, provided Quantum Mechanical (QM) calculations to estimate hydrogen bond strengths for this study. Kathleen Stewart, UR undergraduate student, assisted in the synthesis and chemical characterization of samples produced in this study and the discussion of my results. Chapter 3 was adapted with permission from Macromolecules, 2014, 47 (2), 729–740. Copyright (2014) American Chemical Society. Link: The Influence of Hydrogen Bonding Side-Groups on Viscoelastic Behavior of Linear and Network Polymers

Chapter 4 is a study of the synthesis, swelling behavior, and viscoelastic properties of functional poly(hydroxyethyl methacrylate) with ureidopyrimidinone side-groups. I synthesized and prepared all of the sample materials, performed the thermal
analysis and rheology tests, and analyzed all data. Bausch and Lomb kindly provided the RAFT initiator investigated in this study. Kathleen Stewart provided assistance in making swelling measurements and for useful discussions concerning this work. Chapter 4 is reproduced from Soft Matter, 2013, 9, 4058-4066 by permission of the Royal Society of Chemistry. Link: Synthesis, swelling behavior, and viscoelastic properties of functional poly(hydroxyethyl methacrylate) with ureidopyrimidinone side-groups.

Chapter 5 describes a mathematical model and computer program developed to describe the rheological behavior of linear and crosslinked polymers bearing reversibly associating groups. Professor Anthamatten and I worked on this project with no additional assistance.

Two areas of future work are discussed in Chapter 6. This includes the presentation of preliminary results concerning the behavior of polymer networks bearing the Diels Alder Furan-Maleic cycloadduct side-groups. Secondly, a proposal for an investigation into the influence of hydrogen bonding group structure and binding strength on the glass transition is presented. Professor Anthamatten and I worked on this project with no additional assistance.

Finally, in Chapter 7 my PhD research work is summarized and some concluding remarks are presented.

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Chapter 1: Introduction and Background

1.1 Reversibly Associating Polymers.

Directed self-assembly of materials into hierarchical and functional structures is a major theme in polymer science. Self-assembly is most frequently driven by relatively weak, reversible interactions and has been perfected in the biological realm. For example, protein self-assembly into secondary structures, such as alpha helixes and beta sheets, results from hydrogen-bonding between carbonyls and amide protons.\(^1\) Nature’s remarkable ability to produce highly structured and functional materials has prompted researchers to consider hydrogen bonding and other reversible interactions for development of synthetic materials. Examples of self-assembly within soft materials include block copolymer microphase segregation, micelle formation from surfactants, formation of liquid crystalline mesophases, gelation of organogelators, among many others.\(^1\)\(^-\)\(^3\)

Reversibly associating polymers comprise of macromolecules containing site-specific, reversible binding functionalities. These moieties allow for polymer chains to associate under certain conditions but allow for their release under other conditions. Common stimuli that promote reversibility of these groups include heat, light, or changes in pH. These associating groups are sometimes referred to as “sticky” groups\(^4\)\(^-\)\(^5\) and can
be physical or chemical in nature. Physical interactions include hydrophobic interactions, hydrogen bonding, π-π stacking, and ionic interactions. These interactions are generally weak to moderate in strength (<100 kJ/mol) and often exhibit time-dependent material behavior. Reversible chemical bonds may also form between macromolecules and include, for example, the well-studied Diels-Alder (DA) covalent bond. The reversible nature of these bonds allows for added material functionality when incorporated into polymers. For example, the presence of DA bonds in a self-healing material allows for preferential breakage of the DA bond over the covalent bonds, thereby allowing for a more complete recovery of material properties.

The manner with which reversibly associating groups are incorporated into a polymer can also dramatically influence the observed behavior of these materials. For example, functional groups can be placed at the end or along the length of the chain. The former approach allows for the preservation of characteristics associated with the parent polymer. On the other hand, their presence as constituents along the polymer backbone allows for control of the associating group concentration independent of the polymer molecular weight. Further control can be gained by controlling their placement along the chain—whether they are purposefully placed in certain regions of the chain (e.g. contained within only one segment of a block copolymer) or are randomly distributed.

The inclusion of reversibly associating groups can promote the formation of a transient network assembly and/or the organization into hierarchical structures. For example, the inclusion of reversibly associating side-groups along a polymer chain can result in the formation of temporary networks useful as thermoplastic elastomers and self-
healing materials. For example, low molecular weight monomers and polymers bearing the strong ureidopyrimidinone (UPy) group exhibit rubber-like characteristics at low temperature, but behave as viscous liquids at high temperatures thereby allowing for simplified melt processing. This behavior is not limited to the use of noncovalent interactions. The presence of photo-reversible covalent interactions, such as the cinnamate group, allow for the formation of temporary networks that can be reverted back to a liquid by irradiation with UV.

Reversibly associating functional groups can encourage self-assembly forming supramolecular structures. As is discussed by Ikkala and ten Brinke, hierarchical structures that exhibit organization at several different length scales can be achieved by applying a combination of different self-assembly and self-recognition techniques. For example, hydrogen bonding associations can be used to form a supramolecular structure that subsequently organizes to form a hierarchical structure. This was demonstrated by Frechet and coworkers where hydrogen bonding between polyacrylates bearing carboxylic acid side-groups and hydrogen bonding acceptors such as difunctional pyridines and/or monofunctional stilbazoles promotes the formation of mesogenic three dimensional networks.

The influence of reversibly associating groups on material properties is often investigated in solution, but far fewer studies have investigated the influence of these interactions in the bulk. Differences between condensed and solution phase behavior are expected, a fact highlighted in a recent report comparing the bulk and solution viscoelastic behavior of a polymer containing hydrogen bonding associating groups.
Considering how many of the envisioned end-use applications rely on bulk properties, the study of materials in the condensed phase represents an area of tremendous scientific and commercial importance.

This chapter will begin with a motivation for this work, review some major challenges in the area of polymers bearing reversible associating groups and briefly outline how this work addresses those needs. Next, a tutorial is provided to review relevant reversible interactions with an emphasis on hydrogen bonding. Finally, a review of important topics in the area of polymer rheology will also be provided including a review of several theories concerning the rheology of associating polymers.

1.2 Motivation: Applications of Reversibly Associating Polymers.

The goal of this research is to contribute to our understanding of the structure-property relationships for polymers bearing reversibly associating side-groups. Reversibly binding groups can impart polymeric systems with thermo-responsive behavior, leading to self-healing materials, thermoplastic elastomers and shape-memory polymers (Figure 1.1).

Self-healable materials are able to regain mechanical properties after incurring damage. The conventional approach to self-healing involves “autonomous” crack healing where microcapsules containing a healing agent and catalyst are embedded into a polymer. An advancing crack provides volume for microcapsules to empty healing agents that subsequently polymerize in the presence of a catalyst dispersed in the matrix polymer. As is shown in Figure 1.1, self-healing characteristics can also be imparted
through the use of reversibly associating groups. The advantage of this approach is that self-healing can occur continuously and therefore may prevent the formation of a macroscopic crack.

Self-healing, arising from reversible association of chemical groups has been reported for both small molecular and macromolecular systems. Cordier et al. developed self-healing elastomers derived from low molecular weight di- and tri-functional fatty acids. Reaction of the fatty acids with diethylene triamine followed by urea results in functional oligomers. This study demonstrated that small molecules possessing a high concentration of weak hydrogen bonding groups can give rise to network-like properties and self-healing characteristics. For these supramolecular systems, self-healing is a consequence of noncovalent bond “failure”, and a high concentration of non-associated groups at the fracture surface is critical to the self-repair mechanism.

The ability to self-repair has also been demonstrated for small molecules bearing much stronger reversibly associating groups. For example, a reversible network composed of a Diels-Alder (DA) adduct readily forms upon reaction between a tetrafunctional furan and a trifunctional maleimide. The resulting material is physically hard with mechanical properties resembling that of a conventional thermoset polymer. As in the hydrogen-bonded elastomer example, the reduced strength of the DA bond promotes failure at that site. Experiments showed that only about 57% of the mechanical properties were recovered after mending at 150 °C. However, the authors attributed this inefficiency to misalignment of the two mating surfaces during mending and not to inefficiencies of the DA bond.
The ability to self-repair is apparently not limited to small molecules. Recently it was reported that macromolecules bearing relatively weak hydrogen bonding groups can display self-healing characteristics as well. Here, a phase-separating brush polymer bearing weak hydrogen bonding groups was found to spontaneously self-heal without the need for an external stimulus, healing agent, or solvent.

Figure 1.1. Examples of materials utilizing reversible interactions to achieve improved functionality.

Thermoplastic elastomers (TPEs) display rubber-like elastic properties at room temperature but can be melted and processed at elevated temperatures (Figure 1.1). TPEs by their very nature must be created using reversible associations, and a number of strategies have been investigated. For example, the previously described self-healing materials based on hydrogen bonding dimerization of small molecules and macromolecules exhibit low temperature elastic behavior but flow at sufficiently high temperatures. Likewise, Müller and coworkers demonstrated that the incorporation of phenylurazole or 4-urazoylbenzoic acid hydrogen bonding groups into low T₉ polymers exhibited TPE behavior. Kautz and coworkers showed that supramolecular
thermoplastic elastomers could be prepared by incorporating strongly associating UPy end-groups on a low $T_g$ polymer chain. Long and coworkers demonstrated that the incorporation of UPy side-groups can likewise impart network-like properties at room temperature when incorporated into poly(butyl acrylate) (PBA).

Other reversible associations such as those based on ionic groups and phase separation of block copolymer segments are effective in producing thermoplastic elastomers. For example, ionic groups form strongly associating clusters when incorporated into polymers. Upon heating, these associations weaken sufficiently to allow for melt processing. Ionomers based on ethylene-methacrylic acid and ethylene-acrylic acid have been commercialized by DuPont (Surlyn®) and Exxon-Mobil (Iotek®) respectively. Thermoplastic elastomer behavior is also observed for segmented block copolymers. This results from the phase separation of a high $T_g$ (hard) chain segment from a low $T_g$ (soft) segment. The hard segment represents the minor phase and thereby acts as a physical crosslink at temperatures below its glass transition. Heating to above the $T_g$ of the hard segment allows for conventional melt processing. Kraton® thermoplastic elastomers are based on block copolymers of polybutadiene and polystyrene and have enjoyed commercial success in a number of applications including packaging, footwear, adhesives and sealants, and as polymer modifiers.

Shape-memory polymers (SMPs) are a third example of functional materials that can be formed through the use of reversibly associating polymers. SMPs are able to be deformed and fixed into a stable temporary shape and, upon the application of a stimulus (e.g. heat, light, electrical), are able to recover to their original shape (see Figure 1.1).
Conventionally, shape-fixing is accomplished by cooling beneath a semi-crystalline polymer melting temperature (crystallization) or by cooling beneath a polymer’s glass transition temperature (vitrification). SMPs are capable of memorizing one or two temporary shapes, corresponding to two-way and three-way shape-memory effects, respectively. While two-way shape-memory effects are the most common, three-way shape-memory effects and beyond have been reported in the literature.\textsuperscript{25-27} For example, Luo and Mather recently designed a shape-memory composite material that displayed triple shape-memory effects.\textsuperscript{25} This composite, fabricated by infiltrating an electrospun nonwoven poly(caprolactone) (PCL) network with an epoxy, displayed two transitions, one corresponding to the glass transition of the epoxy matrix and the other corresponding to the melting temperature of the semi-crystalline poly(caprolactone).

Nafion, a well-studied ionomer, has recently been shown to exhibit multi-staged shape-memory.\textsuperscript{28} The capability to stabilize multiple non-equilibrium mechanical states is related to Nafion’s broad transition temperature, which can be viewed as an infinite number of shape-memory element transitions resulting from a distribution of ionomer cluster sizes. Other ionomers may display similar shape-memory behavior, and four or more temporary shapes should be achievable.

Shape-fixing can also be accomplished by reversible bond association. For example, memory effects can result from the presence of strong hydrogen bonding groups acting as the triggering functionality. Extending the work of Long and coworkers\textsuperscript{22}, our group showed that shape-memory elastomers can be created where covalent crosslinks define the permanent shape and the strong hydrogen bonding UPy
groups acts as the temporary net points. More recently, synthesis of UPy-containing shape-memory elastomers was accomplished from photo-crosslinkable polymer precursors. Dynamic mechanical analysis of the materials showed two plateaus in storage modulus: a high-temperature plateau attributed to covalent cross-links, and a lower temperature plateau attributed to both reversible and covalent cross-links. We showed that cooperative H-bonding dynamics are intensified because of the presence of the covalent network.

1.3 Intellectual Challenges.

For polymers bearing reversibly associating side-groups it is desirable to understand how architectural, structural, and environmental variables influence material properties such as mechanical behavior, thermal stability, and degree of reversibility. These properties in turn determine how well the materials will perform in their intended applications. These interdependences are depicted graphically in Figure 1.2. Structural variables are of molecular origin and include polymer backbone type, side-group bond strength, presence of a covalent network, side chain architecture, distance of the group from the polymer backbone, bond density, and positioning of the side-group along the chain, to name a few. Additionally, environmental variables such as operating temperature or the presence and type of solvent are anticipated to influence behavior. The purpose of this thesis is to explore how these variables influence the mechanical and rheological behavior of polymer melts and networks.
Figure 1.2. Demonstrating relationship between molecular and environmental characteristics and material behavior.

Influence of Bond Strength and Side-group Structure. Figure 1.3 depicts the strength of several different covalent and noncovalent interactions relative to thermal energy at room temperature (i.e. $k_B T \approx 2.5 \text{ kJ/mol}$). In order for these interactions to be relevant they must be significantly greater than $k_B T$. For example, the strong UPy group
has a self-complementary bond strength estimated to be $\sim 25\times$ that of $k_B T$ and therefore is anticipated to remain dimerized at room temperature. Indeed, this has been observed for many polymers bearing the UPy group. For example the inclusion of UPy-functionalized end-groups to low molecular weight (ca. 2-3.5 kg/mol) telechelic polymers of poly (ethylene/butenes) resulted in a solid rubbery polymer with a modulus of $\sim 3$ MPa at room temperature and $\sim 1$ GPa in the glassy state. This highlights the strong temperature dependence associated with hydrogen bonding dynamics, where a significant reduction in the melt viscosity is anticipated when the noncovalent transition temperature is exceeded. The zero-shear-rate melt viscosity of end-functionalized polymers was reduced by a factor of four upon a 10 °C increase in temperature—a much greater reduction than expected for analogous high molecular weight polymers. The interaction strength of the Diels-Alder furan maleic anhydride cycloadduct is even greater than the UPy dimer and therefore it is anticipated that properties such as the viscoelastic behavior will be even more influenced by its presence.

**Figure 1.3.** Bond strength relative to thermal energy at room temperature ($k_B T$) for select interactions examined in this study.
The purposeful addition of weak hydrogen bonding groups, such as those based on hydrogen bonding dimers of acrylic acid, with interaction energies several times that of $k_BT$ should be relevant at room temperature as well. The use of these groups is attractive since they are inexpensive and commercially available. While the influence of weak hydrogen bonds on the melt behavior of random copolymers has been discussed for decades, the nature of their influence on polymer properties near room temperature remains unclear. Several investigators have attributed the increase in viscosity resulting from the addition of weak hydrogen bonding groups to the formation of a temporary network.\textsuperscript{32-34} As early as 1958, Longworth observed that the melt viscosity and apparent activation energy for viscous flow increased with increasing methacrylic acid content (varied from 1.5 – 23 mol%). Infrared spectroscopy (IR) was used to show that dimerization equilibrium was quickly established above 100°C but was effectively frozen below 100°C due to the formation of a glass.\textsuperscript{35} The unassociated content of carboxyl groups was measured as a function of temperature and a heat of dimer dissociation of 33-42 kJ/mol was determined. The heat of dimer dissociation for carboxylic acid dimers has been determined for a number of macromolecular compounds and agrees fairly well with these values. A good review of some of this work can be found in the paper by Ostrowska and Narebska,\textsuperscript{36} but, interestingly, all the cases cited utilize polymer backbones that are either glassy or semicrystalline at room temperature. In fact, these materials must be heated to >100°C in order to evaluate their flow properties. For example, Fitzgerald and Neilsen\textsuperscript{37} observed that the copolymerization of methacrylic
acid with PS resulted in an increase in the glass transition. They argued that $T_g$ effects, and not hydrogen bonding dimerization, was responsible for viscosity differences observed. Likewise, Earnest and MacKnight\textsuperscript{38} observed an increase in viscosity over the temperature range of 120-180°C for an ethylene copolymer containing 3.5 mol% of acrylic acid. Again, the observed difference in rheological properties was attributed to a $T_g$ effect. For their polymers they argue that the concentration of dimers is only 10-40% under their experimental conditions but should be nearly 100% at room temp. They speculate that the higher concentration of dimers and the reduced rate of dimer dissociation at room temperature should give rise to a crosslinking effect. These ideas are further supported by a more recent study by Ahn and Shull\textsuperscript{39} who noted that carboxylation of high molecular weight poly(butyl acrylate) (PBA), a low $T_g$ polymer, resulted in an increase in viscosity that they attributed to network formation.

Thus one of the important challenges facing the field of hydrogen bonded polymers is to clarify the role that hydrogen bonds, including weak ones, have on the thermal and viscoelastic behavior of polymers at temperatures relevant to the majority of potential engineering applications (i.e. in the proximity of room temperature). This can only be accomplished through the systematic study of hydrogen bonding groups on a single polymer backbone.

The systematic study of the influence of key hydrogen bonding side-group characteristics on the viscoelastic behavior of low $T_g$ linear polymers and polymer networks will be conducted at temperatures both above and below room temperature (Chapter 3). One major goal of this effort is to determine how the strength of reversible
binding influences the thermal and viscoelastic behavior of polymer melts and network polymers. Additionally, side-group architectural features such as type of H-bond (e.g. OH---H vs. NH---N), side-group length, and/or side-chain rigidity will be related to differences in the thermal and viscoelastic behavior of polymer melts and network polymers.

In a second related effort, experimental data will be compared to a theoretical model to help to explain the viscoelastic and shape-memory behavior of polymers bearing strong hydrogen bonding side-groups (Chapter 5). Finally, rheological data for a polymer bearing even stronger thermoreversible side-groups will be presented. In Chapter 6 preliminary rheological data for polymers bearing side-groups based on the furan-maleic anhydride Diels-Alder cycloadduct will be presented and their thermoreversibility discussed.

**Role of Microenvironment.**

As depicted in Figure 1.2, environment can also play an important role in determining the mechanical behavior of polymers bearing reversibly associating side-groups. Molecular organization within a material can establish micro-environments that strongly influence properties. For example, the formation of ion-pair clusters in ion-containing polymers has a large effect on chain mobility near the ion clusters.\(^{40,41}\) At high concentrations, regions of reduced mobility are sufficiently close to result in an independent glass transition temperature and it is at this concentration that ionomers are said to form clusters.\(^{40,41}\) The efficacy of hydrogen-bonding also depends on the local chemical environment. Despite the presence of water, hydrogen bonding has been
observed in water-swollen systems involving heterogeneous micro-environments. The formation of a hydrophobic micro-environment promotes hydrogen bonding of poly(vinylidiaminotriazine) PVDAT with pyrimidine and purine derivatives in an aqueous environment. Likewise, while UPy dimerization is predicted to be inhibited by water, there is evidence, that under the right circumstances, UPy dimerization is possible. For example, block copolymer pluronics containing hydrophobic domains rich in poly(propylene glycol) were found to offer micro-environments that promote UPy dimerization. In a related study, oligo(ethylene oxide) (oligoEO) chains with UPy end-groups were shown to undergo back-folding to hydrogen bond with UPy, interfering with dimerization. Clearly, dimerization of H-bonding motifs within water-swollen environments, such as in a hydrogel, depends on subtle architectural and structural details, which are poorly understood. This will be examined in Chapter 4, where the swelling and rheological behavior of poly(hydroxyl ethyl methacrylate) (polyHEMA) bearing UPy side-groups will be examined.

1.4 Background.

The following section is intended to provide the unfamiliar reader with the necessary background information. It is organized into the following sections: 1) Reversible interactions commonly used in macromolecular systems; 2) Polymer rheology fundamentals and rheology of associating polymers; and 3) Shape-memory polymers.
1.4.1. Reversible Interactions Utilized in Macromolecular Systems.

**Hydrophobic Interactions.** When water is exposed to a non-polar molecule, its three dimensional, hydrogen bonded dynamic structure is disrupted. This leads to an enhancement in ordering around the non-polar molecule, thereby decreasing entropy and increasing the free energy of the system. A system’s entropy can be maximized by the joining of hydrophobic molecules together to form a hydrophobic cluster. The magnitude of this interaction is ~10-20 J/bond (~6 kJ/mol) and is similar to that of a typical hydrogen bond.\(^1,3\)

Hydrophobic interactions can be used to modify the properties of hydrogels. For example Hao and Weiss recently showed that the properties of N,N-dimethylacrylamide (DMA) hydrogels could be modified through the incorporation of a fluorinated hydrophobic monomer, 2-(N-ethylperfluorooctane sulfonamido) ethyl acrylate (FOSA).\(^4,6\)

The formation of physical crosslinks derived from aggregation of hydrophobic FOSA units resulted in greater modulus, tensile strength, and toughness. Additionally, they found these properties to be strongly dependent on temperature.

Hydrophobic interactions are generally non-directional, and it is difficult to use hydrophobic interactions to design supramolecular polymers in aqueous environments. Recently researchers have circumvented this shortcoming by combining \(\pi-\pi\) stacking with hydrophobic interactions. Directional hydrophobic interactions are afforded through novel molecular design where aromatic amphiphilic perylene diimide units (PDIs)
bearing polyethylene glycol (PEG) substituents are attached to a hexa-substituted benzene (HSB) scaffold through rigid linkers.\textsuperscript{47}

\textbf{Hydrogen Bonding.} A hydrogen bond is the electrostatic attraction between a proton, made partially positive due to its covalent binding to an electronegative atom (i.e. H-bond donor), and an electronegative atom, bearing a partially negative charge (i.e. H-bond acceptor).\textsuperscript{3} The hydrogen bond strength is on the order of \(2-6\times10^{20}\) J/bond or about 8-40 kJ/mol. This corresponds to approximately 3-16 times thermal energy (i.e. \(k_B T\)) at room temperature, and, therefore hydrogen bonds are expected to influence physical properties at room temperature.\textsuperscript{1} Hydrogen bonding derives its strength primarily from the number of bonds involved, although solvent effects, secondary interactions, and preorganizational and tautomeric effects can also play a role in tuning the strength of a given bond.\textsuperscript{48} Hydrogen bonds are generally considered to be short-ranged and directional which is captured in conventional mathematical models of the hydrogen bond. To account for the short range nature of the hydrogen bond, the energy of a hydrogen bond (\(U\)) as a function of atomic distance (\(r\)) can be expressed using a Leonard Jones model such as the following 12-10 model\textsuperscript{49} of the form:

\[
U(r) = \frac{A}{r^{12}} - \frac{B}{r^{10}}
\]

(1.1)

where \(A\) and \(B\) are constants.

In solution, hydrogen bonds constantly break and reform, leading to an average lifetime.\textsuperscript{50} An increase in temperature can significantly increase the rate of H-bond exchange, thereby decreasing the average lifetime.\textsuperscript{12}
Hydrogen bonds have long been recognized as important interactions that influence the behavior of macromolecular systems. For example, the relatively weak hydrogen bonding between the carbonyl group and the amide proton is responsible for crystallization in the case of the commercially important Nylon 6,6 (see Figure 1.4). In the case of Nylon, the presence of these two groups is a serendipitous consequence of the step-growth polymerization between a diamide and a diacid to form a polyamide.

![Figure 1.4](image)

**Figure 1.4.** Organization of nylon 66 molecular chains occurs as a result of hydrogen bonding interactions between amide groups.

In recent years a more purposeful approach to incorporating strong hydrogen bonding groups into polymeric materials has shown to have profound effects on material behavior and properties. Multiple hydrogen-bonding motifs have been applied to purposefully engineer supramolecular polymers and networks. The 2-acrylamidopyridine motif (Figure 1.5A) has two hydrogen bonds and a self-association constant similar to that of carboxylic acids (13.4 M⁻¹ in CHCl₃) (Figure 1.5B). Motifs displaying three, four, or more hydrogen bonds have been synthesized and examined as well and not surprisingly the number of hydrogen bonds...
influences the degree to which the groups associate. For example, the thymine-2,6-diaminotriazine (THY-DAT) motif (Figure 1.5C) exhibits three H-bonds and is reported as having an association constant of $2.6 \times 10^3 \text{M}^{-1}$.\textsuperscript{15} The quadruple hydrogen bonding ureidopyrimidinone (UPy) synthon (Figure 1.5D), developed by Meijer\textsuperscript{55}, provides directionality and strength through an array of four H-bonding donors and acceptors (DDAA). Part of the high bond strength of the UPy group (~70 kJ/mol - in chloroform)\textsuperscript{50} can be attributed to secondary electrostatic interactions as illustrated. The UPy group is a popular synthon because of its ease of synthesis, its ability to be easily introduced onto polymer chains as end and side-groups, and its self-dimerization with remarkably high association constants in nonpolar media (e.g. ~$10^6 \text{M}^{-1}$ in CHCl$_3$).\textsuperscript{55} Another consideration concerning hydrogen bonded dimers is whether they are homocomplementary (i.e. self-associative) or heterocomplementary (i.e. non self-associative). Example of homo- and heterocomplementary quadruple hydrogen bonding systems is shown for the UPy dimer (Figure 1.5D) and UPy-NAPy motifs (Figure 1.5E) respectively. Even stronger interactions with association constants exceeding $10^9 \text{M}^{-1}$ can be achieved by using hydrogen bonding duplexes, which contains six or more cooperative hydrogen bonds such as shown for the Gong’s duplex in Figure 1.5F. The examples presented have demonstrated that the association constant increases with increasing number of hydrogen bonding groups. However, the relationship is more complicated, depending on several additional factors. For example an AADD quadruple hydrogen bonding array has been recently introduced with an association constant of $10^{12}$
Figure 1.5. Examples of hydrogen bonding groups (shown as dimers). A.) Carboxylic Acid; B.) Aminopyridine; C.) Thymine-2,6-diaminotriazine (THY-DAT); D.) Ureido-pyrimidinone (UPy); E.) UPy-NAPY dimer; and F.) Gong’s Duplex. Note: Hydrogen bonds shown as dashed lines. Secondary electrostatic interactions shown for select motifs as arrows (black-attractive; red-repulsive).

in CH$_2$Cl$_2$. As is shown below, the improved association as compared to the UPy group is owed to the fact that secondary electrostatic interactions are attractive for the heterocomplementary AADD system whereas UPy has a repulsive interactions that serve to weaken the attraction. The reader is referred to section 1.2 where several examples illustrating how hydrogen bonds are used to impart interesting functionality in polymers are discussed.
**Ionic Interactions.** Ionic interactions are non-directional, strong interactions resulting from the Coulombic potential between charges. For point charges \( q_1 \) and \( q_2 \) separated by a distance \( r \) the potential can be modeled according to the following expression:

\[
U(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}
\]  

(1.2)

Ionic interactions are generally much stronger than the previously mentioned hydrophobic and hydrogen bond interactions. As a point of reference the magnitude of the interaction between adjacent ions on a crystal lattice are about \( 100 \times 10^{-20} \text{J} \) (approximately 600kJ/mol) and therefore can be as much as two orders of magnitude stronger than a typical hydrogen bond.\(^1\)

Ion containing polymers, or ionomers, are a class of polymers bearing groups that associate through ionic interactions.\(^40,58\) While a number of theories have been proposed concerning their morphology\(^59\) the Eisenberg model\(^41\) appears to have gained acceptance in the field. In this model ionic association has been described as consisting of ion pairs formed together into aggregates called multiplets with polymer chains of reduced mobility immediately surrounding these regions.\(^40,41\) At high concentrations the regions of reduced mobility are sufficiently close to result in an independent glass transition temperature and it is at this concentration that ionomers are said to form clusters.\(^40,41\)

The presence of the ionic group has a profound influence on the observed physical properties of ionomers. This was demonstrated by Fetters *et al* who showed that the zero shear rate viscosity of polyisoprene sodium carboxylates was 14-55X greater that
of the un-functionalized polymers at 25°C for a given molecular weight. Likewise, altering the ionic group has been shown to have a profound influence on the mechanical behavior of the resulting material. For example, an increase in the cluster glass transition temperature of greater than 50°C was observed when comparing carboxylated and sulfonated polystyrene. The mechanical properties of ionomers can also be altered by exchanging with various counterions. For example, Ro et al produced telechelic poly(lactic acid) ionomers where various salts were incorporated into the polymer to promote ion-dipole interactions between metal-carboxylates, which served to increase the glass transition temperature. Additionally it was shown that the glass transition temperature increases as a function of cation valency and concentration thus providing an additional factor for tailoring the viscosity.

Ionomers have enjoyed commercial success since the 1960s where neutralized copolymers of ethylene and acrylic are used in the production of cut-resistant golf balls, membranes, and packaging materials. Another example includes the perfluorosulfonated polymer Nafion® (DuPont™), probably best known for its use in fuel cell applications. The unique charge transport properties of Nafion result from the formation of a network of water swollen clusters.

Their ion transport properties also afford ionomers with the ability to be used as ionic polymer transducers (IPT). IPT’s are composite devices where a swollen ion conducting material is sandwiched between an anode and cathode. The application of a voltage results in the simultaneous migration of cationic counterions toward the cathode and depletion of counterions on the anode. Counterion accumulation at the cathode
boundary layer results in enhanced swelling and deswelling at the anode. Thus when supported at one end this results in the IPT bending toward the anode in a cantilever type motion.\textsuperscript{69}

\textbf{Diels-Alder Adducts: Reversible Covalent Bonds.} Reversible covalent bonds are an additional type of thermoreversible interaction that can be leveraged to create functional materials.\textsuperscript{70-73} The Diels-Alder (DA) bond is one of the most highly studied reversible covalent bond types and has proven useful in synthetic and protein chemistry\textsuperscript{74-76} and as a building block in macromolecular synthesis.\textsuperscript{71,73,77} DA reactions are often characterized as click or click-like type reactions to reflect their efficiency, versatility, and selectively.\textsuperscript{71} DA cycloaddition reactions occur as a result of the reaction of a nucleophilic diene and an electrophilic dienophile where the thermodynamic driving force is the formation of two new sigma bonds at the expense of two less stable pi bonds.\textsuperscript{78} Typical DA reactants include the furan-maleimide, anthracene maleimide, dithioester diene, and tetrazine cyclooctene\textsuperscript{71} (Figure 1.6).

As is shown in Figure 1.7 two isomers are predicted for the cycloaddition of maleic anhydride and furan, where the endo product is the kinetically favored product and the exo product is the thermodynamically favored product. While the exo product exhibits higher stability the kinetically favored endo product is usually observed. DA reactions are highly exothermic with bond formation energies on the order of 125-170 kJ/mol.
Figure 1.6. Several important DA adducts. A. furan-maleimide, B. anthracene maleimide, C. dithioester diene, and D. tetrazine cyclooctene.

Figure 1.7. Diels Alder cycloaddition of maleic anhydride and furan (see Figure 1.6A) to produce endo and exo products.
The DA reaction has been used to produce linear polymer structures in a step-growth manner using homobifunctional monomer units (A-A/B-B type)\textsuperscript{79} or heterobifunctional monomer units (A-B type) as building blocks.\textsuperscript{77, 80} Block copolymers have also been produced using DA chemistry. For example, Durmaz et al showed that polymers end-functionalized with anthracene and maleimide could be used to produce PMMA-\textit{b}-PS, PEG-\textit{b}-PS, PtBA-\textit{b}-PS, and PMMA-\textit{b}-PEG block copolymers.\textsuperscript{81} Researchers have also used DA chemistry to prepare reversible networks; although the strategies for imparting crosslinks vary. One strategy relies on the use of polymers containing a single DA reactant and a multifunctional cross linker containing the second DA reactant such as that described by Jones et al for PET copolymers bearing 2-6-anthracenedicarboxylate crosslinked via a DA cycloaddition with a low molecular weight bismaleimide.\textsuperscript{82} An alternative approach involves synthesizing a difunctional crosslinker that contains a DA adduct. For example, diacrylate crosslinkers containing furan-maleimide DA adducts can be reacted with the end groups of a prepolymer prepared by living polymerization to produce star polymers consisting of a reversibly crosslinked DA core.\textsuperscript{83} Researchers have also investigated the use of DA chemistry to improve the binding of organic to inorganic materials. For example, recognizing that composite mechanical properties are derived through load transfer from high strength fibers to the composite matrix led researchers to apply DA chemistry to improve the matrix-reinforcement interface.\textsuperscript{84} In this study, maleimide functionalized glass fibers were embedded into a furan functionalized epoxy amine matrix. Single fiber microdroplet
pull-out tests showed that the integrity of the polymer fiber interface could be partially restored.

1.4.2. Polymer Rheology Fundamentals.

Dynamic Mechanical Behavior and Time Temperature Equivalence. The temperature dependence for a high molecular weight linear amorphous polymer, a semicrystalline polymer, and a covalently crosslinked rubber is shown in Figure 1.8. At low temperature the materials are stiff and glassy. As the temperature is raised the amorphous fraction begins to soften as it passes through $T_g$. In this region amorphous materials can be generally characterized as tough and leathery. An emergence of the rubbery plateau region follows, named for the mechanical behavior exhibited by amorphous materials in this region. At even higher temperatures the material further softens and begins to flow. As is shown, a covalently crosslinked rubber would be expected to show qualitatively similar rheological behavior except that no flow is observed. Also, the presence of crystals serves to create a stiffer material above $T_g$ and it is not until these crystals melt that the material becomes soft and able to flow.

Polymers are viscoelastic materials meaning that their mechanical behavior is intermediate to that of a solid and a liquid. The degree to which the material behaves as a solid is dependent on temperature as well as the rate at which it is deformed. The child’s toy Silly Putty® is a good example of a material that exhibits this type of behavior. If this material is thrown against a wall it will bounce back as though it was made of rubber.
However, if the ball is allowed to sit on a table for a length of time it will flow like a liquid forming a puddle.

**Figure 1.8.** Idealized temperature dependence of polymer mechanical behavior. Linear amorphous polymer (solid), semicrystalline polymer (dashed) and crosslinked rubber (dotted).

Dynamic mechanical analysis (DMA) can be employed to characterize polymer mechanical behavior. For a strain controlled rheometer, this is accomplished by employing a small, sinusoidal strain on the material and measuring the stress response. For a material subjected to a shearing stress ($\tau$), the degree to which the stress response is out of phase with the strain, $\varepsilon$ can be used to define the storage modulus, $G'$ and the loss modulus $G''$.$^{85,86}$
\[
G' = \frac{\tau}{\varepsilon} \cos \delta \\
G'' = \frac{\tau}{\varepsilon} \sin \delta
\]

where \(\delta\) is the phase lag. The ratio of \(G''/G'\) is equal to \(\tan \delta\) and is a relative measure of the degree to which the materials behave as a liquid or solid. Thus if \(\tan \delta < 1\) then the material behaves more solid-like and if \(>1\) is more liquid-like.

The observation that the mechanical behavior of an amorphous polymer is similarly dependent on both time and temperature led to the concept of time temperature superposition (TTS). In practice this allows for viscoelastic behavior observed at one temperature to be related to another temperature by a change in time scale only by shifting the data using a shift factor, \(a_T\). This approach has the advantage that it allows for the construction of a curve over many orders of magnitude of frequency and allows for the determination of the temperature dependence of the shift factor. This is commonly accomplished by fitting the shift factor to an Arrhenius or Vogel-Fulcher-Tammann (VFT) type relationship to arrive at an apparent flow activation energy.

Oscillatory rheology can also be used to determine the complex viscosity, \(\eta^*\), by relating \(G'\) and \(G''\) with the angular frequency \((\omega)\), according to the relation:

\[
\eta^* = \frac{G''}{\omega} + \frac{G'}{\omega} \cdot i = \eta' + \eta''i
\]

An idealized plot of \(\eta^*\) as a function of \(\omega\) for a typical polymer is shown in Figure 1.9. At low rates of shear the material behaves like a Newtonian fluid, where the viscosity is independent of shear rate. This region is called the zero-shear viscosity.
Figure 1.9. Complex viscosity as a function of frequency.

region. At intermediate frequencies a transition region is observed. Finally at high shear rates the material enters the pseudo plastic or power-law region.

The zero shear melt viscosity, $\eta_0$ of a polymer is a function of the polymer molecular weight, $M$. For a low molecular weight polymer it is observed that the viscosity scales with $M^1$. When the molecular weight exceeds some critical molecular weight the viscosity scales with $M^{3.4}$ (Figure 1.10).\textsuperscript{1,86} It is generally well accepted that the alteration in scaling arises from the presence of topological constraints. These topological constraints, generally referred to as entanglements, establish a temporary network that slows self-diffusion of the polymer molecule.
Figure 1.10. Idealized Relationship between melt viscosity and polymer molecular weight.

Modeling of Polymer Mechanical and Rheological Behavior

Multiple Element Models. Because polymers exhibit both solid and liquid-like behavior their mechanical behavior can often be described by constitutive models based on simple elastic (spring) and viscous (dashpot) elements. The arrangement of these elements in different ways determines the type of material behavior that can be described. This is demonstrated in Figure 1.11 for three of the most popular models. As is shown, the Kelvin model adequately describes the loading and unloading behavior under creep,
Figure 1.11. Constitutive models used to describe polymer viscoelastic behavior. Load and unloading creep curves also shown. A. Kelvin model; B. Maxwell Model; and C. SLS model.

except that the instantaneous elastic response during loading and unloading is not captured. The Maxwell model which includes a dashpot and a spring in series (Figure 1.11B) fairly captures the expected instantaneous elastic response but predicts a Newtonian response during creep and for this reason it is generally not used to describe creep behavior of polymeric materials.
The three element standard Linear Solid (SLS) model shown in Figure 1.11C can adequately capture the initial elastic responses during loading and unloading as well as the transient, non-Newtonian response during creep. This model is also able to predict stress relaxation behavior. The constitutive equations outlined above can often adequately describe the viscoelastic behavior of real materials. In practice it is sometimes necessary to include multiple elements to better replicate the distribution of relaxation times present in real materials.

**Modeling Rubber Elasticity of Solid Polymers.** While the multiple element models adequately describe the viscoelastic behavior of many polymers they do not provide insight into the molecular origins of the mechanical behavior and therefore have limited utility to help establish structure property relationships. An alternative approach to describe material behavior is to derive an equation based on molecular variables. The well-known expression for the entropy of stretching of an elastomer is a good example and will be developed here. The nature of the mechanical reactionary force of a deformed polymer is derived from the change in the entropy of elasticity associated with the macromolecular chain deformation, and not an internal energy change as is the case for other engineering materials such as metals and ceramics. Mathematically, the entropy of stretching can be expressed as:

\[ S_{\text{Strand}} = -\frac{3k_B}{2Na^2} r^2 \]  

(1.6)

where \( k_B \) is Boltzmann’s constant, \( N \) is the number of repeat units in the chain, \( a \) is the bond length, and \( r \) is the end-to-end distance of the polymer coil. If \( r \) is a vector defining
the initial distance of a chain end relative to a fixed chain end located at the origin
(defined by $r_0^2 = x^2 + y^2 + z^2$), then it can be shown that an affine deformation resulting
in chain end displacement from point $r_0$ to $r_1$ results in a change in the entropy of
stretching defined by the equation:

$$
\Delta S_{\text{Strand}} = \frac{-3k_B}{2Na^2} \left[ (\lambda_x^2 - 1)x^2 + (\lambda_y^2 - 1)y^2 + (\lambda_z^2 - 1)z^2 \right] 
$$

(1.7)

Where the extension ratio, $\lambda$, is defined as the ratio of the deformed length to the original
length. Assuming that there is no preferred direction and that the polymer is a freely
jointed chain (i.e. length defined by random walk statistics) then:

$$
\sum r^2 = \sum x^2 + \sum y^2 + \sum z^2
$$

(1.8)

and thus:

$$
\sum x^2 = \sum y^2 = \sum z^2 = \frac{1}{3} \sum r^2 = \frac{1}{3} \sum Na^2
$$

(1.9)

Noting that there are $v$ strands per unit volume:

$$
\Delta S_{\text{Volume}} = \frac{-v \cdot k_B}{2} \left[ \lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right]
$$

(1.10)

Assuming incompressibility (i.e. $l_x l_y l_z = 1$) and $l = l_x$:

$$
\Delta S_{\text{Volume}} = \frac{-v \cdot k_B}{2} \left[ \lambda^2 + \frac{2}{\lambda} - 3 \right]
$$

(1.11)

The change in the Helmholtz Free Energy, $\Delta A$ is simply the product of the temperature
and entropy change and therefore:

$$
\Delta A_{\text{Volume}} = \frac{v \cdot k_B T}{2} \left[ \lambda^2 + \frac{2}{\lambda} - 3 \right]
$$

(1.12)
And since, \( l = l_x / l_{x0} \)

\[
\Delta A_{\text{Volume}} = \frac{V \cdot k_B T}{2} \left[ \left( \frac{l_x}{l_{x0}} \right)^2 + 2 \left( \frac{l_{x0}}{l_x} \right) - 3 \right] \quad (1.13)
\]

Noting \( f = dA/dl \) yields:

\[
f = \frac{d\Delta A}{dl} = \frac{vk_B T}{2} \cdot \left( \frac{2l_x}{l_{x0}^2} - \frac{2l_{x0}}{l_x^2} \right) = vk_B T \cdot \left( \frac{l_x}{l_{x0}^2} - \frac{l_{x0}}{l_x^2} \right) \quad (1.14)
\]

and \( \sigma = \frac{f}{l_x} = \frac{vk_B T}{l_x} \cdot \left( \frac{l_x}{l_{x0}^2} - \frac{l_{x0}}{l_x^2} \right) = \frac{vk_B T}{l_{x0}^2} \cdot \left( \frac{l_x}{l_{x0}^2} - \frac{1}{l_x} \right) \quad (1.15)\]

Simplifying results in the well-known expression for stress resulting from the entropy of stretching:

\[
\sigma = \frac{vk_B T}{V} \cdot \left( \lambda^2 - \frac{1}{\lambda} \right) \quad (1.16)
\]

This model has been shown to approximate rubber elasticity at low to moderate strains and will form the basis of a mathematical model that we develop to describe the viscoelastic and shape-memory behavior of materials bearing strong hydrogen bonding groups.

**Modeling Viscoelasticity of Non-Associating Polymers.** There are a number of models that have been proposed to describe the flow behavior of linear polymer molecules. For unentangled polymer melts the Rouse model, derived originally for polymer solutions, predicts the expected general behavior.
The Rouse model (Figure 1.12) is a coarse grain model developed to account for slow polymer dynamics.\textsuperscript{86, 88} A submolecule consists of a sufficient number of backbone units to approximate a freely jointed, Gaussian chain. In turn, these submolecules are linked together with spring units. For low to moderate extensions, $L$, it can be shown that the spring force is proportional to $L*\kappa B T$. In the Rouse model the frictional drag force is provided by the Stoke’s equation for the dragging of a bead through a Newtonian medium. The recovery following deformation is a result of recovery of the spring. An idealized curve plotted according to the Rouse model is shown in Figure 1.12. In the low frequency terminal region, the Rouse model predicts that modulus will depend on frequency in a predictable fashion where slopes of 1 and 2 are expected for $G''$ and $G'$ respectively. At high frequencies, $G'$ and $G''$ are on the same order with slope =1/2. The transition from the terminal region to high frequency region is related to a distribution of relaxation times, the longest of which determines the onset of the terminal flow region. Very high frequency behavior cannot be predicted, owing to the fact that the short-range motions in this regime cannot be accounted for in the coarse grain Rouse model.
Polymer melts begin to exhibit rubberlike behavior at sufficiently high molecular weight. As indicated in Figure 1.10 a critical entanglement molecular weight is observed where scaling of the zero shear viscosity with molecular weight changes from 1 to about 3.4. The reptation model\textsuperscript{1, 86, 88} more appropriately describes the flow behavior of entangled polymer melts. As is shown in Figure 1.12, an entangled polymer molecule can be conceptually drawn as a string bound in space by a number of other molecules,
shown in Figure 12.B as crosses (to indicate that the chains are coming out of the page). The crossing chains limit the diffusion of the macromolecule much in the same way as it would if it were contained within a tube. The term reptation has been employed to describe the wriggling motion of the polymer chain as it moves through the tube.

**Modeling Viscoelasticity of Associating Polymers.** The sticky Rouse and reptation models\(^5\) represent one of the more popular approaches to describe the behavior of interacting polymers. In this model it is argued that each polymer contains a large number of stickers, where each sticker is either associated or dissociated with exactly one other sticker. It is argued that the binding energy effectively determines the number of stickers bound together and these associations can give rise to network properties with predictable rheological scaling rules.

Rubinstein and Semenov have shown that the dynamics of unentangled polymer solutions bearing associating groups is governed by network strand size and the effective lifetime of reversible junctions. They also showed that multiple recombinations of the same pair of stickers can occur and should result in a higher activation energy than predicted for the dissociation of two stickers.\(^5\) We have observed this for poly(butyl acrylate) copolymers bearing UPy groups.\(^{30}\) While the sticky Rouse model is conceptually a good model to discuss the rheology of reversibly associating polymers it is primarily focused on the behavior of polymer solutions and therefore less applicable to the prediction of polymer melt properties. This is reflected in a recent report where the
sticky Rouse model was not effective in modeling the melt behavior of polymers bearing strong UPy hydrogen bonding groups.\textsuperscript{89}

Green and Tobolsky (1946) developed a transient network theory to describe the behavior of physically crosslinked rubbery networks.\textsuperscript{90} Using the framework of the kinetic theory of rubbery elasticity they modified the equations to account for the fact that net points could break and reform. Only one relaxation time was assumed although the authors acknowledge that inclusion of a distribution of relaxation time could be incorporated into the model. Important to their model was that bonds were hypothesized to form in such a way that they do not contribute to the stress at constant extension. In other words, associations are established in a stress free state. Likewise they assumed that the relaxation rate is independent of the stresses on the elements.

They surmised that the contribution of the stress at time $t$ also arises from chains that have broken and reformed in the time interval $dt'$ (between 0 and $t$) and have not subsequently relaxed. This led to the following expression:\textsuperscript{90}

\[
f = \frac{v_0}{ck_BT} \exp(-kt) \left[ \frac{\lambda(t)}{m_0} - \frac{n_0}{\lambda(t)} \right] + 
\]

\[
v_2 \int_0^t k \exp(-k\tau) \left[ \frac{\lambda(t)}{\lambda(t-\tau)^2} - \frac{\lambda(t-\tau)}{\lambda(t)} \right] d\tau
\]

where $f$ is the force, $c$ is a constant, and $k$ is a rate constant. The transient network theory has gone through several revisions throughout the subsequent decades, mainly aimed at accounting for chain entanglements in non-associating polymers.\textsuperscript{91-94}
In the original transient network theory the rate of dissociation and association are equal. Tanaka and Edwards (1991) proposed a modification to the transient network theory that describes crosslinks that are generated and destroyed.\textsuperscript{4,95-97} In this work the chain breakage rate and the chain recombination rate are independent. This results in the formation of two populations of chains: those engaged in transmitting stress (active) and those that do not (dangling chains).

### 1.4.3. Shape-memory Behavior.

A shape-memory polymer (SMP) is a polymeric material that can be deformed to a temporary shape that is able to recover to its original shape upon the application of an appropriate stimulus.\textsuperscript{98-101} The materials consist of a polymer network that contains both permanent and temporary crosslinks. Permanent crosslinks act as net points to define a sample’s unstrained shape, and, upon cooling, shape-fixing occurs as temporary crosslinks form, thereby locking in entropic stress. The temporary shape is conventionally stabilized by crystallization of chain segments or by the formation of a polymer glass upon cooling. An external stimulus, such as a change in temperature, pH, or light,\textsuperscript{102} can deactivate temporary crosslinks, leading to shape-recovery.\textsuperscript{98-101} Our research group has developed thermally triggered SMPs that utilize hydrogen-bonds to stabilize mechanically deformed shapes.

A typical shape-memory cycle for a shape-memory elastomer bearing reversibly associating side-groups is shown in Figure 1.13.\textsuperscript{29} As is shown, programming of the temporary shape occurs by imposing a strain ($\varepsilon_m$) at high temperature followed by
cooling to a temperature below the shape-memory transition temperature. Upon releasing
the load a partial recovery of the strain ($\varepsilon_u$) occurs followed by slow creep recovery.

Finally, an increase in the temperature allows for recovery of the strain ($\varepsilon_p$).

**Figure 1.13.** Typical shape-memory cycle for a shape-memory elastomer

Metrics used to characterize shape-memory behavior include the strain fixity ratio
($R_f$) and the strain recovery rate ($R_r$). The strain fixity ratio quantifies the ability of
temporary net points to retain the applied strain and is defined by:\textsuperscript{29,103}

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

where $\varepsilon_u(N)$ is the strain of the $N$th cycle immediately following the removal of stress and
$\varepsilon_m$ is the imposed strain. A second metric, the strain recovery ratio, measures an SMP’s
ability to memorize its permanent shape and can be expressed as:\textsuperscript{29,103}

$$R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N - 1)}$$
where $\varepsilon_p(N-1)$ and $\varepsilon_p(N)$ are strains in the stress-free state for two consecutive shape-memory cycles.
1.5 References


Chapter 2: Executive Summary

This thesis establishes new structure-property relationships for polymers bearing hydrogen bonding side-groups. In this work systematic studies on the bulk behavior of both hydrophobic and hydrophilic polymers will be considered. It will be shown that molecular variables, such as the structure and binding strength of side-groups, are critically important in determining viscoelastic and shape memory properties. Further, it will be shown that the mechanical behavior of polymers bearing hydrogen bonding groups depends on the relative rates associated with hydrogen bonding exchange kinetics and the rate of mechanical deformation. Finally, the influence of strong UPy hydrogen bonding groups on the swelling, transport and thermomechanical behavior of a hydrophilic polymer reveal that UPy-binding occurs in these swollen hydrogels and it is surmised that a microenvironment within the hydrogel is necessary to support this hydrogen bonding.

In this executive summary chapter, the research objectives will be briefly discussed and an overview of each chapter will be provided.

2.1. Objectives

Chapter 1 discusses how reversible and/or noncovalent interactions can be used to direct polymer organization and produce stimuli-responsive behavior. These reversible interactions include hydrophobic interactions, hydrogen bonding interactions and ionic
interactions, to name a few. Likewise, thermoreversible covalent interactions such as the Diels-Alder (DA) cycloadduct represent yet another alternative. In this thesis the use of hydrogen bonding side-groups to influence the properties of both hydrophobic and hydrophilic polymers will be the primary focus. As discussed in Chapter 1, many hydrogen bonding groups such as carboxylic acids, while much weaker than covalent bonds, exceed the thermal energy at room temperature and therefore should be able to be sensed using rheological experiments. Also, unlike covalent bonds, hydrogen bonds should be thought of as dynamic and this unique aspect gives rise to time-dependent material behavior. Finally, investigations and theories corresponding to the associative behavior of hydrogen bonding groups are often performed in solution where mobility and solvent effects are expected to differ from that observed in the bulk.

To address these needs the following investigations have been performed:

I) Investigate the influence of side-group bond strength on the viscoelastic properties of a hydrophobic polymer system (Chapter 3);

II) Investigate the influence of water on hydrogels with strong hydrogen bonding groups (Chapter 4);

III) Develop a model to predict viscoelastic and shape memory behavior of polymer networks bearing hydrogen bonding side-groups (Chapter 5).
2.2 Overview and Key Findings

In Chapter 3, the influence of different hydrogen bonding side-groups (HBSGs) on the dynamic behavior of functional poly(n-butyl acrylate) melts and crosslinked networks is presented. The thermal and rheological behavior of random copolymers containing weak and strong HBSGs were synthesized and examined. With respect to thermal behavior it was found that the glass transition temperature ($T_g$) increased nearly linearly with the HBSG concentration for both weak and strong binding groups. All curves shifted to lower frequency with increasing binding group concentration. However, copolymers bearing weak HBSGs behaved as unentangled melts whereas those containing strong HBSGs behaved like entangled networks. Flow activation energies increased linearly with comonomer content; and, for weak hydrogen bonding groups, they depended only on the departure from $T_g$. Similar behavior was observed in crosslinked films as well.

Polymers bearing strong HBSGs exhibited good shape-memory behavior at temperatures greatly exceeding the glass transition temperature whereas polymers bearing weak HBSGs showed little capacity to store energy at temperatures much above the glass transition. These results suggest that weak HBSGs raise $T_g$ but do not create a network.

Chapter 5 describes the development of a transient network model to predict the time-dependent mechanical behavior of a shape-memory elastomer consisting of covalent crosslinks and strong hydrogen bonding groups. The model assumes continuous
mechanical equilibrium between an applied stress and stresses of entropic origin arising from both a permanent network and a transient network.

This model is capable of adequately describing time-dependent mechanical behavior such as creep, dynamic mechanical, and shape-memory responses of poly(butyl acrylate) copolymers bearing strong UPy hydrogen bonding groups. The primary benefit of such an approach is that it provides for a strong connection to molecular variables, thereby greatly improving its ability to explain the physics governing these complex systems. For example, the model was used to demonstrate that the dynamic mechanical behavior for these materials is related to two important time scales: the transient network characteristic relaxation time and the time scale associated with the deformation. This result supports the hypothesis advanced in Chapter 3 to explain why polymers bearing weak hydrogen bonding side-groups, though present as dimers, do not contribute to the observed mechanical behavior. The model also demonstrated the ability to replicate key stages of the shape-memory curve. Of particular interest was that the “state-of-ease” was found to be independent of the shape-memory fixing temperature for polymers bearing strong hydrogen bonding groups, a fact confirmed experimentally (Chapter 3). The limited capacity of the model to capture transient behavior was also revealed in the time-dependent creep behavior following the state-of-ease and became more prominent as the shape fixing temperature was increased.

UPy’s ability to self-associate to form hydrogen-bonded dimers (DDAA) in a polar environment is examined in Chapter 4. Poly(hydroxyethyl methacrylate) (poly(HEMA)) polymers with varying UPy side-group content were prepared and the
swelling and viscoelastic properties were measured. Water swelling experiments revealed that UPy side-groups retard early time (< 24 h) Fickian-like swelling and lead to two-stage, temperature-dependent, water sorption. At longer times UPy side-groups promote water swelling. Rheological studies show that the material’s viscosity and viscous relaxation time both increase with increasing UPy-content. The activation energy of the shear-induced flow scales linearly with UPy-content, suggesting cooperative dynamics. These results are similar to observations made for hydrophobic polymers bearing hydrogen-bonding side-groups. The swelling and mechanical behavior suggests that at least some UPy hydrogen-bonding occurs in hydrated poly(HEMA), despite competitive H-bonding with water, a fact confirmed using FTIR spectroscopy. Experimental observations can be explained by reversible association of UPy side-groups within water-excluded domains of poly(HEMA)’s secondary structure.
Chapter 3: The Influence of Hydrogen Bonding Side-groups on Viscoelastic Behavior of Linear and Network Polymers

3.1 Introduction.

Polymer chains connected by hydrogen bonds have been thoroughly investigated and remain a topic of elevated interest. The thermoreversibility of hydrogen bonds can result in transient supramolecular networks with topologies and dynamics that are highly sensitive to environmental variables, especially temperature. At high temperatures, hydrogen bond exchange is fast, and intermolecular bonds have little impact on viscoelastic properties. However, at low temperatures, the hydrogen bond lifetime can exceed experimental time-scales, and the resulting dynamic networks behave as crosslinked systems. The ability to apply heat, light, or other stimuli to invoke stress relaxation of neat polymer melts has been the key to developing classes of thermally mendable polymers, shape-memory elastomers and thermoplastic elastomers. Architectural control of supramolecular sub-units through intermolecular H-bonding dynamics also offers approaches to developing biomimetic and semiconducting nanostructures.

The melt behavior of linear polymers containing hydrogen bonding groups is distinctly different from their solution behavior. In solution, end-to-end association of telechelic polymers and the reversible assembly of comb polymers have been
described by simple association models. There, the concentration of formed bonds is determined by an association constant ($K_a = k_a/k_d$), and the average bond lifetime is determined by the inverse of the dissociation rate constant ($1/k_d$). For chains that have multiple (>2) hydrogen bonding sites, reversible networks can form in solution. The inter-chain binding strength can be modulated by solvent polarity; more polar solvents tend to reduce the equilibrium association constant.\textsuperscript{12,13} However, systems containing both polar and nonpolar components can organize in a way to shield binding sites from polar solvents, including water.\textsuperscript{14-16} Solution dynamics and rheological properties near and above the gel point have been predicted by the “sticky” Rouse model in which chains contain both non-bonding monomer segments and “sticky” sites.\textsuperscript{17,18} The sticky Rouse model predicts that, above the gel point, multiple bond dissociation events are required for a single change in network topology; hence, renormalized bond lifetimes, leading to apparent activation energies, are required to predict mechanical properties. While these ideas have been observed across a range of supramolecular gels and melts, few studies have quantitatively confirmed the predicted scaling. Moreover, subtle differences, such as whether the reversible crosslinking groups are covalently bonded to the supramolecular chains, influence scaling.\textsuperscript{3,19} In supramolecular polymer melts, the situation is even more complex due to reduction of chain mobility, chain entanglements, phase-segregation of macromolecular parts, and aggregation or crystallization of hydrogen bonding groups.\textsuperscript{20} Most experimental studies of supramolecular polymer melts deviate significantly from the idealized picture of reversibly binding chains. Very few
studies have been conducted on model systems that isolate how specific variables influence H-bond network dynamics within polymer melts.

Hydrogen bond strength and density of side-groups are critical design variables that influence the formation of supramolecular networks from linear polymers. The most prominent examples of strong, multi-site H-bonding motifs include the self-complementary ureidopyrimidinone group, the complementary thymine / 2,6-diaminotriazine and the Hamilton-receptor/barbituric acid system, and the recently introduced AAAA-DDDD+ quadruple hydrogen bond complex.\(^1,21\) Larger, higher strength H-bonding groups tend to be more susceptible to aggregation, phase segregation and stacking. However, even weak, monovalent and bivalent hydrogen bonding groups can increase melt viscosity, compatibilize binary blends, and introduce hierarchal structure into amorphous melts. Examples of such labile hydrogen bonding side-groups that modify melt behavior include carboxylic acids, uradiazoles, and amide groups. Interchain bonding of these groups is highly unpredictable but depends on the system’s physical state and the concentration of binding groups. For example, there is evidence that stable H-bonding networks of poly(styrene-co-acrylic acid) are viscoelastically relevant in the glassy and melt states, even at temperatures exceeding 100 °C.\(^22\)

Understanding the degree to which weak, yet highly concentrated, hydrogen bonding side-groups are comparable to strong, yet dilute, binding groups is the topic of our current investigation.

Here, we report the synthesis and characterization of model copolymers and crosslinked networks synthesized from butyl acrylate and monomers containing different
self-complementary H-bonding groups shown in Figure 3.1. We examine how the density, molecular structure, and strength of H-bonds affect network dynamics in linear polymer melts and in elastomeric rubbers bearing covalent crosslinks. Poly(butyl acrylate) (PBA) was chosen as the backbone because it is weakly polar and has a low glass transition temperature ($T_g \sim -50 \, ^\circ C$), to enable sufficient chain mobility to support H-bonding. Moreover, since PBA has a relatively high entanglement molecular weight ($M_e \sim 20 \, \text{kg/mol}$)\textsuperscript{23}, the influence of chain entanglements can be minimized by synthesizing low molecular weight polymers. H-bonding monomers were selected to evaluate the influence of strength and structure and include acrylic acid (AA), carboxy ethyl acrylate (CEA), aminopyridine (AP), and ureidopyrimidinone-functionalized acrylate (UPy). Of these, AA, CEA, and AP all form two-point (AD:DA) hydrogen bonded dimers and have much lower solution dimerization energies (~25-40 kJ/mol)\textsuperscript{24-28} than the four-point (AADD:AADD) UPy dimer (70 kJ/mol).\textsuperscript{29} CEA’s carboxylic acid group contains two methylene spacers further from the backbone than AA, and AP contains a pyridyl ring, limiting its configurational freedom.

![Figure 3.1](image-url)  

**Figure 3.1.** Cartoon depicting reversible association in a melt of copolymers bearing self-complementary hydrogen bonding side-groups.
3.2 Results and Discussion.

**Bond Strength.** Table 3.1 displays the experimentally determined hydrogen bond energies of monomer units employed in this study. To confirm relative bond strengths, experimental values were compared to quantum mechanical (QM) calculations (Appendix A). The QM results are consistently a factor of ~2.6 greater than the experimental results. The data show that acrylic acid (AA), carboxy ethyl acrylate (CEA), and aminopyridine (AP) have bond strengths that are less than half the ureidopyrimidinone (UPy) monomer. Thus, monomers AA, CEA, and AP will be termed “weak” hydrogen bonding groups and UPy will be termed “strong” hydrogen bonding groups. Using experimental values of hydrogen bond energies, we define the side-group energy density (SGED) according to the following equation:

\[
SGED = \frac{\Delta H_d \cdot x_{HB}}{m_{HB} \cdot x_{HB} + m_{BA} \cdot (1-x_{HB})}
\]  

(3.1)

where \(\Delta H_d\) is the bond dissociation energy taken from Table 3.1, \(x_{HB}\) is the molar fraction for the hydrogen bonding comonomer, and \(m_{BA}\) and \(m_{HB}\) are the molecular weights for butyl acrylate and the comonomer bearing hydrogen bonding groups respectively. SGED reflects the additional cohesive energy density of the material, per unit mass, due to hydrogen bonding.
Table 3.1. Bond strength and structure for different functional monomers bearing hydrogen bonding groups.

<table>
<thead>
<tr>
<th>Hydrogen Bonding Comonomer</th>
<th>Structure</th>
<th>Bond Energy, $\Delta H$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamidopyridine (AP) $^a$</td>
<td><img src="image" alt="Structure" /></td>
<td>25.1 $^{24}$</td>
</tr>
<tr>
<td>Acrylic acid (AA) $^b$</td>
<td><img src="image" alt="Structure" /></td>
<td>30 $^{25,28}$</td>
</tr>
<tr>
<td>Carboxyethylacrylate (CEA) $^b$</td>
<td><img src="image" alt="Structure" /></td>
<td>30 $^{25,28}$</td>
</tr>
<tr>
<td>Ureidopyrimidinone acrylate (UPy) $^c$</td>
<td><img src="image" alt="Structure" /></td>
<td>70 $^{29}$</td>
</tr>
</tbody>
</table>

a) Determined by $^1$H-NMR dilution experiments; b) based on FTIR (gas phase) study of acrylic acid coupled with theoretical calculation. FTIR studies of polymers bearing acrylic and methacrylic acid groups and analogous low molecular weight acids show good agreement (~30-45kJ/mol)$^{30}$; c) values are based on the activation energy for dimer dissociation determined by dynamic NMR spectroscopy.

Copolymer Synthesis. Copolymers bearing hydrogen bonding side-groups were prepared by copolymerizing $n$-butyl acrylate with different comonomers. The composition, molecular weight characteristics, and glass transition temperatures of synthesized polymers are summarized in Table 3.2. The samples’ average molecular weights ($M_n$) were approximately 30 kg/mol, slightly higher than the PBA’s entanglement molecular weight of 20 kg/mol. The product composition nearly matched the comonomer feed ratio though the copolymers containing AA were somewhat lean in
acrylic acid. Infrared spectroscopy (ATR) confirmed the presence of hydrogen bonded
groups (Appendix A). The average number of stickers per chain, \( n_{HB} \), listed in Table 3.2,
was determined according to relation:

\[
n_{HB} = DP \cdot x_{HB} = \frac{M_n \cdot x_{HB}}{m_{HB} \cdot x_{HB} + m_{BA} \cdot (1-x_{HB})}
\]  

(3.2)

where \( m_i \) and \( x_i \) are the monomer molecular weights and monomer mole fractions in the
product copolymers. All polymers contained more than two hydrogen bonding groups per
chain, and, if association between side-groups is thermodynamically favored, chains
should form a supramolecular network.

The glass transition temperature \( (T_g) \) of synthesized polymers, determined by
DSC, depends nearly linearly on the number of hydrogen bonding side-groups as shown
in Figure 3.2. Interestingly, weak binding side-groups influence \( T_g \) nearly the same as
strong UPy side-groups. The slopes obtained by linear least-square fitting for each
comonomer are comparable, and the coefficient of determination among each data set is
high (\( R^2 > 0.99 \)). The \( T_g \) results of UPy-containing samples are in good agreement with
other studies which extend to UPy compositions as high as 15 mol\%.

\(^{31,32}\)
**Table 3.2.** Composition and molecular weight characteristics of synthesized copolymers containing hydrogen bonding side-groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H-bonding monomer feed [mol %]</th>
<th>$x_{HB}^a$ [mol %]</th>
<th>$n_{HB}$ [number /chain]</th>
<th>SGED [J/g]</th>
<th>$M_o^b$ [kg/mol]</th>
<th>$M_w/M_n^b$</th>
<th>$T_g^c$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>32.9</td>
<td>2.5</td>
<td>-49.0</td>
</tr>
<tr>
<td>AP5</td>
<td>5.4</td>
<td>4.7</td>
<td>11.9</td>
<td>9.0</td>
<td>28.4</td>
<td>2.6</td>
<td>-39.1</td>
</tr>
<tr>
<td>AP10</td>
<td>10</td>
<td>10.0</td>
<td>21.4</td>
<td>18.9</td>
<td>27.8</td>
<td>2.4</td>
<td>-25.2</td>
</tr>
<tr>
<td>AP15</td>
<td>15</td>
<td>14.7</td>
<td>31.7</td>
<td>27.7</td>
<td>27.7</td>
<td>2.5</td>
<td>-12.7</td>
</tr>
<tr>
<td>AA6</td>
<td>7</td>
<td>5.6</td>
<td>14.2</td>
<td>13.5</td>
<td>25.3</td>
<td>2.3</td>
<td>-40.2</td>
</tr>
<tr>
<td>AA10</td>
<td>13</td>
<td>10.2</td>
<td>32.8</td>
<td>25.0</td>
<td>30.9</td>
<td>2.5</td>
<td>-34.5</td>
</tr>
<tr>
<td>AA23</td>
<td>25</td>
<td>23.1</td>
<td>60.8</td>
<td>60.2</td>
<td>28.0</td>
<td>2.7</td>
<td>-14.6</td>
</tr>
<tr>
<td>CEA5</td>
<td>5</td>
<td>4.5</td>
<td>11.7</td>
<td>10.5</td>
<td>30.1</td>
<td>2.7</td>
<td>-43.4</td>
</tr>
<tr>
<td>CEA12</td>
<td>12</td>
<td>11.9</td>
<td>30.5</td>
<td>27.5</td>
<td>33.0</td>
<td>2.4</td>
<td>-36.9</td>
</tr>
<tr>
<td>UPy1</td>
<td>1</td>
<td>1.0</td>
<td>2.7</td>
<td>5.4</td>
<td>34.4</td>
<td>2.4</td>
<td>-46.5</td>
</tr>
<tr>
<td>UPy2</td>
<td>2</td>
<td>2.2</td>
<td>4.9</td>
<td>11.7</td>
<td>32.1</td>
<td>2.4</td>
<td>-43.6</td>
</tr>
<tr>
<td>UPy5</td>
<td>5</td>
<td>5.3</td>
<td>11.4</td>
<td>27.3</td>
<td>31.1</td>
<td>2.4</td>
<td>-38.7</td>
</tr>
</tbody>
</table>

a) $x_{HB}$ is the mole fraction of H-bonding monomer, determined from $^1$H NMR.
b) Determined by GPC.
c) Determined by DSC.

In the glassy state, structural relaxation requires molecular mobility and available free volume. In polymeric systems, intermolecular hydrogen bonds can act as temporary crosslinks which can restrict motion and decrease free volume, although sometimes unexpectedly.\(^{33-35}\) In most cases, introducing hydrogen bonds onto a polymer increases $T_g$, a concept well supported in the literature.\(^{36}\) Qualitatively, this trend is well supported by our observations.
In addition to hydrogen bonding, the chemical structure of the comonomer side-group is believed to play an important role in determining $T_g$. For example, the AP monomer presents a bulky group close to the polymer backbone, raising $T_g$ more than the bulky UPy monomer, which is separated from the backbone by a flexible spacer. The influence of the flexible spacer on $T_g$ is also evident when comparing the AA and CEA containing copolymers. Similar effects have been observed in unfunctionalized homopolymers $^{37,38}$

**Figure 3.2.** Plot of $T_g$ versus mole fraction of hydrogen bonding side-group ($x_{HB}$) for different binding groups. Least-squares linear fits are shown as dashed lines, and they have similar slopes ($m_{AP} = 264$ K; $m_{AA} = 148$ K; $m_{CEA} = 87$ K; $m_{UPy} = 176$ K).
**Rheology of Linear Copolymers.** Storage modulus master curves as a function of frequency for a reference temperature of 25 °C are shown in Figures 3.3a-d for the linear copolymers. Each acquired dataset obeys time-temperature superposition fairly well over the experimental temperature range (5-145 °C). For samples containing the weaker hydrogen bonding side-groups (AA, AP, CEA), the curves appear similar to the PBA homopolymer curve, although they are shifted to lower frequency with increasing comonomer content. In contrast, the UPy-containing samples exhibit a distinct plateau modulus, even for samples containing as little as 1 mol% UPy.

Samples containing different types of hydrogen bonding groups at nearly the same value of SGED are compared in Figure 3.4. Samples AA6, AP5, and CEA5 have about 5 mol% of hydrogen bonding side-group and an SGED of about 10 J/g, and they exhibit nearly identical behavior in G’. However, the polymer containing only 2 mol% of UPy comonomer, with nearly the same SGED, behaves very differently and displays a clear plateau. Thus, SGED alone is not deterministic; a higher concentration of weakly bonding groups is not equivalent to a smaller number of strong bonding groups.

Representative curves illustrating the relationship between G’ and G” are shown in Figure 3.5. The complete data set of G’ and G” master curves are included as Appendix A. For the copolymers bearing weakly bonding side-groups (e.g. AA10), G” exceeds G’ at low frequencies, indicating liquid-like behavior; and at higher frequencies, G’ and G” nearly lay directly ontop of one another. For UPy-containing copolymers, G’ is similar to G” at low frequency, and solid-like behavior (G’ > G”) is encountered at
intermediate frequencies through the plateau region. At even higher frequencies, $G''$ is again on the same order as $G'$.

Power-law fits to $G'$ and $G''$ master curves were made in the terminal region and in the high frequency region. These regions are separated by the characteristic “knee” appearing in all of the master curves at a frequency corresponding to the longest Rouse relaxation time. Resulting power-law exponents are shown in Table 3.3. Poly(butyl acrylate) behaves nearly Rouse-like with the expected terminal power-law exponents of nearly 1 and 2 for $G''$ and $G'$ and a common higher frequency power-law exponent of $\frac{1}{2}$.

An increase in comonomer concentration consistently results in a lower exponent in the terminal region for both $G'$ and $G''$. The presence of the UPy side-group results in the largest differences in the value of the limiting exponents. For example, the UPy5 sample exhibits terminal region exponents of 0.65 and 0.56 for $G''$ and $G'$ respectively.

The appearance of a plateau modulus in UPy-containing copolymers allows for the determination of effective strand density, $\nu_x$:

$$\nu_x = \frac{G_N}{RT}$$

(3.3)

where $G_N$ is the plateau modulus, $T$ is the temperature, and $R$ is the gas constant. Using the plateau modulus—determined from $G'$ curves at frequencies corresponding to minima in $G''$—the number of effective crosslinks from Equation 3.3 is then 26.7, 71.8, and 206.3 mol/m$^3$ for the UPy1, 2, and 5 samples respectively. These numbers can be
Figure 3.3. Storage modulus master curves referenced to 25 °C of linear copolymers containing (a) acrylamidopyridine, (b) acrylic acid, (c) carboxyethylacrylate, and (d) UPy acrylate monomers.
Figure 3.4. Storage modulus master curves of polymers, referenced at 25 °C, with nearly equivalent SGED (values in parenthesis).

Figure 3.5. Selected storage and loss modulus master curves referenced at 25 °C for PBA, AA13, and UPy5 samples.
Table 3.3. Summary of power-law exponents obtained from fitting $G'$ and $G''$ master curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power-law exponent in terminal regime [Pa-s/rad]</th>
<th>Power-law exponent in high frequency regime [Pa-s/rad]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G''$</td>
<td>$G'$</td>
</tr>
<tr>
<td>PBA</td>
<td>1.00±0.02</td>
<td>1.85±0.02</td>
</tr>
<tr>
<td>AP5</td>
<td>0.94±0.02</td>
<td>1.57±0.02</td>
</tr>
<tr>
<td>AP10</td>
<td>0.95±0.02</td>
<td>1.52±0.02</td>
</tr>
<tr>
<td>AP15</td>
<td>0.93±0.02</td>
<td>1.52±0.04</td>
</tr>
<tr>
<td>AA6</td>
<td>1.04±0.02</td>
<td>1.65±0.03</td>
</tr>
<tr>
<td>AA10</td>
<td>0.86±0.02</td>
<td>1.42±0.02</td>
</tr>
<tr>
<td>AA23</td>
<td>0.85±0.01</td>
<td>1.42±0.01</td>
</tr>
<tr>
<td>CEA5</td>
<td>0.97±0.01</td>
<td>1.76±0.01</td>
</tr>
<tr>
<td>CEA12</td>
<td>0.89±0.01</td>
<td>1.54±0.01</td>
</tr>
<tr>
<td>UPy1</td>
<td>0.91±0.01</td>
<td>1.55±0.03</td>
</tr>
<tr>
<td>UPy2</td>
<td>0.67±0.01</td>
<td>0.94±0.02</td>
</tr>
<tr>
<td>UPy5</td>
<td>0.65±0.02</td>
<td>0.56±0.02</td>
</tr>
</tbody>
</table>

compared to the maximum possible number of crosslinks formed by UPy dimerization based on $^1$H-NMR data:

$$\nu_{x,\text{max}} = \frac{1}{2} \frac{x_{UPy} \cdot \rho}{m_{HB} \cdot x_{HB} + m_{BA} \cdot (1 - x_{HB})}$$

(3.4)
where the factor of $\frac{1}{2}$ accounts for the fact that two UPy dimers are required to make one net-point. Using this equation, one obtains theoretical values of 34.7, 79.1 and 175.3 mol/m$^3$ which agrees fairly well with values based on $G'$, indicating that dimerization of UPy groups are responsible for network properties observed at intermediate frequencies.

Complex viscosity ($\eta^*$) curves derived from rheology experiments, and shifted by the same factors as $G'$ and $G''$, are plotted in Figure 3.6 for PBA and selected copolymers. Newtonian behavior is observed in the zero-shear viscosity region, and shear-thinning behavior is observed at higher frequencies. Complex viscosity data were fit to the empirical Cross model\textsuperscript{39}:

$$\eta^*(\omega) = \frac{\eta_0}{1 + \left(\frac{\tau_0\omega}{2\pi}\right)^{1-n}} \quad (3.5)$$

where $\eta_0$ is the characteristic zero-shear viscosity, $\tau_0$ is an average relaxation time, and $n$ is the power-law index (see Appendix A). Fitted model parameters are plotted against copolymer content in Figure 3.7. The zero-shear viscosity increases exponentially with the amount of hydrogen bonding comonomer; however UPy-containing copolymers show values that are orders of magnitude higher than the weakly bonding copolymers. Similar trends are observed for relaxation times. Fitted values of $n$ were all $< 1$, indicating shear-thinning behavior. UPy-containing copolymers exhibit the greatest shear-rate dependency with $n \approx 0.1$. In contrast, the copolymers with weak bonding groups all showed similar values of $n \approx 0.5$, even at high H-bonding monomer concentration.
Table 3.4 compares the average relaxation times $\tau_0$ to the Rouse relaxation times for unentangled melts and the Doi-Edwards relaxation times for entangled melts.\textsuperscript{40} The Rouse relaxation time is given by:

$$\tau_R = \frac{6\eta_0 M}{\pi^2 \rho RT}$$

(3.6)

where $M$ is the polymer molecular weight and $\rho$ is density (taken as 0.9 g/cm$^3$). For PBA and copolymers with weak bonding groups, $\tau_0$ roughly agrees with $\tau_R$ indicating that the Cross model provides a good estimate for the longest Rouse relaxation time. This agreement is also evident by comparing the position of the “knee” in plots of modulus and complex viscosity master curves. In contrast, for UPy-containing copolymers, $\tau_R$ exceeds $\tau_0$ with increasing side-group content, suggesting that UPy dimers act like chain entanglements. The Doi-Edwards relaxation time is given by

$$\tau_{DE} = \frac{15\eta_0 M_e}{\pi^2 \rho RT}$$

(3.7)

where $M_e$ is the molecular weight between entanglements. If hydrogen bonding side-groups are fully associated and chain ends are neglected then $M_e = M_n/(n_{HB}-1)$. The Doi-Edwards relaxation time is in better agreement with $\tau_0$ for UPy samples than for the copolymers bearing weak side-groups.
Figure 3.6. Selected complex viscosity curves referenced at 25 °C.

Table 3.4. Comparison of the average relaxation time obtained from fits to experimental data to the Rouse and Doi-Edwards relaxation times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_0$ [s]</th>
<th>$\tau_R$ [s]</th>
<th>$\tau_{DE}$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>AP5</td>
<td>0.09</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>AP10</td>
<td>0.60</td>
<td>0.26</td>
<td>0.03</td>
</tr>
<tr>
<td>AP15</td>
<td>5.5</td>
<td>2.8</td>
<td>0.23</td>
</tr>
<tr>
<td>AA6</td>
<td>0.02</td>
<td>0.02</td>
<td>0.003</td>
</tr>
<tr>
<td>AA10</td>
<td>0.33</td>
<td>0.20</td>
<td>0.02</td>
</tr>
<tr>
<td>AA23</td>
<td>63</td>
<td>30</td>
<td>1.2</td>
</tr>
<tr>
<td>CEA5</td>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>CEA12</td>
<td>0.18</td>
<td>0.17</td>
<td>0.01</td>
</tr>
<tr>
<td>UPy1</td>
<td>11</td>
<td>7.4</td>
<td>11</td>
</tr>
<tr>
<td>UPy2</td>
<td>21</td>
<td>110</td>
<td>72</td>
</tr>
<tr>
<td>UPy5</td>
<td>258</td>
<td>2500</td>
<td>594</td>
</tr>
</tbody>
</table>
Figure 3.7. Parameters obtained by fitting complex viscosity to the Cross-model plotted against mole fraction of hydrogen bonding side-group, $x_{\text{HB}}$. a) average relaxation time, $\tau_0$; b) zero-shear viscosity, $\eta_0$; and c) the power-law index, $n$.

For thermorheologically simple polymer melts, the temperature-dependence of the superposition shift factor, $a_T$, can aid in elucidating the mode of chain relaxation. Selected plots of the time-temperature superposition shift factors $a_T$ as a function of
reciprocal temperature are shown in Figure 3.8. A complete collection of plots, including curve fits, is provided in Appendix A. For PBA and polymers containing weak hydrogen bonding groups, a non-linear relationship is observed; and data fit well with the Vogel-Fulcher-Tammann (VFT) relationship:

$$\log a_r = A + \frac{B}{T - T_0}$$  \hspace{1cm} (3.8)

where \(T_0\) is a reference temperature and \(A\) and \(B\) are empirical constants. The VFT equation describes the temperature dependence of viscosity over a wide range of temperatures, and it predicts the same temperature dependence as the WLF equation. The physical significance of the VFT constants \(A\) and \(B\) can be interpreted as a viscosity term and a temperature-dependent activation energy respectively. While the polymers containing weak hydrogen bonds broadly conform to the VFT equation, the UPy-containing samples conform better to the Arrhenius relationship:

$$\ln a_r = \frac{-E_a}{RT} + C$$  \hspace{1cm} (3.9)

where \(E_a\) is the apparent flow activation energy and \(C\) is a constant.

To compare flow activation energies between the different copolymers, the superposition shift factors for each melt were fit to the Arrhenius expression, and results are compiled in Figure 3.9. The flow activation energy increases with comonomer content for each type of hydrogen bonding group. For copolymers with weak hydrogen bonding groups, the relationship is nearly linear. Polymers with the strong, UPy hydrogen bonding groups exhibit the highest activation energies that are most dependent on side-group content.
Figure 3.8. Temperature dependence of time-temperature superposition shift factors, $a_T$ for representative samples. a) PBA; b) AA23; c) UPy5. Lines are least-squares fits to the Arrhenius model (dashed) and VFT model (solid).

For samples containing weak hydrogen bonding groups, the apparent flow activation energy is predominately influenced by changes in $T_g$. Figure 3.9b shows that, regardless of the type of weak hydrogen bonding group, these activation energies depend linearly on the departure of the reference temperature from $T_g$. Interestingly, a data point from the literature for poly (butyl acrylate-co-methyl methacrylate) without hydrogen bonding side-groups, is plotted and resides on the same trend-line. This finding is important because it indicates that, for polymers with weak bonding groups, the
rheological relaxation at the timescales investigated is independent of hydrogen bonding dynamics. Instead, the rheology is determined by common (VFT) behavior of molten polymers near their $T_g$. Unlike the weakly bonding copolymers, UPy-containing polymers exhibit much higher flow activation energies that fail to collocate on the trend-line in Figure 3.9b.

**Synthesis of crosslinked elastomers.** Crosslinked poly(butyl acrylate) elastomers containing different hydrogen bonding side-groups were prepared using 0.5 mol% TMPTMA as a crosslinker. The measured glass transition temperature and the calculated side-group energy density (SGED), determined by feed composition, are shown in Table 3.5. Following the reaction, infrared spectroscopy confirmed that unreacted monomers were absent and hydrogen bonding comonomers were present as dimers (see Appendix A). Since solution $^1$H NMR could not be performed on crosslinked films, the composition of crosslinked films was assessed using elemental analysis, showing good agreement with the feed composition (see Appendix A).

The $T_g$ values of crosslinked films are slightly elevated (~3.5°C) compared to uncrosslinked melts with the same composition. The presence of hydrogen bonding side-groups elevates the $T_g$ as observed in the uncrosslinked melts. The $T_g$’s of crosslinked samples containing about 5 mol% of AA, CEA, and UPy are similar to one another (-35 to -40 °C). The $T_g$ of the AA21-X sample is greatly increased as a result of its high acrylic acid concentration, but is within about 5°C of the analogous linear polymer AA25. In general, the agreement between the $T_g$ values of linear versus the lightly crosslinked elastomers at a given comonomer concentration is expected.
Figure 3.9. Apparent flow activation energies of linear polymer melts containing hydrogen bonding side-groups as a function of: a) comonomer composition and b) the departure of the reference temperature (25 °C) from the material’s glass transition ($T_{ref} - T_g$). The dashed trend line is drawn to guide the eye. The data point “MMA” is poly(butyl acrylate-co-methyl methacrylate) with 39 mol% methyl methacrylate point taken from reference 42.
Table 3.5. Characteristics of crosslinked poly(butyl acrylate) with hydrogen bonding side-groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comonomer feed [mol %]</th>
<th>SGED [J/g]</th>
<th>T_g [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA-X</td>
<td>0</td>
<td>0</td>
<td>-45.8</td>
</tr>
<tr>
<td>AP5-X</td>
<td>5</td>
<td>10.1</td>
<td>-35.4</td>
</tr>
<tr>
<td>AA5-X</td>
<td>5</td>
<td>10.8</td>
<td>-38.5</td>
</tr>
<tr>
<td>AA21-X</td>
<td>21</td>
<td>48.8</td>
<td>-9.76</td>
</tr>
<tr>
<td>CEA5-X</td>
<td>5</td>
<td>11.6</td>
<td>-39.4</td>
</tr>
<tr>
<td>UPy2-X</td>
<td>2</td>
<td>10.7</td>
<td>-39.6</td>
</tr>
</tbody>
</table>

a) Determined by DSC.

Viscoelasticity of crosslinked networks. Storage modulus (E’) and tan δ mastercurves of representative crosslinked materials are shown in Figures 3.10 (see Appendix A for additional curves). All materials exhibit a low frequency plateau in E’ that is attributed to the formed crosslinked network. At frequencies above this plateau, the storage modulus rapidly rises with increasing frequency as the glass transition is approached. In general, curves of networks containing weak hydrogen bonding groups are shifted to lower frequencies relative to the unsubstituted PBA network. For AA21-X, the glass transition, evident by the peak in tan δ, was experimentally accessible. UPy2-X displays a second storage modulus plateau at intermediate frequencies, and, at high frequencies, glassy behavior is observed. The UPy transition at low frequencies is also evident from a peak in tan δ at approximately 10³ rad/sec.
Figure 3.10. Representative rheological master curves referenced to 25 °C of crosslinked polymers containing hydrogen bonding side-groups. a) storage modulus and b) loss tangent.
The flow activation energy of crosslinked samples was determined by fitting superposition shift factors to the Arrhenius relationship, and results are plotted in Figure 3.11. Like the linear copolymer melts, the apparent flow activation energies of samples containing weak hydrogen bonding groups is dominated by changes in $T_g$. This indicates that viscoelastic properties of the networks, like the melts, are independent of hydrogen bonding dynamics. However, the copolymer containing the UPy side-groups is distinct, and this sample does not collocate on the dashed trend-line.

In our earlier study, we demonstrated that the presence of a covalent network can support cooperative hydrogen bonding of UPy side-groups, leading to higher flow activation energies. In the present study, this effect can be examined for other hydrogen bonding groups because each crosslinked sample was designed with nearly the same concentration of hydrogen bonding groups as an uncrosslinked sample. Table 3.6 summarizes the results. For poly(butyl acrylate) and copolymers containing weak hydrogen bonding groups the introduction of a crosslinked network had little effect on the flow activation energy. Subtle difference in activation energies between these crosslinked networks and copolymer melts is attributed to composition differences. As observed earlier, crosslinks significantly raised the activation energy of UPy-containing copolymers.
Figure 3.11. Apparent flow activation energies of crosslinked samples containing hydrogen bonding side-groups as a function of the departure of the reference temperature (25°C) from the material’s glass transition ($T_{ref}-T_g$). The dashed trend line is drawn to guide the eye through networks containing weak hydrogen bonding groups.
Table 3.6. Comparison of Flow Activation Energies flow for selected linear and crosslinked samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>x&lt;sup&gt;a&lt;/sup&gt; [mol %]</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>-</td>
<td>53.0</td>
</tr>
<tr>
<td>PBA-X</td>
<td>-</td>
<td>54.0</td>
</tr>
<tr>
<td>AP5</td>
<td>5.2</td>
<td>68.0</td>
</tr>
<tr>
<td>AP5-X</td>
<td>5.0</td>
<td>69.5</td>
</tr>
<tr>
<td>AA5</td>
<td>5.6</td>
<td>62.7</td>
</tr>
<tr>
<td>AA5-X</td>
<td>5.0</td>
<td>58.4</td>
</tr>
<tr>
<td>AA23</td>
<td>23.1</td>
<td>96.5</td>
</tr>
<tr>
<td>AA21-X</td>
<td>21.0</td>
<td>80.8</td>
</tr>
<tr>
<td>CEA5</td>
<td>4.6</td>
<td>55.6</td>
</tr>
<tr>
<td>CEA5-X</td>
<td>5.0</td>
<td>60.2</td>
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<tr>
<td>UPy2</td>
<td>2.2</td>
<td>79.7</td>
</tr>
<tr>
<td>UPy2-X</td>
<td>2.0</td>
<td>93.4</td>
</tr>
</tbody>
</table>

a) For crosslinked samples the fraction of hydrogen bonding group is based on the feed composition.

**Shape-memory.** Crosslinked samples near their glass transition temperature were subjected to thermomechanical analysis to study shape-memory behavior. A typical shape-memory cycle is shown in Figure 3.12. A temporary shape is first achieved by stretching the sample to a specified maximum strain, <i>ε</i><sub>m</sub> at a programming temperature, <i>T</i><sub>p</sub>. The sample is then cooled, while under tension, to a lower, fixing temperature, <i>T</i><sub>f</sub>. Upon releasing the load, the shape immediately recovers a fraction of its strain and then further recovers by slow elastomeric creep. The partial shape recovery following load removal is due to a combination of slow relaxation near <i>T</i><sub>g</sub> and slow reshuffling of temporary net-points which act to maintain the temporary shape. Finally, an increase in the temperature allows for rapid and complete recovery of the strain. Samples were
cycled multiple times (>3) and did not show any signs of degradation or shape training; they fully recovered after multiple cycles.

**Figure 3.12.** Shape-memory cycle of AA21-X.

The time-dependence of strain following load removal is displayed in Figure 3.13 for selected samples, AA21-X and UPy2-X. Fixing temperatures closer to the glass transition temperature most effectively stabilized the imposed strains. All samples exhibit an instantaneous response upon removal of the load, followed by elastomeric creep recovery that is dependent on $T_f$; although the instantaneous response observed in the UPy sample is especially abrupt and is identical for every temperature examined.

To compare different samples’ strain behavior following load removal, the strain fixity ratio thirty minutes after load removal ($R_{f,30}$) is plotted against $T_f - T_g$ in Figure 3.14. Regardless of the type of bonding group, the strain response for networks containing
weak bonding groups depends linearly on the departure from $T_g$. Even the datum from the PBA-X polymer, without hydrogen bonding side-groups, lies on the same trend-line. Collectively, these results suggest that the presence of a glass transition, and not hydrogen bond exchange dynamics, is responsible for shape stabilization of networks containing weak hydrogen bonding groups. In contrast, the UPy2-X sample deviates from the trend-line and shows higher strain fixity at much higher temperatures. For the UPy sample, hydrogen bond dynamics occur on timescales that are similar or exceed the experiment, leading to shape stabilization. In other investigations, shape-memory effects have been reported for polymers modified with weak hydrogen bonding groups, including poly(methyl acrylate)-co-(acrylic acid) networks$^{43}$ and complexes of a poly(methacrylic acid-co-methyl methacrylate) network with poly(ethylene glycol)$^{44}$. Memory in these systems is attributed to shape fixing near the glass transition temperature.

3.3 The Influence of Weak and Strong Hydrogen Bonding Side-Groups.

This study provides a body of dynamic mechanical data and examines how side-group hydrogen bonding affects the polymer glass transition as well as viscoelastic behavior of linear copolymer melts and network elastomers.
Figure 3.13. Strain transients following load removal at various temperatures of a) AA21-X and b) UPy2-X.

Figure 3.14. Shape fixity ratio thirty minutes after load removal (Rf,30) plotted as function of the departure from Tg. A trend line is provided to guide the eye through data corresponding to networks with weak hydrogen bonding side-groups.
For a given comonomer, $T_g$ increases in a near linear fashion with the density of hydrogen bonding groups. The differences in slope for the weak hydrogen bonding groups suggests that side-group structural factors such as length of flexible spacers and side-group rigidity also play an important role in influencing $T_g$. Although hydrogen bonding may not be the dominant factor, we hypothesize that hydrogen bonds, regardless of their strength, can reduce segmental motion associated with the slowest mode of the glass transition, i.e. the $\alpha$ relaxation. We suspect that hydrogen bonding reduces chain motion by either decreasing the available free volume or increasing the amount of chain friction. Accordingly, hydrogen bonding must be relevant beneath the glass transition, and the equilibrium number of dimerized hydrogen bonds, and not their exchange kinetics, should determine the extent that $T_g$ is influenced. While there is ample evidence that hydrogen bonds form beneath $T_g$, to our knowledge no studies have investigated their exchange rate in the glassy state.

Our second notable finding is that weak hydrogen bonds have little effect on rheological relaxation modes. PBA and copolymers containing weak hydrogen bonding groups exhibit characteristics of unentangled melts as indicated by their Rouse-like behavior. The dominance of $G''$ over $G'$ implies that weak hydrogen bonding side-groups are unable to form a percolated network at room temperature. Moreover, the viscoelasticity above $T_g$ is determined by the proximity to $T_g$. Figures 3.9, 3.11, and 3.14 show that, for weak hydrogen bonding copolymers, activation energies and elastomeric creep scale linearly with $T-T_g$. Similar effects, often termed the “$T_g$ effect”, have been reported in several early studies of melts including poly(styrene) modified with
methacrylic acid \(^{46,47}\) ethylene-acrylic acid copolymers\(^ {48}\) and ethylene-methacrylic acid copolymers\(^ {49}\). Those studies involved high \(T_g\)'s and were performed at elevated temperatures (>100 °C) where the lifetimes of hydrogen bonds are obviously short. It was speculated that a higher concentration of bonding groups with reduced exchange rates at room temperature should give rise to a crosslinking effect\(^ {49}\). However, our results show no such effect for the weak hydrogen-bonding systems examined. Instead, the rheological behavior of copolymers containing weak hydrogen bonding groups can be attributed to monomeric friction independent of the presence of hydrogen bonds indicating that hydrogen bond exchange is fast relative to the experimental time scale. Indeed, the temperature dependence of superposition shift factors (Figure 3.8) is consistent with the VFT dependence of the monomeric friction factor\(^ {45}\), suggesting free volume effects play a critical role. We may conclude that melt behavior is determined by the proximity to \(T_g\), which is elevated due to a number of factors, including hydrogen bonding.

UPy-containing polymers are rheologically distinct from the other copolymers because they exhibit network-like properties at short time scales, including a plateau in \(G'\). This difference is attributed to the long lifetime of UPy dimers. The viscoelastic relaxation times for UPy-containing copolymers exceed 10 seconds (Figure 3.7). We view these relaxation times as measures of the apparent UPy bond lifetime for the following reasons: unlike all other copolymers, viscous relaxation of UPy-copolymers is thermally activated and shows Arrhenius temperature dependence (Figure 3.8); network-like properties are observed only for UPy-containing copolymers (Figures 3.5 and 3.10).
and are consistent with the number density of UPy binding units, a fact further supported by shape-memory testing (Figure 3.14); and cooperative dynamics are observed due to the presence of a network (Table 3.6).

The distinct behavior of UPy-containing melts suggests that interchain associations are mechanically relevant, beyond the \( T_g \) effect, above a critical hydrogen-bond strength. Recent investigations of copolymer solutions containing different side-group hydrogen bonding motifs arrive at a similar understanding. Norbornene-based copolymer solutions containing cyanuric acid or thymine side-groups were crosslinked by adding small molecule complements; and thymine’s higher binding strength resulted in elastic gels, whereas cyanuric acid resulted in viscous liquids.\(^5\) Similarly, Hackelbusch \textit{et al.} varied the associating side-group motif in poly(butyl acrylate) copolymers and studied solution mobility of tracer chains.\(^3\) Their results agreed with the theoretical “sticky” Rouse model, but only above a threshold equilibrium association constant of \( K_a \sim 10^9 \). However, solution rheological behavior cannot always be used to infer melt behavior. Herbst discovered drastic differences between melt and solution behavior of end-functional poly(butyl acrylate) copolymers bearing the moderately strong (i.e. \( K_a = 10^3 \) \( M^{-1} \)) THY/DAT pair, with network formation in solution but only viscoelastic thickening in the melt.\(^5\)

\textbf{3.4 Conclusions.}

In summary, poly(butyl acrylate) copolymers and elastomers bearing different amounts and types of hydrogen bonding side-groups were synthesized, and a large body
of dynamic mechanical data were collected. The presence of hydrogen bonding groups elevates the material’s glass transition temperature; this is attributed to comonomer structure and the formation of inter-chain hydrogen bonds. Copolymer melts containing weak hydrogen-bonding side-groups (AA, CEA, and AP) behaved like unentangled melts, with no indication of network formation. For copolymers containing weak hydrogen bonding groups, hydrogen bond dynamics are fast compared to rheological chain relaxation. On the other hand, copolymers bearing strong hydrogen bonding groups (UPy) behaved as soft, elastic solids. The rheologically distinct behavior of UPy-containing copolymers is attributed to dimer lifetimes exceeding the experimental timescale. Considering the behavior of strongly and weakly binding copolymers together, we can conclude that side-group dimerization alone is not sufficient to form a mechanically relevant network.

The results presented here are relevant to developing adaptable materials including shape-memory polymers, self-healing materials, damping materials and adhesives that utilize hydrogen bonding to influence bulk mechanical properties. This study highlights the complexity of hydrogen bonding in melts and elastomers. Other factors such as side-group molecular structure, polarity, microphase segregation, etc., may have greater influence on viscoelastic properties than hydrogen bonding dimerization. Future comparative studies involving a single polymer backbone are needed to elucidate structure-property relationships of hydrogen bonding polymers and to better define the threshold hydrogen-bond strength for network formation within specific systems. This study also raises important questions regarding hydrogen bonding
dynamics within the glassy state. Experiments are needed to quantify free volume, molecular motion, and structural reorganization within a hydrogen bonded glass.

3.5 Methods.

**Quantum Mechanical Calculations.** Geometry optimizations were performed using the Gaussian 09 software package. Density functional theory with an empirical correction for dispersion (B97D) was used with the 6-31G* basis set and the default polarizable PCM continuum solvent model. Solvent parameters for butylethanoate, one of predefined solvents, were chosen except for the dielectric constant which was set to that of butylacrylate (5.38).

**Materials.** Dimethyl formamide (DMF), 2-amino-4-hydroxyl-6-methyl pyridine (AHMP), 2-aminopyridine, acryloyl chloride, and 1-methyl-2-pyrrolidone (NMP) were obtained from Alfa Aesar. Hexane was obtained from Macron. Ethyl acetate, diethyl ether, methanol, and isopropyl alcohol were obtained from Fisher Scientific. Azobisisobutyronitrile (AIBN), aminoethanol, trimethylpropane trimethyacrylate (TMPTMA) and 2-isocyanatoethyl methacrylate (ICEMA) were obtained from Sigma Aldrich. These reagents were all used as-received, without further purification. Acrylic acid was obtained from Alfa Aesar and distilled immediately prior to use. Toluene and chloroform were obtained from JT Baker and purified using a PureSolv PS-MD-3 monomer purification system. Triethylamine was obtained from Sigma Aldrich, dried over KOH and then distilled. N-butyl acrylate (BA) and carboxyethyl acrylate (CEA)
were obtained from Sigma Aldrich and distilled immediately prior to use. The UPy-substituted methacrylate monomer and acrylamidopyridine were prepared according to the literature.

**Polymer Synthesis.** Linear copolymers were prepared using conventional free-radical polymerization. As an example, a copolymer containing ~2mol% UPy monomer was prepared as follows: freshly distilled n-butyl acrylate monomer (5 g, 39.1 mmol) was first added to a round bottom flask. UPy monomer (223.2 mg, 0.8 mmol) and 30 ml DMF were sequentially added, and dry nitrogen was bubbled through the resulting solution for 20 minutes. The flask was placed under nitrogen purge in an oil bath set at 60 °C. AIBN (32.7 mg, 0.2 mmol) dissolved in 1 ml of DMF was added drop-wise, and the reaction proceeded for 6 hours. Polymer purification involved precipitation of the reaction mixture in 10× excess cold methanol/water (10:1), reprecipitation in methanol/water, and vacuum drying for 48 hours at 65 °C. The final products were transparent with mechanical properties ranging from viscous polymer melts to soft elastomeric solids, depending on the comonomer type and concentration. A typical overall yield for the reaction was ~65% (3.3g). Chemical structures and monomer concentrations were determined using $^1$H NMR (Bruker 400) and molecular weight and polydispersity were measured by size exclusion chromatography (PolyAnalytik PAS103-L and PAS104-L GPC columns and Viscotek TPA301 detector) using THF as an eluent and polystyrene standards. FTIR analysis was also performed to qualitatively assess the state of hydrogen bonding (see Appendix A).
**Polymer Network Synthesis.** Lightly crosslinked networks bearing different levels of reversible side-group substitution were prepared using a custom mold consisting of a 1.5 mm thick silicone spacer with a 40 × 30 mm window sandwiched between two 1 mm thick quartz slides. As an example, a network polymer with 2 mol% UPy monomer in the feed and 0.5 mol% TMPTMA will be described. UPy monomer (89.6 mg, 0.32 mmol) was first dissolved in 2.1 ml NMP with mild heating. Freshly distilled and sparged n-butyl acrylate monomer (2 ml, 14.1 mmol) was then added along with the 0.5 mol% TMPTMA and 0.25 wt% 2,2-Dimethoxy-2-phenylacetophenone (DMPA). The photoinitiator concentration was selected so as to minimize the spatial variation of UV light intensity during cure. The mold was purged with dry nitrogen and then the monomer solution was transferred to the mold through a syringe equipped with a 20 gage needle. Samples were irradiated using an Oriel 66002 UV lamp equipped with a 150 W Hg bulb and an Edmund Optics UV360 filter. Samples were irradiated for 13 minutes (6.5 minutes each side) at an intensity of ~3.6 mW at 325 nm (measured using a Liconix 45PM laser power meter). These conditions were selected as they resulted in approximately 90% conversion for a linear polymer not containing the crosslinker (determined using \(^1\)H-NMR). Following irradiation, the swollen films were placed in a vacuum oven (65 °C/24 hours), subjected to 6 hours of soxhlet extraction, and dried for an additional 48 hours at 65 °C. The final sample masses for the rubbery, transparent network films ranged from 0.8 – 1.2g, which agreed with estimates based on mold volumes and monomer/solvent feed ratios. Chemical characterization of resulting
networks was accomplished using elemental analysis and infrared spectroscopy (see Appendix A).

**Thermal Analysis.** Thermal characterization was performed on dry samples using a TA Instruments Q2000 Differential Scanning Calorimeter (DSC). Approximately 10 mg of sample was placed in a hermetically sealed aluminum DSC pan and subjected to a heat/cool/heat cycle over the temperature range -60 – 150°C at a linear heating rate of 5 °C/min. The polymer glass transition temperature was determined from the second heating curve and analyzed using the commercially available Universal Analysis software (TA Instruments).

**Dynamic Mechanical Analysis.** The viscoelastic behavior of linear polymers was evaluated using a TA Instruments DHR-2 rheometer equipped with a Peltier plate. To ensure accuracy the instrument calibration was verified periodically during the course of experimentation by measuring the crossover modulus and crossover frequency of a traceable silicone standard (TA instruments 700.01011 PDMS Standard). A parallel plate, 25 mm diameter tool with a 1000 micron gap was used for all experiments.

The thermal behavior was characterized by performing temperature ramps from 25 to 150°C at constant frequency (1Hz) (see Appendix A). Frequency scans were obtained by subjecting samples to oscillatory shear rates (0.1-100 rad/sec) in the linear viscoelastic regime over the temperature range of 5-145 °C in 10 °C increments. Mastercurves at a reference temperature of 25°C were generated using time temperature superposition (TTS) using the commercially available software package TRIOS (TA Instruments). A frequency sweep conducted at 25°C following experimentation matched
the curve measured at the beginning of the experiment indicating that these polymers had not degraded during experimentation.

The viscoelastic behavior of network polymers was performed using a Perkin Elmer DMA 8000 dynamic mechanical analyzer (DMA). Samples were measured in tensile mode with a 2 mm gage length. Mastercurves were obtained using the same frequency and temperature ranges as described for polymer melts. Resulting curves were qualitatively similar to temperature scans recorded at 1Hz. TTS was performed using commercially available software supplied by Perkin Elmer.

**Shape-memory Studies.** Shape-memory behavior of network polymers was studied using a Perkin Elmer Diamond TMA thermomechanical analyzer (TMA) equipped with a liquid nitrogen cooling unit. Samples ∼1 mm thick × 3-4 mm wide and a gage length of 5 mm were measured in tension according to a specified thermal/force program. It was necessary to contemplate the differences in material behavior for the different crosslinked samples in the experimental design of the SMP program. For instance, the applied stress at the beginning of the experiment was varied accordingly in order to maintain a constant strain (∼23%). Also, the crosslinked specimens with low bond strength displayed a reduced fracture resistance when subjected to strains at high temperature. Therefore the value of $T_{\text{max}} = 85 \, ^{\circ}C$ was used for the UPy-containing samples, but had to be decreased to $62 \, ^{\circ}C$ for the low bond strength samples and $52 ^{\circ}C$ for the PBA-X sample to avoid breakage in the TMA grips.

An important metric used to define the ability of the material to retain its temporary shape is the strain fixity ratio, $R_{f,t} = \varepsilon_{m}(t)/\varepsilon_{m}$, where $\varepsilon_{m}$ is the programmed
strain, and \( \varepsilon_a(t) \) is the instantaneous strain at some time following removal of the applied load.
3.6 References


Chapter 4: Synthesis, Swelling Behavior, and Viscoelastic Properties of Functional Poly(hydroxyethyl methacrylate) with Ureidopyrimidinone Side-groups

4.1 Introduction.

In the previous chapter, molecular parameters such the strength of the hydrogen bonding group and the stiffness and length of the side-group were shown to influence the rheology of a hydrophobic polymer. In this chapter we turn our attention to a hydrophilic polymer copolymerized with strongly hydrogen bonding side-groups and study the influence of microenvironment on the resulting swelling and viscoelastic properties.

Hydrogels are important biomaterials comprising of three-dimensional hydrophilic networks that swell upon immersion in water, forming highly permeable, soft solids. Improving control over hydrogel swelling and viscoelastic properties is essential for advancing biomedical applications in areas such as wound dressing\textsuperscript{1,2}, prosthetics\textsuperscript{3,4}, tissue engineering scaffolds\textsuperscript{5,6}, as well as drug delivery and release systems.\textsuperscript{7}

Conventional hydrogels, when swollen, are typically weak and brittle because they cannot effectively dissipate energy. However, a swollen hydrogel’s modulus and toughness can be substantially improved by introducing untreated nanoparticles\textsuperscript{8}, surface-active inorganic nanoparticles\textsuperscript{9,10} and by employing “double network” topologies to
eliminate network heterogeneity.\textsuperscript{11} Recently, hydrophobic associating groups have been integrated into hydrogels.\textsuperscript{12,13} Such hydrophobic groups form temporary junctions that are effective in dissipating energy. The current study examines how site-specific, reversibly binding functional groups can modify swelling and viscoelastic properties of poly(hydroxyethyl methacrylate) (poly(HEMA)), a well-known hydrophilic polymer.

Multiple hydrogen bonding motifs have been extensively applied to engineer supramolecular polymers and networks.\textsuperscript{14,15} The ureidopyrimidinone (UPy) group, for example, provides directionality and strength through an array of H-bonding donors and acceptors (DDAA).\textsuperscript{16} UPy groups are popular synthons because they are easily introduced onto polymer chains as end-groups and side-groups, and they are capable of self-dimerization with remarkably high association constants. We have recently investigated the viscoelastic properties of low glass transition temperature polymers and elastomers that contain UPy-terminated side-groups.\textsuperscript{17-19} The combination of covalent and non-covalent crosslinks gives rise to a broad dynamic viscoelastic transition, forming the basis for novel shape-memory elastomers.

The efficacy of hydrogen bonding depends on the polarity and mobility of the local chemical environment. Density functional theory studies of UPy binding indicate that dimerization should not occur in water, although dimerization readily occurs in chloroform.\textsuperscript{20} However, UPy association has been observed in water-swollen systems involving microphase segregated environments. For example, the non-polar microenvironments within UPy-containing block copolymer pluronic and aliphatic dendritic dimers promote UPy dimerization.\textsuperscript{21,22} Structural studies of oligo(ethylene
oxide) (oligoEO) systems with UPy end-groups, separated by aliphatic spacers, have shown that backfolding of the oligoEO chain can bond with UPy, interfering with dimerization.\textsuperscript{23} Clearly, dimerization of H-bonding motifs within water-swollen environments depends on local composition, structure, and dynamics; and these relationships are not completely understood.

Here we report the synthesis and properties of nearly linear poly(hydroxyethyl methacrylate) (poly(HEMA)) functionalized with UPy side-groups. A controlled radical polymerization technique was employed to prepare samples at low molecular weights to minimize chain entanglement effects and to limit disproportionation reactions that lead to inter-chain covalent bonds. Our objective is to understand how UPy side-groups can influence swelling and viscoelastic properties of poly(HEMA) and to assess the state of UPy side-group dimerization within a water-swollen hydrophilic polymer. Crosslinked poly(HEMA) is a technologically important, non-degradable hydrogel that can be processed into different forms and is best known for its role in contact lenses. Establishing control over poly(HEMA)’s viscoelastic properties will be helpful in developing novel biomaterials.\textsuperscript{24-27}

\textbf{4.2 Experimental.}

\textit{Materials.} Dimethyl formamide (DMF), 2-amino-4-hydroxyl-6-methyl pyridine (AHMP) and 1-methyl-2-pyrrolidone (NMP) were obtained from Alfa Aesar. Azobisisobutyronitrile (AIBN) and 2-isocyanatoethyl methacrylate (ICEMA) were obtained from Sigma Aldrich. UPy-substituted methacrylate monomer was prepared
according to the literature. The RAFT chain transfer agent, ethyl 2-phenyl-2-((phenylcarbonothioyl)thio)acetate (EPCTA), was provided by Bausch and Lomb. These reagents were all used as-received, without further purification. HEMA monomer, obtained from Alfa Aesar, was carefully purified to minimize the amount of ethylene glycol dimethacrylate (EGDMA) and methacrylic acid contained in the polymer. These impurities can lead to branching and crosslinking during polymerization. Purification involved passing through an alumina column followed by extraction with cyclohexane and fractional distillation. This procedure has been shown to reduce both EGDMA and methacrylic acid impurities to very low levels (~0.01%).

**Polymer Synthesis.** Nearly linear poly(HEMA) macromolecules bearing different levels of UPy side-group substitution were prepared using reversible addition fragmentation transfer (RAFT) polymerization according to Figure 4.1. Freshly distilled HEMA monomer (77 mmol) was added to a round bottom flask. UPy monomer (4.6 mmol), EPCTA (0.83 mmol) and 50 ml DMF were sequentially added, and dry nitrogen was bubbled through the resulting solution for 30 minutes. The flask was placed under nitrogen purge and transferred to an oil bath at 60 °C. AIBN (0.08 mmol) was dissolved in a small amount of DMF and added dropwise to the reaction flask, and the reaction proceeded for 21 hours (~ 80% conversion). The polymer product was precipitated in chloroform followed by centrifugation and vacuum drying, resulting in a red powder. A typical overall yield was ~65% (~6 g). Chemical structures and monomer concentrations were determined using 1H NMR (Bruker 400) and molecular weight and polydispersity.
were measured by size exclusion chromatography (Shimadzu CTO-20A GPC with RID-10A RI detector) using PMMA standards and DMF with 0.05 M LiBr as an eluent.

**Figure 4.1.** Synthesis and melt processing of poly(HEMA) copolymers containing UPy-side-groups.

**Thermal Analysis.** Thermal characterization was performed on dry samples using a TA Instruments Q2000 Differential Scanning Calorimeter (DSC). Samples were prepared by first swelling in deionized water with periodic water changes for at least one month to ensure all residual solvent and monomer had been extracted. Samples were then placed in a vacuum oven at 100 °C for several days to ensure all water was removed. Approximately 7-9 mg of sample was placed in a hermetically sealed aluminum DSC pan and subjected to a heat/cool/heat cycle over the temperature range 20 – 160 °C at a linear heating rate of 2 °C/min. The glass transition temperature was determined from the second heating curve and analyzed using the commercially available Universal Analysis software (TA Instruments).

**Swelling Studies.** Synthesized poly(HEMA) samples were formed into disks, and water-swelling was studied gravimetrically. Samples were melt processed into disks
(\( h = 1.0 \text{ mm}, D = 10.4 \text{ mm} \)) using a custom-made compression mold. Dried product powder (~ 150 mg) was charged into the preheated mold, and the mold was moved to an oven under full vacuum (135 °C, 30 min.). The mold was then transferred to a hydraulic press with heated platens (135 °C) and pressure was increased to about 30 MPa. With the pressure still applied, the platen heaters were turned off and allowed to cool to 110 °C. This temperature was chosen to eliminate crack formation during demolding. Transparent, glassy samples were immediately removed from the mold, and excess flash was removed from the samples. GPC was performed before and after molding and confirmed that negligible crosslinking had occurred during molding.

Swelling studies were performed on molded samples according to the following conditions. Sub-ambient and room temperature samples were prepared by individually exposing specimens to 125 mL of deionized water. A fine mesh stainless steel screen was used to suspend samples above the base of the container to ensure adequate water exposure to all sides of the specimen. Specimens were removed from water and blotted dry. The change in mass was recorded as a function of time. The water was exchanged every two to three days to remove trace amounts of residual monomer and solvent. Elevated temperature exposures were accomplished by immersing the entire solvent exposure vessel into a temperature-controlled oil bath. Sub-ambient exposures were performed by placing the sealed glass containers in a refrigerator. Experiments were repeated in duplicate or triplicate; in most instances the coefficient of variation is less than 10%.
The swelling ratio $S_w$ is defined as:

$$S_w = \frac{(m_w - m_0)}{m_0}$$  \hspace{1cm} (4.1)

where $m_w$ and $m_0$ are sample weights in their wet and original, dry states, respectively.

Since poly(HEMA) can be extracted following long swelling times \(^{33}\) (> 7 days), reported swelling ratios were verified by vacuum drying sample for several days and recalculating the swelling ratio on the dry basis. The equilibrium swelling ratio was determined in the same manner on samples that ceased to increase in weight following several days of exposure time.

**Rheological Characterization.** Rheology studies were performed on hydrated samples (> 3 months exposure time) using a TA Instruments DHR-2 rheometer equipped with a Peltier plate. A parallel plate, 25 mm diameter tool was used with a 1 mm gap. To prevent slip, 220 grit sandpaper was super-glued to both the tool and Peltier plate surfaces. Samples were subjected to oscillatory shear rates (0.1-100 rad/sec) in the linear viscoelastic regime over the temperature range of 5-75 °C in 10 °C increments. Resulting curves were shifted along the abscissa to a reference temperature of 35 °C using time temperature superposition (TTS) using the commercially available software package TRIOS (TA Instruments).

**Infrared Spectroscopy.** Infrared (IR) spectra in the mid IR range (750-4000 cm\(^{-1}\)) were collected for dry and swollen samples using a Shimadzu IRR Prestige-21 FT-IR equipped with a Pike Technologies MIRacle ATR unit. 64 scans were collected at 4 cm\(^{-1}\) resolution with background correction and analysis performed using Shimadzu IR
Solution software. Dry samples were tested as molding powders and swollen samples were blotted dry prior to analysis.

4.3 Results and Discussion.

Synthesis. Nearly linear poly(HEMA) containing different levels of UPy side-group substitution were prepared using RAFT polymerization. Table 4.1 summarizes molecular weight characteristics of synthesized polymers. Samples are named according to HG-Un where “n” indicates the mol % of UPy in the feed. The mol fraction of UPy monomer in product polymers was slightly lower than that in the feed, indicating a lower reactivity of UPy-containing monomer compared to HEMA monomer. Low polydispersity indices (PDI) and fairly consistent molecular weights were observed. It should be noted that a significant discrepancy between molecular weights obtained using gel permeation chromatography (GPC) and those obtained using end-group analysis from \(^1\)H NMR is evident from Table 4.1. A similar discrepancy was reported for poly(HEMA) synthesized using ATRP and is attributed to poly(HEMA) having a higher hydrodynamic volume than the GPC calibration standards.\(^{33,34}\) Assuming that every RAFT chain transfer agent is active and remains at the end of the chain, and neglecting side reactions, then the theoretical molecular weight at full conversion is about 13,000 g/mol for all reactions conducted. This value is closer to the molecular weight obtained using NMR.
<table>
<thead>
<tr>
<th>Sample</th>
<th>UPy feed (mol %)</th>
<th>UPy meas. (^a) (mol%)</th>
<th>GPC</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(M_n) (g/mol)</td>
<td>(M_w) (g/mol)</td>
</tr>
<tr>
<td>HG-U0</td>
<td>0</td>
<td>0</td>
<td>50,500</td>
<td>61,900</td>
</tr>
<tr>
<td>HG-U2</td>
<td>2</td>
<td>1.4</td>
<td>48,300</td>
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</tr>
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<td>HG-U6</td>
<td>6</td>
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<td>50,200</td>
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<td>10</td>
<td>8.6</td>
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<td>56,200</td>
</tr>
</tbody>
</table>

\(^a\) determined using \(^1\)H NMR.

RAFT polymerization was monitored as a function of time to study reaction kinetics. The logarithm of the ratio of instantaneous monomer concentration to initial monomer concentration, \(c/c_0\), is plotted against time in Figure 4.2a. The linearity of the data is consistent with pseudo-first-order kinetics associated with controlled radical polymerization. Single-mode GPC peaks (not shown) were observed at all reaction times, and molecular weights grew linearly with conversion, \(1-c/c_0\), as shown in Figure 4.2b. A least-square linear fit to the data intersects the ordinate at about 10 kg/mol. This kind of behavior is indicative of a hybrid polymerization, where the molecular weight first increases rapidly in a manner consistent with a conventional free radical polymerization, followed by a slow, steady growth associated with controlled radical polymerization.\(^35\)
Figure 4.2. Kinetic plots for RAFT polymerization of HG-U6: a) reduced monomer concentration versus time; b) Mn versus degree of conversion, (1-c/c₀). Dashed lines are linear least squares fit to data (R² > 0.99). The monomer / chain transfer agent / initiator molar ratio was 1000:10:1. Molecular weights were determined using GPC and were corrected for the discrepancy between GPC and NMR described in the text.

Covalent branching during polymerization was minimized to enable effects of reversible crosslinks to be directly studied. HEMA monomer was carefully purified to minimize diacrylate and acid impurities that may lead to crosslinking, and RAFT polymerization was chosen to limit disproportionation reactions. The RAFT technique also offers good control over molecular weight; and low molecular weight materials were prepared to minimize entanglement effects. Chain entanglements behave as physical crosslinks and could obfuscate the effects of reversible crosslinks. Several observations
suggest that nearly linear poly(HEMA) was achieved. The number average molecular weight determined from end-group analysis agrees fairly well with the designed molecular weight of 13,000 g/mol. Furthermore, after drying, all samples were melt-processable, and even after compression molding at 135 °C, GPC spectra were unchanged, indicating that an insignificant amount of crosslinking by ester formation from residual acrylic acid had occurred. Finally, the storage modulus curve of poly(HEMA) homopolymer did not show a significant plateau modulus at low frequency, again indicating the absence of appreciable crosslinking.

The measured glass transition temperature ($T_g$) for dried samples, listed in Table 4.1, increases with increasing UPy-concentration. A similar increase in $T_g$ was observed previously following end-functionalization of PMMA with UPy.$^{36}$ The $T_g$ of poly(HEMA) is in the range of ~ 90-110 °C.$^{37-39}$ The slightly lower $T_g$ observed for poly(HEMA) homopolymer in this study is thought to be a consequence of its near-linear structure and relatively low molecular weight.

**Water Swelling Behavior.** The initial water-swelling dynamics of two representative samples with different UPy-contents are shown in Figure 4.3. Data were fit to the power-law rate expression, $S_w = k t^n$, where $k$ is a rate constant, $t$ is experimental time (minutes), and $n$ is a power-law exponent. At short times ($t < 24$ hrs), the data agreed with power-law scaling ($R^2 \geq 0.99$), with $n$ ranging between 0.43 and 0.48. Fickian diffusion corresponds to a power-law exponent of one-half, and, therefore water transport into the materials is nearly Fickian.$^{40}$ Figure 4.4a shows that the swelling rate constant $k$ decreases with increasing UPy-content. This indicates that, during short times
(t < 24 hrs), UPy side-groups retard poly(HEMA) chain relaxation or diffusive transport of water. The observed water absorption rate constants for poly(HEMA) are higher than those reported by others.\textsuperscript{41, 42} However, in those studies, HEMA monomer was not purified, and the prepared hydrogels likely contain crosslinks that should decrease swelling kinetics.

\textbf{Figure 4.3.} Examples of room temperature water swelling curves of UPy-modified polymers. Lines are least-square fits to the power-law equation $S_w = kt^n$.

Experiments at elevated temperatures indicate that early-time swelling is thermally activated. This is especially apparent for UPy-containing samples. Figure 4.4b displays a plot of $\ln k$ as a function of reciprocal temperature for \textbf{HG-U0} and \textbf{HG-U6}. The activation energy, determined by linear fitting to the data, of \textbf{HG-U6} (9.0 kJ/mol)
was approximately twice that of \textbf{HG-U0} (4.3 kJ/mol). Extrapolation of linear fits suggests that hydration kinetics of the two samples is nearly equal at about 100 °C.

Trends in initial swelling can be explained on the basis of UPy dissociation kinetics. Prior to swelling, UPy side-groups form a network of reversible crosslinks. Unlike covalent crosslinks, reversible crosslinks can dissociate at one locus and reform at another. The ability of crosslinks to rearrange can significantly retard polymer chain relaxation. For example, our group and others have previously shown that viscous relaxation in hydrophobic polymers bearing UPy side-groups is limited by the H-bonding dissociation rate.\footnote{18,28} For samples bearing UPy side-groups, swelling is significantly slower and the thermal activation barrier is higher. Higher temperatures correspond to faster side-group rearrangement thereby hastening viscous relaxation, and, consequently, swelling.
Figure 4.4. Influence of UPy-content on initial swelling (t < 24 hrs) of poly(HEMA) copolymers. (a) swelling rate constant versus mol% UPy-content from $^1$H NMR for experiments conducted at room temperature, and (b) swelling rate constants versus inverse temperature for HG-U0 and HG-U6.
A plot of the swelling ratio versus time over all experimental times is shown in Figure 4.5. **HG-U0** displays a single hydration process followed by attainment of equilibrium swelling of ~ 63 wt% in approximately one day. For this sample, the water content did not change, even after six months of exposure. In contrast, UPy-containing samples display a two-stage swelling process. A rapid increase in water content occurred over the first several days of exposure followed by a second, slower absorption process that continued, in some cases even after several months. UPy-containing samples swell more than poly(HEMA) homopolymer after long exposure times, and the attained swelling ratios increase with increasing UPy-content for the 0, 2, and 6% samples. Even after this long exposure time, **HG-U6** and **HG-U10** appear not to be at equilibrium, perhaps explaining why **HG-U10** has a lower swelling ratio than the **HG-U6** material in Figure 4.5a.

While equilibrium swelling at room temperature was not attained following months of exposure, equilibrium swelling could be achieved in less than 15 days when swelling was conducted at temperatures above 40 °C. The elevated temperature equilibrium water contents $S_{w_e}$ for **HG-U0** and **HG-U6** are shown in Figure 4.5b. The equilibrium swelling values for both **HG-U0** and **HG-U6** appear to be insensitive to temperature over the range investigated. Poly(HEMA) homopolymer has been shown to exhibit a relatively small temperature dependence (about 3-4wt%) with a minimum equilibrium swelling value at around 60°C. The weak dependence on temperature in our data is attributed to experimental error from our measurement technique. For **HG-**
Figure 4.5. Influence of UPy-content on equilibrium swelling of poly(HEMA) copolymers: (a) swelling ratio of UPy-containing polymers versus time for experiments conducted at room temperature, and (b) equilibrium swelling versus temperature for HG-U0 and HG-U6. Error bars correspond to the standard deviation of multiple swollen specimens.

HG-U6, the insensitivity to temperature might be expected because UPy dimerization strongly favors the associated state, even as high as 120 °C.\textsuperscript{44}

Figure 4.5b indicates that HG-U6 exhibits greater equilibrium swelling than poly(HEMA) at all temperatures investigated. This was an unexpected result since the UPy monomer is hydrophobic. Peppas and coworkers showed that a decrease in equilibrium swelling is observed when a hydrophobic monomer such as methyl
methacrylate (MMA) is copolymerized with HEMA, whereas copolymerization with hydrophilic monomers such as N-vinyl-2-pyrrolidone (NVP) and N,N-dimethylacrylamide (DMac) resulted in increased swelling. One explanation for the heightened swelling observed in the current study is that the UPy group, which is quite hydrophobic and exhibits poor room temperature solubility in even some of the best polar solvents, disrupts poly(HEMA)’s native hydrophobic secondary structure.

Poly(HEMA)’s ability to absorb water is based on hydrogen bonding interactions between pendant hydroxyl groups and water molecules. The morphology of swollen poly(HEMA) is described as being composed of a secondary, noncovalent network based on hydrophobic interactions from the \( \alpha \)-methyl group and/or the polymer backbone. Ratner and Miller proposed an alternative explanation describing the secondary, noncovalent network as hydrogen-bonded hydroxyl groups buried in water-excluded regions. An insensitivity of swelling to the degree of crosslinking suggests that the secondary structure is primarily responsible for the observed swelling behavior. We suspect that hydrophobic UPy side-groups occupy water-excluded regions, disrupting poly(HEMA)’s native structure. For example, side-groups may interfere with poly(HEMA)’s backbone interaction or may increase the availability of pendent hydroxyl groups to interact with water.

**Rheological Behavior.** Master curves from oscillatory shear studies are displayed in Figure 4.6. The knee in the material’s storage modulus \( G' \) (at about 10-50 Pa) indicates the onset of temporary crosslinks such as chain entanglements. For UPy-containing samples, this knee occurs at significantly lower frequencies. One explanation
for this behavior is that UPy hydrogen bonded dimers act as chain entanglements or temporary crosslinks. At frequencies beyond the knee, the storage modulus increases sharply and begins to plateau as the polymer’s relaxation time-scale exceeds that of the applied oscillatory shear. Remarkably, the UPy side-groups affect the storage modulus at all frequencies—shifting the entire curve to lower frequencies. UPy side-groups affect the loss modulus $G''$ curves in a similar way.

Both HG-U10 and HG-U6 exhibit a crossover in $G'$ over $G''$ indicating solid-like behavior whereas HG-U0 and HG-U2 display liquid-like behavior over all frequencies and temperatures investigated. In UPy-functionalized hydrophobic polymers, hydrogen bonding of UPy groups can result in network formation at relatively low UPy concentrations. For example, Feldman and coworkers observed $G' > G''$, indicating solid-like behavior, over a similar range of frequencies for poly(butyl acrylate)s (PBA) containing as low as 4.1 mol% UPy. The molecular weight of PBA was beneath the entanglement molecular weight and network formation could be attributed to UPy interactions and not chain entanglements. In the current study, the absence of solid-like behavior in samples with low UPy-content indicate a reduced effectiveness of UPy-binding compared to the PBA study.
Figure 4.6. Plots of a) storage modulus, b) loss modulus, and c) loss ratio for synthesized polymers. Data were shifted to form master curves at a reference temperature $T_{ref} = 35^\circ C$.

The complex viscosity $\eta^*$, calculated by:

$$
\eta^*(\omega) = \frac{G''}{\omega} - i\frac{G'}{\omega},
$$

(4.2)
is plotted versus frequency in Figure 4.7a. At low frequencies, $\eta^*$ is independent of frequency, defining the material’s zero-shear viscosity, $\eta_0^*$. UPy side-groups increase the zero-shear viscosity by up to four orders of magnitude. The zero-shear viscosity increases in an exponential fashion with increasing UPy-content (Figure 4.7b), an observation made for other polymers bearing reversibly associating hydrogen bonded side-groups,\textsuperscript{49, 50} and may suggest that UPy side-groups act like chain entanglements. With increasing frequency, shear thinning occurs and is attributed to the inability of stretched chains with anisotropic backbone configurations to relax over the time-scale of oscillatory shear. Shear thinning is significantly enhanced in samples containing UPy side-groups. The complex viscosity in the shear-thinning region was fitted using the Ostwald–de Waele power-law equation:

$$\eta^*(\omega) = c \omega^{x-1}$$  \hspace{1cm} (4.3)

where $\omega$ is the frequency, $c$ is the consistency index, and $x$ is a power-law index that is less than one for shear-thinning fluids. Figure 4.7c, shows that the power-law index decreases with increasing UPy-content, indicating a more non-Newtonian response with increasing UPy-concentration. An explanation for enhanced shear thinning is that, above a characteristic frequency, the rate of deformation exceeds the UPy dimerization rate.
Figure 4.7. Plots of a) complex viscosity, b) zero shear viscosity and c) power-law index as a function of UPy-content from $^1$H NMR for synthesized materials.

The rheology data shows strong similarities to the previously mentioned studies involving hydrophobic polymers bearing UPy side-groups, suggesting that UPy side-group association occurs in poly(HEMA)’s complex hydrated environment. At low temperatures, functionalized materials behave like highly viscous liquids, and, at high temperatures, viscous relaxation is accelerated. The characteristic time associated with
the transition from Newtonian to shear-thinning behavior increases from ~1 s for \textbf{HG-U0} to over $10^4$ s for \textbf{HG-U10}. Shift factors ($a_T$) determined using TTS were plotted versus inverse temperature to obtain thermal activation energies ($E_a$). As shown in Figure 4.8, a quality fit was obtained ($R^2 > 0.99$) for each material, and the activation energy increases linearly with increasing UPy-content. This behavior is comparable to that observed in poly(butyl acrylate) copolymers and crosslinked networks bearing UPy.\textsuperscript{17,48} We attribute the increasing trend in activation energy to cooperative dynamics of UPy binding, and we suspect that the secondary structure of poly(HEMA) may further enhance UPy association and cooperativity in these materials.

**Infrared Spectroscopy.** The state of hydrogen bonding of \textbf{HG-U0} and \textbf{HG-U10} in dry and swollen states was studied using IR spectroscopy. The N-H stretch (3212 and 3147 cm\textsuperscript{-1})\textsuperscript{51} and the isocytosine carbonyl stretch ($\sim 1702$ cm\textsuperscript{-1}) were not observed due to interferences by both water and poly(HEMA)’s strong hydroxyl absorbance for the former and by acrylic carbonyl groups in various bound states for the latter. However, absorptions attributed to UPy’s urea carbonyl ($\sim 1667$ cm\textsuperscript{-1}) and amide II band ($\sim 1580$ cm\textsuperscript{-1}) associated with C-N stretching and C-N-H bending are both evident in \textbf{HG-U10} and are depicted in Figure 4.9.\textsuperscript{52} Although the urea absorption is present in both dry and hydrated \textbf{HG-U10}, it cannot be used to examine the state of hydrogen bonding—an interference peak around 1650 cm\textsuperscript{-1} appears in swollen samples, arising from water in various bound states in poly(HEMA).\textsuperscript{53} Fortunately, the amide II absorption is also sensitive to the state of hydrogen bonding.\textsuperscript{54} For UPy-containing samples, the amide II absorption is often observed and has been used to distinguish between dimerized and
Figure 4.8. Dependence of shear activation energy on UPy-content. a) Arrhenius plot of time-temperature-superposition shift factor $a_T$ and b) plot of activation energies versus UPy-content from $^1$H NMR for experiments.
monomeric forms.\textsuperscript{55} Appel et al. recently observed that the amide II band shifts to lower wavenumbers when UPy model compounds are heated, presumably disrupting UPy dimers.\textsuperscript{52} An earlier study showed that competitive binding of UPy with ethylene oxide groups results in a similar shift, from 1580 cm\textsuperscript{-1} to 1560 cm\textsuperscript{-1}.\textsuperscript{23,56} The presence of the amide II peak and the absence of a shift upon hydration confirms that some hydrogen bonded dimers exist in the swollen state.

\textbf{Figure 4.9.} FTIR spectra showing the amide II region for dry HG-U0 (top), dry HG-U10 (middle), and swollen HG-U10 samples. Curves have been shifted vertically for clarity.
4.4 Conclusions

This study demonstrates how UPy side-groups can modify a technologically important hydrophilic polymer’s swelling and viscoelastic properties. RAFT polymerization was applied to functionalize near-linear poly(HEMA) macromolecules with strong hydrogen bonding groups. Ureidopyrimidinone (UPy) side-groups significantly decrease the rate of water absorption at early times (< 24 h) and prolong the attainment of equilibrium swelling. These observations are consistent with the idea that UPy-dimers form a hydrogen-bonded, reversible network which retards swelling due to imposed osmotic stresses. The equilibrium degree of swelling increases with increasing UPy-content, and we suspect that hydrophobic UPy-groups may interfere with poly(HEMA)’s native secondary structure. Rheology studies of water-swollen UPy-containing materials showed that the zero-shear viscosity exponentially increases with UPy-content. The shear activation energy was found to scale linearly with UPy-content, suggesting cooperative dynamics of UPy association. These results are similar to those found for UPy-modified hydrophobic polymers and suggest that UPy dimerization is relevant in hydrated poly(HEMA), despite competitive H-bonding with water. The use of UPy dimerization to control viscous relaxation could be valuable for injectable polymers or surgical biomaterials that fill voids and become more solid-like once introduced into the body. FTIR studies provided further evidence of UPy dimerization within poly(HEMA)’s water-swollen state. To fully understand swelling and viscoelastic properties within water-swollen hydrogels will require careful study of the interplay between poly(HEMA)s microstructural organization and UPy binding. Further
modification of this or other hydrophilic polymers with reversibly binding groups will be valuable in developing end-use applications that demand controlled drug release, controlled swelling, improved mechanical damping, or improved toughness.
4.5 References


Chapter 5: A Transient Network, State-of-ease Model to Describe Shape-memory Behavior of Elastomers Bearing Dynamic Bonding Side-groups

5.1 Introduction.

Most developments in the field of shape-memory polymers have only occurred within the last few decades; and only a few efforts, dating back to the mid-90s, have been devoted to modeling the observed behavior. Most models rely on mechanical spring and dashpot style elements such as those discussed in Chapter 1. For example, Tobushi and coworkers\(^1,2\) have demonstrated that the addition of a friction element to the standard linear solid (SLS) model can accurately predict various thermomechanical responses for amorphous SMP’s where \(T_g\) is used as the switching mechanism.

Criticism of mechanical analog models is that many attempts only qualitatively capture SMP behavior without providing a strong connection to factors influencing the underlying physical behavior of these systems. An alternative method to the modeling of SMPs is to utilize molecular variables through the use of thermodynamic arguments\(^3,4\) thereby providing a means to better predict SMP behavior from first principles. The work by Liu et al, later refined by Chen and Lagoudos is a notable example that will be briefly described.\(^5,7\) At the core of this model is that the polymer is composed of two distinct phases consisting of “frozen” and “active” bonds. Frozen bonds, which are the
majority below \( T_g \), prevent entropic stretching whereas active (soft) bonds allow for large scale chain conformational changes. Thus frozen bonds are related to internal energy whereas active bonds have an entropic origin. The temperature dependent SMP behavior is related to the temperature dependence of active bonds where entropic changes can be stored temporarily after unloading (i.e. a certain number of active bonds exist at the setting temperature that are transformed to frozen bonds when the load is removed).

While the bulk of the modeling work reported is focused on amorphous SMPs where \( T_g \) acts as the switching mechanism, models describing polymer crystallization as the switching mechanism have also been developed.\(^8\) Other, molecular switches to trigger SMP behavior have also been discussed in the literature such as those based on photo-reversible\(^9,10\) and ionomer groups.\(^11\) Noncovalent dynamic bonds such as those based on hydrogen bonding and certain metal-ligand covalent bonds provide yet another strategy to produce responsive materials.\(^12\) We have investigated the use and efficacy of hydrogen bonding groups as a means to alter the viscoelastic behavior of linear and network hydrophobic polymers, hydrophilic polymers\(^13,14\) as well as shape-memory polymer networks.\(^15,16\) For the latter we have investigated the influence of hydrogen bonding side-groups on the SMP and viscoelastic behavior of amorphous, low \( T_g \) polymers. Being well above \( T_g \), these polymers are either melts (linear polymers) or elastomers (polymer networks) under all test conditions and therefore the theories previously mentioned are not appropriate to describe the observed behavior as the rheological “thickening” mechanism is governed by very different physics.
We have demonstrated that the viscoelastic behavior of our SMP’s can be described qualitatively by a simple SLS type model. Our goal here is to develop and apply a mathematical relationship with physics more strongly based on molecular parameters. This effort will allow not only for predictive behavior but also will more adequately reveal the nature of the viscoelastic behavior observed for these interesting materials. In particular we demonstrate that the rheological properties of polymers bearing strong hydrogen bonding groups can be described through the use of a double-network based theory. Because all macromolecules are above $T_g$ we assume that the forces observed are entropic in origin. The permanent and temporary shapes of the SMP are thereby governed by rubber elasticity theory; except that the latter is composed of bonds with temporary lifetimes that are on the order of the measurement time scale. A consequence of the time-dependent nature of the hydrogen bonded network is that remodeling can occur and this has consequences on the temporary shape of the SMP. We have used a transient network based approach to satisfy this requirement. Following development of the model, its ability to predict creep, dynamic mechanical behavior, and finally isothermal steps of the shape-memory curve will be explored. The double network theory utilized is further justified by the emergence of a “state-of-ease” following removal of the load during SMP experiments, a phenomena that is predicted experimentally and observed in the model.
5.2 Model Development.

An idealized shape-memory curve for a low glass transition polymer bearing covalent crosslinks and strong hydrogen bonding side-groups is depicted in Figure 5.1. Note that the presence of covalent crosslinks allow for the establishment of a permanent shape whereas the noncovalent, strong H-bonding groups act as temporary crosslinks resulting from homocomplementary associations with long lifetimes. A simplified view of the molecular process is also depicted in Figure 5.1 as a cartoon describing the state of the pendant hydrogen bonding groups during each characteristic stage of the shape-memory cycle.

Prior to beginning the experiment the material is heated to a sufficiently high temperature where the hydrogen bonding dynamics are fast. Under these conditions the material responds as a soft rubber with crosslink density approximately equal to the concentration of covalent crosslinks in the network. When the material is stressed during stage 2 the fast H-bond dynamics allow for rearrangement. The material is then cooled to a lower temperature (Stage 3). During cooling the material lengthens slightly in accordance to the temperature dependence of the rubbery modulus which is governed by the entropy of elasticity. With a temperature reduction the hydrogen bonding dynamics become slowed such that the effective lifetime of a dimer is now on a time scale where their presence can be sensed. Provided that the interaction is sufficiently strong the dimerization of the hydrogen bonding groups can result in the formation of a temporary network. This is evident when the load is removed (stage 4) and the network responds instantaneously to a reduced strain. This “state-of-ease” is due to the force balance that
arises between two networks. The material then slowly recovers a portion of the strain due to rearrangement of the temporary network. Finally, the sample is reheated (stage 5) and the increased H-bond dynamics allow for a rapid recovery of the strain. Because these materials are essentially rubbers at all temperatures and contain covalent crosslinks the system exhibits high reversibility with nearly 100% of the strain recovered even after numerous cycles.\textsuperscript{16}

\textbf{Figure 5.1.} Idealized shape-memory curve for an elastomer bearing strong hydrogen bonding side-groups.

Given the presence of two distinct bond types we employ a double network model to describe the shape-memory behavior of these systems. A force balance can be formulated where an external stress, $\sigma_{ext}$ is balanced by the sum of the stresses resulting from the permanent, $\sigma_p$ and temporary networks, $\sigma_t$.

$$\sigma_{ext} = \sigma_p + \sigma_t$$  \hspace{1cm} (5.1)
Because our polymers are uniquely amorphous and above $T_g$ the nature of the mechanical reactionary force is derived solely from the change in the entropy of elasticity associated with the macromolecular chain deformation. Mathematically, the entropy of stretching can be expressed as:

$$\Delta S_{Strand} = \frac{-3k_B}{2Na^2}r^2$$  \hspace{1cm} (5.2)

where $k_B$ is Boltzmann’s constant, $N$ is the number of repeat units in the chain, $a$ is the bond length, and $r$ is the end-to-end distance of the polymer coil. From this is derived the well-known expression for the stress resulting from an affine deformation:

$$\sigma = \frac{V k_B T}{V} \left( \lambda^2 - \frac{1}{\lambda^2} \right)$$  \hspace{1cm} (5.3)

where $V$ is the volume, $T$ is the temperature, $\lambda$ is the extension ratio, and $\nu$ is the strand density. Equation 5.3 will be used as the expression to describe the stress resulting from stretching of the permanent network, $\sigma_p$.

Analogous to the classic “State-of-ease” models\textsuperscript{20-22} a force balance between two independent networks can give rise to a network deformation intermediate to the deformed and relaxed states. It is hypothesized that such a model would adequately predict the viscoelastic and resulting shape-memory behavior of polymers containing permanent crosslinks and reversibly associating groups, provided that the temporary nature of the reversibly associating groups is accounted for in the model.

In this model shape-memory fixation and any subsequent relaxation of that strain are balanced by the forces resulting from the deformation of the permanent and temporary networks; the former begin governed by the classic entropy of chain stretching
expression developed in equation 5.3 and the latter arising from a similar, yet distinct entropy of stretching expression which accounts for the temporary nature of the reversibly associating groups.

The stress resulting from the temporary network can be expressed as a constant multiplied by the product of the extension ratio term and a probability distribution function; the latter, which accounts for the temporary nature of the bonds:

$$p(t, \tau) = \delta(t - \tau)\exp(-kt) + k\exp(-k\tau)$$  \hspace{1cm} (5.4)

where $k$ is the rate constant (associated with the bond lifetime), $t$ is the experimental time scale, and $\tau$ is the reversible bond age (i.e. the elapsed time since the reversible bond was formed in the stress-free state).

Mathematically, the stress balance of the permanent and reversible bonds must be equal to an externally applied stress. After integrating over all possible values of $t$ and $\tau$ the following final expression for rubbery elasticity of a polymer containing permanent and reversibly associating net points is obtained:

$$v_1 \left( \lambda(t)^2 - \frac{1}{\lambda(t)} \right) + v_2 \int_0^t p(t, \tau) \left[ \frac{\lambda(t)^2}{\lambda(t-\tau)^2} - \frac{\lambda(t-\tau)}{\lambda(t)} \right] d\tau = \frac{\sigma}{k_B T}$$  \hspace{1cm} (5.5)

Note that the first term of the integral involving the delta function has an analytical solution:

$$v_2 \int_0^t \delta(t - \tau)\exp(-kt) \left[ \frac{\lambda(t)^2}{\lambda(t-\tau)^2} - \frac{\lambda(t-\tau)}{\lambda(t)} \right] d\tau = v_2 \exp(-kt) \left[ \frac{\lambda(t)^2}{\lambda^0} - \frac{\lambda^0}{\lambda(t)} \right]$$  \hspace{1cm} (5.6)
Substituting 5.4 and 5.6 into equation 5.5 yields the following final expression:

\[
\begin{align*}
\text{Covalent network} & \quad + v_2 \exp(-k_t) \left[ \frac{\lambda(t)}{\lambda^0} - \frac{\lambda^0}{\lambda(t)} \right] \\
\text{Delta function} & \quad \int_0^t k \exp(-k \tau) \left[ \frac{\lambda(\tau)}{\lambda(t-\tau)} - \frac{\lambda(t-\tau)}{\lambda(t)} \right] d\tau = \frac{\sigma}{k_BT}
\end{align*}
\]

Note that equation 5.7 is an equivalent expression to the transient network theory offered by Green and Tobolsky\textsuperscript{17} except that it includes an additional term to account for the presence of the covalent network. The delta function term can be interpreted as the component that pertains to those bonds initially formed at time, \( t=0 \). The delay integral term pertains to the population of new, stress-free bonds formed at a later time following the onset of the experiment and it is this term that allows for relaxations to occur. An implicit assumption to this model is that following dissociation reversible bonds immediately reform. Likewise, chain entanglements have been ignored assuming that all net points can be attributed solely to either permanent or reversible crosslinks. Thus another implicit assumption of this model is that the relaxation time associated with the temporary bonds is much greater than Rouse or reptation relaxation times.

Equation 5.7 was solved numerically using a computer program written using the commercial software package IGOR. Only the strand density for the reversible and irreversible crosslinks (\( v_1 \) and \( v_2 \)) and the rate constant \( k \) are required inputs to solve the stress balance shown in equation 5.7. As will be shown our numerical approach allows not only for a reasonable prediction of the stress/strain behavior but also allows for
further insight into the nature of the mechanical relaxations by plotting the time evolution of the covalent and temporary network components.

5.3 Results and Discussion.

Case I: Modeling of Simple Creep. Modeling results for tensile creep ($T=47\,^\circ C$) are presented in Figure 5.2 along with data reported from an earlier study$^{16}$ for a polymer bearing 2mol% UPy and 1.5mol% TMPTMA in the feed. For these samples a thermal polymerization technique in an open vessel was employed and therefore the composition in the feed likely differs from the final copolymers as a result of monomer evaporation during polymerization. In this case we employed equation 5.7 as a three parameter model where a curve fitting technique is applied to the experimental data to estimate the strand densities and rate constant. The strand density of the permanent network ($v_1$) was first determined by fitting the long time response of the material with the temporary network strand density ($v_2$)=0, since:

$$v_1 = \frac{\sigma}{k_bT} \left( \lambda(t)^2 - \frac{1}{\lambda(t)} \right)^{-1}$$

(5.8)

Using equation 5.8 a best fit value of approximately 4.5 moles of covalent strands per m$^3$ was obtained. The temporary network strand density can then be fit to the short time response and finally the rate constant $k$ fit to the experimental data to produce the desired decay between the two extremes. With this we obtain a value of $\sim 28$mol/m$^3$ and $k=0.2$ sec$^{-1}$. Using this technique we see good qualitative agreement with experimental data as indicated by the normalized residuals of no greater than 4%. It is notable to mention that
similar results were also obtained using a conventional three parameter standard linear solid model (SLS) with best fit parameters for the elastic and viscous components of the model (Figure 5.2). While the SLS model fit to experimental data is reasonable, it is not well connected to molecular variables and therefore the interpretation of the fit parameters are not useful. On the other hand our model offers the advantage of a connection to polymer architecture through the entropy of elasticity term. More specifically this model demonstrates how the instantaneous elastic response is a consequence of the presence of both networks and the time dependency is related to the kinetics of remodeling of the temporary network. Further, it is revealed that the source of this response is due to the entropy of stretching of a distribution of chains, each bearing its own stress history, and thus contributing uniquely to the overall temporary network force.

The contribution made by the permanent and temporary networks subjected to creep can be decoupled (Figure 5.3). The normalized stress response (\(\sigma/RT\)) is plotted as a function of time. As is shown the applied normalized stress of 3 mol/m\(^3\) is borne primarily by the reversible network at short times with a small contribution made by the permanent crosslinks. At later times the reversible network stress remodels and in doing so relaxes the stress. If the experiment were conducted for a sufficiently long time the system would achieve an equilibrium condition where only the permanent network bears all the stress and all reversible binding groups are in a stress-free state.
Figure 5.2. Comparison of experimental results for extension ratio ($\lambda$) and normalized residuals ($\varepsilon$) to state-of-ease model and standard linear solid (SLS) modeling results.

**Modeling Conditions:**
- $\sigma/RT=3\text{mol/m}^3$,
- $k=0.02\ \text{sec}^{-1}$,
- Initial extension ratio = 1.00,
- $v_1 = 4.5\ \text{mol of covalent strands/m}^3$,
- $v_2 = 28\ \text{mol of reversible strands/m}^3$,
- $T=47^\circ\text{C}$

Figure 5.3. Normalized stress response for each component as a function of experimental time. Note: Reversible network stress=delta function + delay integral.
Case II: Dynamic Mechanical Response. Experimentally we have shown that a hydrogen bonded network will only display network properties provided that the time scale of bond associations are on the order of the experimental timescale. This behavior is also captured in our model as is shown in Figure 5.4. Here the dynamic mechanical behavior of a shape-memory elastomer bearing an equal concentration of covalent and thermoreversible crosslinks with a relaxation time \((1/k)\) of 5 seconds is plotted at select frequencies spanning several decades. At low frequency \((0.002 \text{ rad/sec})\), the observed mechanical behavior is related primarily to the covalent network with no significant contribution provided by the temporary bonds. This is a result of the dynamics of hydrogen bonding—>the rate of deformation and therefore chain dynamics are relatively unaffected by the dynamic load. As the frequency is increased to \(0.02 \text{ rad/sec}\), the time scale of deformation comes on the order of the time scale of the temporary network relaxation. As shown the temporary network begins to respond to the applied load, though the permanent network still dominates the mechanical behavior. At this frequency the temporary network is nearly completely out of phase with the applied load. This model predicts that a network containing only covalent bonds will be in phase at all frequencies. Interestingly the primary network is also slightly out of phase owing to the mechanical damping of the temporary network. At \(\omega=0.2 \text{ rad/sec} = 1/\tau\) the temporary network contributes to an even greater extent to the mechanical response of the system. Also, the population of initially formed bonds begins to takes a longer time to relax though the dynamic nature of the system ensures that relaxation of the temporary network cannot take place and this behavior is captured by the delay integral. At this frequency
both networks are out of phase with the applied load to a greater extent than observed at 0.02 rad/sec. The condition of maximum damping is expected to occur at this frequency, though the phase lag of the temporary network is less than at 0.02 rad/sec. At even higher frequency (2 rad/sec) relaxation of temporal bonds formed at the beginning of the experiment are not fully relaxed after a single cycle. Additionally the temporary and covalent networks are close to being in-phase and they contribute nearly equally to the mechanical response of the material. At 200 rad/sec, the time rate of deformation greatly exceeds the rate of hydrogen bond dynamics and the temporal network behaves like a permanent network. This is evidenced both in the magnitude of the mechanical response and that both networks are in phase with the sinusoidal loading program. Likewise, over a single cycle there is insufficient time for even the originally formed bonds to relax at this rapid experimentally timescale.

The transient network dynamics during oscillatory experiments exhibit a unique start-up response but the ever changing stress field results in a steady state condition with regard to magnitude and position of strain. This is shown in Figure 5.5 for a polymer containing only reversible bonds. From 0 to \( \pi \) the delta function, which relates to the population of bonds that were present from the onset of the experiment, is dominant. As the experiment continues this population decreases in magnitude at the expense of bonds that dissociate and reform during the experiment (evidenced in the delay integral). Interestingly, the composite stress response of the transient network remains unchanged due to the ever changing stress. At sufficiently long times it is anticipated that
Figure 5.4. Dynamic mechanical behavior of shape-memory polymer bearing covalent and hydrogen bonding groups as a function of frequency.
the delta function would decay to zero though it will be inconsequential in terms of the macroscopically observed mechanical behavior.

The input stress and output strain are plotted for one complete stress cycle in Figure 5.6. In this example the strain lags the input stress by a phase angle $\delta$. For viscoelastic materials the storage ($E'$) relates to the elastic, Hookean response of the material while the loss ($E''$) modulus relates to the viscous, time-dependent component. The determination of $\delta$ allows for the determination of these two quantities using the following well-known relations:

\[
E' = \frac{\sigma}{\varepsilon} \cos \delta \tag{5.9}
\]

\[
E'' = \frac{\sigma}{\varepsilon} \sin \delta \tag{5.10}
\]

The loss decrement can also be determined according to the following:

\[
\tan \delta = \frac{E''}{E'} \tag{5.11}
\]

The ability of this model to quantitatively predict the dynamic mechanical behavior of a shape-memory elastomer is demonstrated by analyzing data taken from a recent report on the dynamic mechanical behavior of PBA bearing UPy and benzophenone (BP) moieties, the latter which can establish permanent crosslinks through a photo-crosslinking reaction mechanism. In this example we will examine the dynamic mechanical behavior of PBA bearing 2mol% UPy and 1 mol% BP.
Figure 5.5. Response of permanent and temporary network over several DMA cycles.

Note that the mechanical response of the initially formed bonds (delta function) decays while the signal attributed to bonds formed during the experiment (delay integral) increases. Note also that the overall mechanical response of the dynamic network reaches steady-state.

As we discussed in an earlier paper the temperature dependent modulus for these elastomers should be a function of the crosslink density according to the relation:

\[ E = 3\nu RT \]  

(5.12)

where \( \nu \) is the strand density, \( R \) is the gas constant, and \( T \) is the temperature. As discussed in the previous example, at low frequencies (or sufficiently high temperatures) hydrogen bonding dynamics should be rapid and therefore \( \nu \) should be attributable exclusively to the permanent crosslink density \( (\nu_f) \) whereas at higher frequencies (or low
temperatures) the modulus should be a function of both covalent and temporary
crosslinks ($v_1 + v_2$). As such modeling parameters were determined by first adjusting $v_1$
until the low frequency modulus obtained by modeling reasonably matched the
experimental value. Following this $v_2$ and $k$ were adjusted until a qualitatively
satisfactory fit was obtained. Using this method model parameters of 73 and 57 mol/m$^3$
and $k=0.2$ sec$^{-1}$ were obtained.

**Figure 5.6.** A. Dynamic stress-strain response for a shape-memory elastomer; B.
Zoomed-in view showing phase lag.
As shown the model satisfactorily predicts the high and low frequency limiting cases. For example, at low frequency it is expected that the modulus is related primarily to the permanent network. Given the value of $\nu_l=73$ mol/m$^3$ a modulus $\sim 600$ kPa is anticipated according to equation 5.12. Likewise at high frequency the rate of UPy dimerization is slow relative to the rate of deformation and therefore the modulus should be proportional to the total crosslink density (i.e. $\nu_l+\nu_2$). For $\nu=130$ mol/m$^3$ equation 5.12 predicts a high frequency modulus of $\sim 1.1$ MPa, which agrees well with experiment.

Because the compositions of these copolymers are well characterized it is expected that the crosslink densities determined by curve fitting should closely resemble theoretical predictions. During photopolymerization one BP group reacts to form a single tetrafunctional crosslink whereas two UPy hydrogen bonding groups (HB) are required to make one tetrafunctional crosslinker. Therefore $\nu_l$ and $\nu_2$ can be estimated based on the following:

\[
\nu_l = \frac{x_{BP} \cdot \rho}{m_{HB} \cdot x_{HB} + m_{BA} \cdot x_{BA} + m_{BP} \cdot x_{BP}} \quad (5.13)
\]

\[
\nu_2 = \frac{1}{2} \cdot \frac{x_{UPy} \cdot \rho}{m_{HB} \cdot x_{HB} + m_{BA} \cdot x_{BA} + m_{BP} \cdot x_{BP}} \quad (5.14)
\]

where $m_i$ is the molecular weight of the $i$th component, $x_j$ is the molar fraction of the $j$th component, and $\rho$ is the density of the polymer (taken to be 0.9 g/ml). Results based on feed and NMR ratios indicate a compositional range of 0.8 - 1 mol% for BP and 1.7-2
mol% for UPy. Thus the theoretical values of the strand density for BP and UPy are in the range 46-68 and 51-68 mol/m³ respectively which agrees well with the values determined according to the model fitting method described above.

**Figure 5.7.** Demonstrating ability of state-of-ease modeling results to predict dynamic mechanical behavior.

The transient network, state-of-ease model supports not only the limiting cases of the high and low modulus regimes but also provides a reasonable prediction of the transition region. Firstly it is notable that the peak value of tan delta determined experimentally is well approximated by the model both in magnitude and frequency.

**Modeling Conditions:** $\sigma/RT = \sin(\omega t)$,

$k = 0.2 \text{ sec}^{-1}$, Initial extension ratio $= 1.00$, $\nu_1 = 73$ mol of covalent strands / m³, $\nu_2 = 57$ mol of reversible strands / m³, $T = 60^\circ\text{C}$. 
(Figure 5.7). In fact the frequency where tan delta is at its maximum value is the reciprocal of the rate constant, \(k\). Therefore \(k\) can be interpreted as the inverse of the average effective bond lifetime. Interestingly it is revealed that tan delta is broader than that predicted by the model. This is thought to be a consequence of the use of a rate constant that represents a single relaxation time.

To further explore the model behavior in the transition regions we compare the model predictions to experimental data taken for a PBA linear copolymer containing approximately 2.2 mol% UPy. Based on NMR data and the observed plateau modulus value \((G_N)\) the strand density of reversible crosslinks was estimated to be in the range of 70-80 mol/m\(^3\). A fit of the model to this experimental data is shown in Figure 5.8. As shown, the model accurately captures the high frequency behavior of \(G'\) beyond the crossover frequency. Likewise, using a value of \(k=0.015\) sec\(^{-1}\) allows for a prediction of the crossover behavior. However, the model prediction fails to predict the low frequency behavior of \(G'\) and the behavior of \(G''\) at both high and low frequencies. Tanaka and Edwards\(^{23}\) modified the transient network theory to account for a chain breakage rate \(\beta\) and called the condition of constant chain breakage the Green Tobolsky limit (GT limit).\(^{24-26}\) At this limit the chain is considered to snap back from the junction at a constant rate, irrespective of its chain end-to-end distance. In this limit they find that the expression reduces to a Maxwell model:

\[
G'(\omega, T) = \nu k_B T \frac{\omega^2}{\omega^2 + \beta^2} \quad (5.15)
\]

\[
G'(\omega, T) = \nu k_B T \frac{k \cdot \omega}{\omega^2 + \beta^2} \quad (5.16)
\]
In our model, the chain breakage and recombination is embodied in the expression $\exp(-k\tau)$ where $k$ is the chain breakage rate. As such our model shows fairly good linearity when data taken from the low frequency regime is plotted according to the GT limit expressions above (Figure 5.9). Tanaka and Edwards suggested that a more realistic form of the chain breakage rate would be one that takes into account a distribution of relaxation times and molecular weight. Departure from the model behavior at high frequencies may be an indication that other relaxation processes also begin to become significant. For example we have shown experimentally that unentangled polymers bearing weak hydrogen bonds display Rouse-like behavior at intermediate frequencies and glassy behavior at even higher frequencies akin to that expected for conventional polymers. While our model in its current form agrees reasonably well with our experimental findings we suspect that a modification to include a more detailed expression for the chain breakage rate would improve the quality of fit to the experimental data.
**Figure 5.8.** Plot of $G'$ (red) and $G''$ (blue) for PBA linear copolymer bearing 2.2mol% UPy side-groups (solid lined) and model predictions (points).

**Case III: Isothermal Shape-memory Behavior.** The isothermal shape-memory behavior can also be predicted using this model (Figure 5.10). As is shown, this model is effective in predicting the instantaneous response of the polymer during high temperature loading (stage 2 of the shape-memory cycle). The instantaneous response following removal of the load (i.e. “State-of-ease”) and the subsequent creep behavior are also predicted by this model.
Figure 5.9. Plot of low frequency storage and loss modulus determined from “state-of-ease” model plotted as functions of equations 5.12 and 5.13. The good linearity obtained demonstrates that a Maxwell relaxation process is predicted by our model.

As discussed, it was necessary to apply curve fitting parameters that greatly differed from the expected values for the thermally polymerized samples. In a recent effort we showed that the state-of-ease value was a constant irrespective of the fixing temperature for a PBA containing 2mol% UPy and 0.5mol%TMPTMA in the feed. On the other hand the fixing temperature greatly influenced the creep behavior following load removal. These data are reproduced below along with modeling predictions. This model reveals that the temperature independence of the “state-of-ease” arises from the fact that at the instant the load is removed both networks behave as though are permanent. However, the subsequent creep behavior can be explained as arising from the temporary nature of the hydrogen bonded network. Interestingly, the nonlinear creep behavior is not fully
**Figure 5.10.** Demonstrating ability of model to predict isothermal shape-memory behavior.

**Figure 5.11.** Model prediction of “state-of-ease” and creep behavior of shape-memory relaxation following removal of the load at three fixing temperatures.
captured by the state-of-ease model. As is shown in Figure 5.11 the model’s ability to accurately predict the creep relaxation is reduced as the fixing temperature is increased.

It is suspected that this is due to the fact that stress relaxation in these systems is governed by a distribution of relaxation times, whereas the model in its current form only accounts for a single relaxation time. Nevertheless, the order of magnitude approximation provided by the model suggests that the observed behavior can be primarily attributed to the transient network dynamics. This is reflected in the fact that a logarithmic plot of the relaxation time vs. the reciprocal temperature exhibits good linearity ($R^2=0.99$) and predicts an activation energy of ~70kJ/mol which is of the right order, albeit somewhat lower than the experimental value reported for this material (~90kJ/mol).

Interestingly, this temperature-independent state-of-ease was not observed for elastomers bearing weaker carboxylic acids and aminopyridine side-groups, thus indicating that a true network was not obtained for those materials (Chapter 3). It is suspected that the physics governing networks bearing these weak hydrogen bonding groups would be better represented by the use of an SMP model where $T_g$ is used as the switching mechanism.

### 5.4 Conclusions.

In this work a double network model consisting of a permanent network and a reversible network composed of bonds that continuously reform under stress free conditions was presented. This model was shown to be effective in describing the
viscoelastic behavior of elastomers bearing strong hydrogen bonding groups including creep, dynamic mechanical behavior, and isothermal shape-memory behavior. Further this model was used to elucidate the role that each network plays in determining the mechanical behavior. The satisfactory behavior of this model should enable it to be used to predict the complex viscoelastic behavior of shape-memory gels and elastomers where strong reversibly associating dynamic bonds are used to alter the timescale of viscous relaxation processes.
5.5 References


Chapter 6: Future Work

6.1. Introduction.

In this chapter two areas for future work will be presented. The first involves the use of the noncovalent, thermoreversible binding Diels Alder (DA) group to form transient networks in bulk polymers. Some preliminary data concerning the bulk thermoreversibility of two different DA groups based on the furan and maleic anhydride Diels Alder (F-MA DA) adduct will be presented and some suggestions for extending this work will be discussed. A second opportunity for future research involves an investigation of the influence of reversibly associating groups on the observed glass transition temperature.

6.2. Polymers Bearing Diels Alder Side-groups to Improve Shape-memory Fixity.

One of the shortcomings of the use of hydrogen bonds, even strong ones like the UPy group, as the switching mechanism for shape-memory polymers is that the temporary nature of the bonds allow for relaxation to occur. This is demonstrated in Figure 3.13 for a PBA polymer bearing UPy side-groups. As is shown a fairly substantial
amount of creep is observed near room temperature and this will most certainly limit the number of viable commercial applications.

Alternative mechanisms to promote better shape fixity include the use of high $T_g$ amorphous or crystallizable chain segments. However, the use of these approaches result in stiff materials above the transition temperature. Further they require a relatively high concentration of the polymer group responsible for shape fixing to achieve a percolated network sufficient to pin the temporary shape.

One potential solution to produce soft, thermoresponsive shape-memory materials is to use stronger thermoreversible binding groups. Ideally this approach would be based on an alternative chemistry that could easily be turned on and off but that does not exhibit a time dependency. One potential motif that shows promise to achieve these goals is the Diels Alder bond. As mentioned in Chapter 1, these bonds have often been described as click-like implying a high level of efficiency. Also, their use in polymers is well established in the literature and therefore they are good candidates for use as a switching mechanism.

A few examples have been presented in the literature where DA units have been used as a strategy for shape-memory applications. In many instances the DA units are not used as the switching segment but instead are used to establish the permanent shape of the shape-memory material. For example a series of papers were recently published where a recyclable shape-memory polymer based on poly(lactic acid) (PLA) and a thermoreversible DA bond were reported.\textsuperscript{1,2} In this study multifunctional PLA macromers bearing furanyl groups were crosslinked with di- and tri-functional
crosslinkers bearing maleimidyl groups. As a control, a PLA based polymer crosslinked via conventional means (i.e. isocyanate chemistry) was also examined. Because the glass transition of the PLA was used as the switching mechanism, both the DA containing sample and control sample exhibited shape-memory behavior when heated to above the $T_g$ of PLA. However, the DA chemistry allows for recyclability, a feature not present in the covalently crosslinked control sample.

The thermoreversibility of the DA bond is well established, particularly in solution. However the thermoreversibility in the bulk still remains a question. For example, in solution the popular furan maleic anhydride DA bond is well known to favor the formation of cycloadducts at 50-60°C but favors the retro DA reaction to form the two reactants at higher temperature (ca. 120°C). It has been demonstrated that even higher temperatures (ca. 150-175°C) are required to form the retroDA reaction in the bulk and that the retro temperature is dependent on the structure of the group attached to the DA units.\(^3\) In one particularly interesting example Wouters et al showed that a coating based on the F-MA DA bond exhibited good reversibility; the coating exhibited a high modulus at room temperature, but would revert to a self-leveling liquid upon heating to approximately 175°C.\(^4\) The material displayed good reversibility when it was thermally cycled between 30-175°C several times. It was mentioned that the degree of reversibility was dependent on the structure of the segment adjacent to the DA group. In particular it was shown that structures with aromatic groups adjacent to the DA units showed poor reversibility as compared to those containing flexible, aliphatic groups.
A lack of thermoreversibility for bulk materials has also been observed by Syrett and coworkers. In their study cycloadducts based on both the F-MA DA and the anthracene-MA Diels Alder adducts exhibited less than ideal reversibility. Likewise, Wudl et al in their groundbreaking work on self-healing of polymer networks bearing the F-MA DA bond, displayed only 50% return of properties during self-healing. It was explained that the less than ideal healing behavior was a consequence of the manner of testing but one wonders if limitations of the DA bond in a bulk polymer may have had an influence on the reduced self-healing capability of the material.

Thus one potential area of future work is the study of the structure property relationships governing the DA bond to impart self-healing and shape-memory properties on bulk materials. The goal of this study would be to develop an understanding of the key variables that influence thermoreversibility of the DA bond. Factors that could be examined include:

1.) **The type of DA bond:** The F-MA DA bond represents one of the more well studied bonds. However, its high retroDA temperature may yield it unsatisfactory for certain applications, such as those requiring a lower transition temperature and/or for certain thermally sensitive polymer backbones. It is proposed that a cyclopentadiene adduct also be considered as it has a lower retroDA temperature (ca. 90°C).

2.) **Influence of the structure of the pendant group.** DSC results of a number of model compounds and the coating study by Wouters and coworkers both
suggest that the structure of the group directly attached to the DA functional
group influences the retroDA temperature and the thermoreversibility.

3.) *Chain attachment of both the diene and dienophile vs. the use of a difunctional
dienophile additive.* In many of the instances where good reversibility has been
cited, furan groups have been attached directly to the chain and a difunctional
dienophile has been incorporated as an additive.

Two monomers, based on the F-MA DA adduct have been synthesized. Monomer 1 was synthesized according to the method described by Syrett⁵ (see Figure 6.1) and a second, novel difunctional monomer was prepared as shown in Figure 6.2 (see Appendix D for ¹H-NMR results). Monomer 2 was produced by dissolving 1 molar equivalent of bismaleimide with excess furan (2x) in chloroform. While the reaction proceeded slowly at room temperature it did not go to completion even after several days. Stirring at 50°C for 5 days under nitrogen purge did allow for complete conversion of the bismaleimide. Purification was easily performed by precipitation in acetone (2x). The ¹H-NMR spectra indicates both endo and exo forms of the DA cycloadduct. One advantage of this approach is that networks made using these monomers will be stoichiometric balanced with respect to the two reactive groups. This has the advantage that all DA groups are paired at the onset of the experiment and that any losses in properties observed during the course of the experiment can be attributed to inefficiencies in the DA unit upon reforming the cycloadduct. This is in contrast to the common
approach taken for difunctional monomer additives, where a furan containing polymer is first produced followed by the addition of a bismaleimide.\(^9\)

Network polymers bearing approximately 2 mol% DA in the feed and 0.5mol% of the trifunctional TMPTMA crosslinker were prepared with PBA as the polymer backbone according to the thermal polymerization technique established by Li et al\(^{10}\) (Figure 6.2). The resulting polymers were subjected to oscillatory dynamic mechanical analysis.

Preliminary rheological results (Figure 6.3) suggest that the factors listed above are important in determining thermoreversibility in the bulk. For example, polymer 1 exhibited a relatively flat curve over the range 50°C to 200°C suggesting that a retroDA reaction did not occur. Also, the fact that the sample remained relatively stiff immediately following removal from the test apparatus at 200°C further indicates a lack of the Diels Alder retro reaction. This is in contrast to that displayed by polymer 2, where a high and low temperature modulus was observed, indicating a retroDA reaction had occurred. However, the high temperature plateau modulus of polymer 2 still exceeds that of a polymer bearing 1mol% TMPTMA crosslinker. Had all of the DA units undergone the retroDA reaction then the high temperature plateau modulus would be slightly lower than the polymer bearing 1mol% TMPTMA.
Figure 6.1. Synthetic Approach for Diels-Alder Monomer Preparation. A. Furan Maleic Anhydride Difunctional Monomer based on Syrett et al. B. Novel Diacrylate monomer based on bismaleimide.
A. Polymer 1

B. Polymer 2

Figure 6.2. Synthesis of network polymers bearing DA side-groups. A. Furan Maleic Anhydride Difunctional Monomer based on Syrett et al. B. Novel Diacrylate monomer based on bismaleimide.

These preliminary results support the idea that differences in the molecular structure of the DA side-group result in differences in the reversibility in the bulk. Further research in this area should reveal the important parameters that give rise to this reversibility. As a next step it is recommended that a bismaleimide linker be produced containing an aliphatic spacer. If the results follow that observed by Wouters and coworkers it is expected that good reversibility would be obtained. This would make for an interesting platform to study the structure property relationships of shape-memory polymers bearing the F-MA DA adduct.
Figure 6.3 Dynamic mechanical data for DA containing polymers and a network polymer containing only 1mol% TMPTMA. Note: Polymer 2 measured using shear rheometry with $E' = 3G'$ plotted.

6.3 Influence of hydrogen bonding group strength on the glass transition.

A second area proposed for future study pertains to the influence of monomer structure and hydrogen bonding strength on the glass transition temperature. As discussed in Chapter 3 if the strength of the hydrogen bond were exclusively important in determining the glass transition, then the UPy containing polymers would be expected to exhibit a significantly higher $T_g$ than that of the weaker binding groups. However, this was not observed but rather monomer structural factors such as the length of the pendant group, and the bulkiness of the side-group appeared to play at least as significant of a
role. This led us to the conclusion that hydrogen bond strength is less important than the equilibrium concentration of dimers below $T_g$ so long as the strength of the binding group exceeds $k_B T$.

To study this effect it is proposed that the copolymers bearing weak and strong HBSGs reported in Chapter 3 be subjected to the following additional analysis:

1.) **Temperature dependent FTIR:** In chapter 3 we mentioned that all samples exhibit characteristic IR spectra that indicate the presence of a high concentration of dimers. However, our work was performed using an ATR probe with data collected at room temperature. The use of ATR did not allow for the quantitative evaluation of the number of dimers formed. Carefully IR transmission measurements, performed as a function of temperature, such as those reported by Ostrowska and Narebska\textsuperscript{11} would allow for a better understanding of the number of hydrogen bonded groups as a function of temperature. This approach also has the added advantage that it would also allow for the experimental assessment of the binding energy in the polymer system.

2.) **Differential Scanning Calorimetry:** Our DSC results allowed for the experimental determination of the glass transition temperatures reported in Chapter 3 (see also Appendix A). This work could be extended by preparing copolymers over a wider range of HBSG concentrations. This would have two main advantages. The first is that it would allow for the use of models such as the one proposed by Kwei:\textsuperscript{12}

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2$$  \hspace{1cm} (6.1)
where $W_i$ is the weight fractions of $i$th constituent, $T_{gi}$ is the glass transition of the $i$th constituent, and $k$ and $q$ are fitting constants. The quantity $k_{gi}W_iW_2$ can be interpreted as the excess energy by which the average stabilization of the backbones in the blend (or copolymer) is greater than that of the corresponding homopolymers and therefore $q$ should be reflective of the interaction strength of the bond.\textsuperscript{13} This equation, while its intended purpose was to describe the behavior of polymer blends bearing hydrogen bonding interactions, has been successfully applied to copolymers bearing pendant hydrogen bonding groups as well.\textsuperscript{14,15} This would allow for a more accurate determination of the influence of the hydrogen bonding group on the glass transition. A second advantage to performing this study is that the change in heat capacity, $\Delta C_p$, and the breadth of the glass transition can also be related to the strength of the hydrogen bonding interaction.\textsuperscript{16} The synthesis of materials with increased side-group concentrations would also ensure that subtle changes in the heat capacity with increasing monomer concentration are elucidated. Unfortunately for the PBA homopolymer and several of the copolymers bearing low monomer concentrations we were not able to obtain reliable $\Delta C_p$ measurements due to a lack of a baseline stability for many of the samples prior to the glass transition (upon heating) and following the achievement of the glass transition (upon cooling) (See Appendix A). We suspect that this is a consequence of the low temperature limit of our current DSC system that utilizes an intercooler, as well as the relatively high heating rate employed (5°C/min). The use of a liquid nitrogen cooling unit should allow for lower
temperatures to be achieved thereby allowing for more stable baselines to be obtained.

3.) **Positron Annihilation Lifetime Spectroscopy**: Positron Annihilation Lifetime Spectroscopy (PALS) is a technique that allows for the measurement of the free volume in polymers. The difference in time between a positron emission and its annihilation is measured and three characteristic times are measured, each relating to different annihilation pathways. The time \( \tau_1 \) relates to the time for a positron to couple with an electron to form a parapositronium atom (p-PS), \( \tau_2 \) relates to the time for annihilation of free positrons, and \( \tau_3 \) to the time for a positron to couple with an electron to form an orthopositronium atom (o-PS). Because o-PS atoms tend to localize in areas of low electron density the characteristic time \( \tau_3 \) and the measured intensity \( I_3 \) can be used to estimate polymer free volume. It is envisioned that PALS would be applied to select samples of varying comonomer content (i.e. high and low concentrations of H-bonding groups) at temperatures above and below \( T_g \) and related to the DSC and FTIR data described above.

The results obtained from such experiments should make for an important contribution to the understanding of the nature of the glass transition of polymers bearing hydrogen bonding groups.
6.4 References

Chapter 7: Concluding Remarks

7.1 Concluding Remarks.

Polymers containing hydrogen bonding side-groups (HBSGs) can form transient supra-macromolecular networks that exhibit technologically useful viscoelastic properties. In this thesis the influence of different HBSGs on the dynamic behavior of functional poly(n-butyl acrylate) melts and crosslinked networks was investigated. To the best of our knowledge this is the first study where the influence of weak HBSGs on viscoelastic behavior is examined for a low glass transition model polymer system in the condensed phase. The use of side-groups of similar bond strength but different structure allowed us to decouple the influence of hydrogen bonding and structure and revealed that the rheological behavior of polymers bearing these weak HBSGs is derived primarily from \( T_g \) effects, even at sub ambient temperatures very near \( T_g \).

Random copolymers containing weak and strong HBSGs were synthesized and subjected to thermal and dynamic mechanical analysis. The glass transition temperature \( (T_g) \) increased nearly linearly with the HBSG concentration, and this effect was similar for both weak and strong binding groups. Copolymers containing weak HBSGs behaved as unentangled melts and exhibited higher storage and loss modulus with increasing amounts of binding group. In contrast, copolymers containing strong HBSGs behaved like entangled networks. Flow activation energies increased linearly with comonomer
content; and, for weak hydrogen bonding groups, they depended only on the departure from $T_g$. Similar behavior was observed in crosslinked films and this is the first study to directly examine the influence of hydrogen bonding groups in linear and network systems utilizing the same polymer backbone.

Differences between weak and strong HBSGs were also apparent from shape-memory cycles. To our knowledge, this is the first investigation of the combined role of hydrogen bonding strength and side-group structure on SMP properties. Polymers bearing strong HBSGs exhibited good shape-memory behavior at temperatures greatly exceeding the glass transition temperature whereas polymers bearing weak HBSGs showed little capacity to store energy at temperatures much above the glass transition. These results suggest that weak HBSGs raise $T_g$ but do not create a network.

A transient network model was developed to predict the time-dependent mechanical behavior of a shape-memory elastomer consisting of covalent crosslinks and strong hydrogen bonding groups. To our knowledge this is the first attempt to model shape-memory behavior for these types of network polymers using a thermodynamic approach. The model assumes continuous mechanical equilibrium between an applied stress and stresses of entropic origin arising from a permanent network and a second, independent network composed of reversible bonds. Bonds forming the reversible network are assumed to rearrange at a constant rate, and newly formed bonds are created in a stress-free state. This gives rise to a time-dependent distribution of bond ages and corresponding stresses, and both are accounted for in the model using a delay integral approach.
This model is capable of adequately describing creep, dynamic mechanical, and shape-memory responses of poly(butyl acrylate) copolymers bearing strong UPy hydrogen bonding groups. For creep it was demonstrated that the quality of fit to the experimental data was qualitatively similar to the three parameter standard linear solid (SLS) model. However, the primary benefit of our model is the strong connection to molecular variables afforded through the thermodynamic framework. In addition, the numerical approach employed allows for a thorough characterization of the role of reversible bonds. For example, the model was modified in order to predict the dynamic mechanical behavior thus allowing us to probe the role of the relaxation time relative to the rate of deformation. It was shown that at relatively low frequencies the presence of dimerized hydrogen bonding groups does not necessarily imply that they will be sensed in dynamic experiments. This result supports the hypothesis advanced in Chapter 3 to explain why polymers bearing weak hydrogen bonding side-groups, though present as dimers, do not contribute to the observed mechanical behavior. The phase lag between stress and strain allowed for the determination of storage and loss modulus values, and it was shown that these results quantitatively agree with theoretical predictions based on monomer feed ratios. While DMA predictions agree well with theory for the limiting cases of low and high frequency some departure from experiment was observed in the transition region. This is thought to be a consequence of the simplified expression for the rate constant used in our model. It was suggested that a more elaborate expression for the rate constant that assumes a distribution of relaxation times and considers molecular weight effects (for linear polymers) would more adequately describe the transition
behavior. The model also demonstrated the ability to replicate key stages of the shape-memory curve. Of particular interest was that the “state-of-ease” was found to be independent of the shape-memory fixing temperature for polymers bearing strong hydrogen bonding groups, a fact confirmed experimentally (Chapter 3). The limited capacity of the model to capture transient behavior was also revealed in the time-dependent creep behavior following the state-of-ease and became more prominent as the shape fixing temperature was increased.

UPy’s ability to self-associate to form hydrogen-bonded dimers (DDAA) in non-polar media was also established. This was accomplished by preparing a series of poly(hydroxyethyl methacrylate) (poly(HEMA)) polymers, with varying UPy side-group content, using a reversible addition-fragmentation chain transfer (RAFT) polymerization and measuring the swelling and viscoelastic properties. To the best of our knowledge this is the first example where the influence of water was evaluated on UPy containing hydrogels. Water swelling experiments revealed that UPy side-groups retard early time (< 24 h) Fickian-like swelling and lead to two-stage, temperature-dependent, water sorption. At longer times UPy side-groups promote water swelling. Rheological studies show that the material’s viscosity and viscous relaxation time both increase with increasing UPy-content. The activation energy of the shear-induced flow scales linearly with UPy-content, suggesting cooperative dynamics. These results are similar to observations made for hydrophobic polymers bearing hydrogen-bonding side-groups and suggest some UPy hydrogen-bonding occurs in hydrated poly(HEMA), despite competitive H-bonding with water. Experimental observations can be explained by
reversible association of UPy side-groups within water-excluded domains of poly(HEMA)’s secondary structure.

This thesis establishes new structure-property relationships for polymers bearing hydrogen bonding side-groups for both hydrophobic and hydrophilic polymers. It has been demonstrated that molecular variables such as the structure and binding strength of the side-group and the microenvironment where the hydrogen bonding groups reside, are critically important parameters in determining the observed thermal, mechanical, and transport properties.

Two areas of additional study were briefly presented in Chapter 6. This first involves the systematic study of the influence of thermoreversible covalent side-groups based on the Diels Alder (DA) cycloadduct. Such strong, thermoreversible interactions promise many of the benefits afforded by strong HBSGs while eliminating the time-dependent creep observed for hydrogen bonded systems. A second future work area outlined in Chapter 6 involves the study of the role of hydrogen bonding groups on the glass transition temperature.

The structure property relationships outlined in this work should serve as a platform for additional study. Additionally, the lessons learned in this thesis should serve as a guide to the development of new functional materials for specific engineering applications such as membranes, shape-memory materials, thermoplastic elastomers, self-healing materials, and functional hydrogels.
Appendix A: Supplemental Documents for Chapter 3

A.1. FTIR Characterization of Linear and Crosslinked Films.

Infrared (IR) spectra in the mid IR range (750-4000 cm\(^{-1}\)) were collected using a Shimadzu IRR Prestige-21 FT-IR equipped with a Pike Technologies MIRacle ATR unit. 64 scans were collected at 4 cm\(^{-1}\) resolution with background correction.

FTIR of Linear Polymers.

_Ureidopyrimidinone (UPy) containing copolymers:

Figure A.1. FTIR of UPy containing linear copolymers.

For PBA we observe a band centered around \(\sim 1730\) cm\(^{-1}\) attributed to the acrylate carbonyl. Several new peaks were observed with increasing UPy concentration. Of these
the characteristics UPy absorptions attributed to UPy’s isocytosine carbonyl stretch (~1702 cm\(^{-1}\)), urea carbonyl (~1667 cm\(^{-1}\)) and amide II band (~1590 cm\(^{-1}\)) associated with C-N stretching and C-N-H bending indicate that UPy groups are present as dimers. For more information concerning the IR peak references listed above it is recommended that the reader consult the following articles.\(^1\)-\(^5\)

**Carboxylic acid containing copolymers**

![Figure A.2. FTIR of carboxylic acid containing linear copolymers.](image)

For PBA a band centered around ~1730 cm\(^{-1}\) attributed to the acrylate carbonyl is observed. For copolymers bearing carboxylic acid side-groups the emergence of a shoulder centered around ~1710 cm\(^{-1}\) is observed. This peak increases in intensity with increasing carboxylic acid concentration and has been assigned to the carbonyl groups associated with hydrogen bonded acid dimers.\(^6\), \(^7\)
**Acrylamidopyridine (AP) containing copolymers:**

![FTIR spectrum of AP containing linear copolymers](image)

**Figure A.3.** FTIR of AP containing linear copolymers.

Several new peaks were observed in the FTIR that increased in intensity as the AP monomer concentration was increased. The state of hydrogen bonding of the NH---N bond in the AP precursor has been studied extensively and generally the NH stretch region for the 2-aminopyridine dimer is investigated as it exhibits a strong peak characteristic of a primary amine.\(^8\,^9\) Unfortunately, the NH stretch IR absorption is much less intense for a secondary amine. Given this, and that our copolymers bear relatively low concentrations of the acrylamidopyridine comonomer, it is fortuitous that a weak band at \(\sim 3320\,\text{cm}^{-1}\) is still resolvable (see inset) not present in the PBA homopolymer sample. The location of this band is in good agreement to that assigned to the NH---N hydrogen bond for hydrogen bonded proton of the 2-aminopyridine precursor.\(^10\)
AP is well known to form hydrogen bonds with other species as well, such as carboxylic acids.\textsuperscript{11,12} While acidic species should not be present in these copolymers, the presence of the amide linkage (CONH) could result in the formation of a hydrogen bond between the carbonyl oxygen and the secondary amine. The shoulder present in the range 1670-1690cm\(^{-1}\) occurs very near the same location as the solid AP monomer and we attribute this peak to the AP carbonyl group. It has been shown that for nylon 11 bearing amide linkages, hydrogen bonded amide carbonyl groups exhibit peaks at \(~1650\text{cm}^{-1}\), whereas “free” amide carbonyls show peaks at much higher frequencies (\(~1680\text{cm}^{-1}\)).\textsuperscript{13} Therefore we associate the peak centered at 1690cm\(^{-1}\) as belonging to free amide carbonyl groups. Taken together, these results suggest that the AP group is dimerized at room temperature.

\textit{FTIR of Crosslinked Polymers.}

Qualitatively similar results were obtained for crosslinked specimens as was observed for linear specimens. The results are provided below. It is recommended that the reader refer to the previous section for peak assignments and further discussion.
Figure A.4. FTIR of UPy containing networks.

Figure A.5. FTIR of AA containing networks.
Figure A.6. FTIR of AP containing networks.

A.2. Elemental Analysis of Linear and Crosslinked Films.

Procedure:

Elemental analysis (C, H, N) was performed according to the following procedure: Samples (~2 mg) were weighed with a PerkinElmer Model AD-6 Auto balance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Also all measurements were made on the same instrument on the same day.

The interpretation of elemental analysis of very pure substances generally involves the comparison of calculated to measured weight fractions of elements contained in a sample. Given that the side-groups are present in relatively low concentrations and consist of similar atoms to the butyl acrylate monomer (present as the primary component) we have elected to also analyze select linear polymers with known
compositions (determined using $^1$H-NMR) to serve as an additional comparison (see Table A.1).

**Results:**

The PBA-X sample shows good agreement to the theoretical prediction (C=65.6%, H=9.4%). In general, good agreement between linear and crosslinked samples indicates that the composition of the crosslinked films is approximately equal to the feed ratio. As is shown, the AA6 linear polymer sample (theoretical C=65.1wt%, H=9.2wt%) exhibits a similar C and H concentration to the crosslinked AA5-X sample, and a slightly higher C and H concentration compared to the CEA5-X (theoretical C=64.7%, H=9.1wt%). At even greater acrylic acid concentrations the experimental values for AA21-X agree reasonably well with the theoretical prediction (C=63.6wt%, H=8.9wt%). Very good agreement between the AP5 and AP5-X was observed, with the N concentration serving as a further indication of the presence of this monomer in the expected amounts. This is also indicated in the good agreement of the experimental result with the theoretical C, N, H values of 65.6, 1.1, and 9.1wt% respectively. This was also true for the UPy2 and UPy2-X samples where the experimental values agree reasonably well with the theoretical prediction for a 2mol% containing copolymer (C, N, and H are 65.0, 0.8, and 9.2wt% respectively).

These results, taken together with the IR and DSC results, indicate that the actual hydrogen bonding side-group concentration in crosslinked samples closely matches that of the feed composition.
<table>
<thead>
<tr>
<th>Sample</th>
<th>% Hydrogen Bonding Group (¹H-NMR)</th>
<th>Elemental Analysis Result, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>PBA-X</td>
<td>Unknown</td>
<td>65.6</td>
</tr>
<tr>
<td>AA6</td>
<td>5.6</td>
<td>64.6</td>
</tr>
<tr>
<td>AA5-X</td>
<td>Unknown</td>
<td>64.9</td>
</tr>
<tr>
<td>CEA5-X</td>
<td>Unknown</td>
<td>64.4</td>
</tr>
<tr>
<td>AA21-X</td>
<td>Unknown</td>
<td>63.1</td>
</tr>
<tr>
<td>AP5</td>
<td>5.2</td>
<td>65.3</td>
</tr>
<tr>
<td>AP5-X</td>
<td>Unknown</td>
<td>65.4</td>
</tr>
<tr>
<td>UPy2</td>
<td>2.2</td>
<td>64.6</td>
</tr>
<tr>
<td>UPy2-X</td>
<td>Unknown</td>
<td>64.6</td>
</tr>
</tbody>
</table>
A.3. Summary of Rheological $G'$ and $G''$ Mastercurves for All Linear Polymers

$G'$ and $G''$ for all linear copolymers are plotted below.

Figure A.7. Storage ($G'$) and Loss ($G''$) modulus for linear copolymers
Figure A.7. (continued) Storage ($G'$) and Loss ($G''$) modulus for linear copolymers
A.4. Storage Modulus and tan delta for AA5-X and CEA5-X crosslinked specimens.

Storage modulus and tan delta for samples AA5-X and CEA5-X are included below. As is shown, these materials exhibit similar viscoelastic behavior as the other network polymers bearing weak hydrogen bonding groups.

![Graph showing storage (E') and loss (E'') modulus for AA5-X and CEA5-X network polymers.]

Figure A.8. Storage (E') and Loss (E'') modulus for AA5-X and CEA5-X network polymers.

A.5. Curve fits for PBA homopolymer and select copolymers according to Arrhenius and Vogel-Fulcher-Tammann (VFT) equations.

Curve fitting was performed using the commercially available software program IGOR. As is discussed in chapter 3, the nonlinearity in the plot of ln a_T vs. 1/T is better captured by the VFT equation for PBA and copolymers bearing weak hydrogen bonds whereas the Arrhenius equation better captures the behavior for copolymers bearing high concentrations of UPy. In all cases the value of T_0 is taken to be T_g-52K according to
that found for a number of polymers.\textsuperscript{14} A qualitative assessment of the quality of fit is most apparent by comparing plots for each equation made on the same curve (see Chapter 3). The following curves show the curve fits according to $1/T$ and $1/(T-T_0)$ with fitting parameters listed (average +/-standard deviation). Interestingly, the PBA and copolymers bearing weak hydrogen bonding groups all display a concave up nonlinearity whereas the UPy1 (and UPy2) copolymers exhibit a concave down behavior. The UPy5 copolymer exhibits a strong linear dependence between $\ln a_T$ and the reciprocal temperature with very little concavity and poor conformance to the VFT equation.
### Arrhenius

<table>
<thead>
<tr>
<th>Coefficient values ± one standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a/RT = -49304 \pm 1.5e+003$</td>
</tr>
<tr>
<td>$C = -19.918 \pm 0.531$</td>
</tr>
</tbody>
</table>

### VFT

<table>
<thead>
<tr>
<th>Coefficient values ± one standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A = -4.7346 \pm 0.0291$</td>
</tr>
<tr>
<td>$B = 593.32 \pm 4.64$</td>
</tr>
</tbody>
</table>

**Figure A.9.** Curve fits according to Arrhenius and VFT equations.
<table>
<thead>
<tr>
<th>Arrhenius</th>
<th>VFT</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="https://via.placeholder.com/150" alt="Figure" /></td>
<td><img src="https://via.placeholder.com/150" alt="Figure" /></td>
</tr>
<tr>
<td><img src="https://via.placeholder.com/150" alt="Figure" /></td>
<td><img src="https://via.placeholder.com/150" alt="Figure" /></td>
</tr>
</tbody>
</table>

**Figure A.9. (continued)** Curve fits according to Arrhenius and VFT equations
A.6. Storage (G’) and Loss Modulus (G’’') as a function of Temperature.

The storage and loss modulus were measured as a function of temperature at a constant frequency \((f = 1\text{Hz})\) for all linear polymers samples over the range 25-150°C according to that described in chapter 3. As is shown these curves are qualitatively similar to the mastercurves presented.

![Graph](image)

**Figure A.10.** Storage (G’) and Loss (G’’') modulus as a function of temperature for AP containing linear copolymers.
Figure A.11. Storage ($G'$) and Loss ($G''$) modulus as a function of temperature for AA containing linear copolymers.

Figure A.12. Storage ($G'$) and Loss ($G''$) modulus as a function of temperature for CEA containing linear copolymers.
Figure A.13. Storage ($G'$) and Loss ($G''$) modulus as a function of temperature for UPy containing linear copolymers.
A.7. Complex Viscosity Curves and Fit to the Cross Model

Individual linear polymer curves showing fits to the Cross model (as well as fit parameters expressed as an average+/standard deviation) are provided below. Fits were performed using the commercially available software IGOR.

Figure A.14. Complex viscosity and fit according to Cross-model as a function of temperature for linear copolymers.
Figure A.14. Complex viscosity and fit according to Cross-model as a function of temperature for linear copolymers (continued).
**Figure A.14.** Complex viscosity and fit according to Cross-model as a function of temperature for linear copolymers (continued).
A.8. Quantum Mechanical Calculation Results.

The QM calculations are presented below. For convenience the experimental values listed in Table 1 of chapter 3 are also included. As is shown, the experimental and QM calculations differ by a factor of 2.4-2.9X.

Table A.2. Hydrogen Bonding Strength for Monomers Used in this Study

<table>
<thead>
<tr>
<th>Hydrogen Bonding Comonomer</th>
<th>Structure</th>
<th>Bond Energy, ΔH experimental [kJ/mol]</th>
<th>Bond Energy, ΔH QM calculations [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamidopyridine (AP)</td>
<td><img src="image" alt="Structure of AP" /></td>
<td>25.1</td>
<td>72.6</td>
</tr>
<tr>
<td>Acrylic acid (AA)</td>
<td><img src="image" alt="Structure of AA" /></td>
<td>30</td>
<td>73.0</td>
</tr>
<tr>
<td>Carboxyethylacrylate (CEA)</td>
<td><img src="image" alt="Structure of CEA" /></td>
<td>30</td>
<td>73.0</td>
</tr>
<tr>
<td>Ureidopyrimidinone acrylate (UPy)</td>
<td><img src="image" alt="Structure of UPy" /></td>
<td>70</td>
<td>171.0</td>
</tr>
</tbody>
</table>
Figure A.15. Acrylamidopyridine (AP) monomer synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 
Figure A.16. Ureidopyrimidinone (UPy) monomer synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 
Figure A.17. Poly(butyl acrylate) (PBA) linear homopolymer synthesis scheme and 1H-NMR spectrum in CDCl$_3$. 
Figure A.18. PBA-co-UPy linear copolymer synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 
Figure A.19. PBA-co-(carboxyethyl acrylate) (CEA) linear copolymer synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 
Figure A.20. PBA-co-(acrylic acid) (AA) linear copolymer synthesis scheme and $^1$H-NMR spectrum in dmso-d6.
Figure A.21. PBA-co-(acrylamidopyridine)(AP) linear copolymer synthesis scheme and \textsuperscript{1}H-NMR spectrum in CDCl\textsubscript{3}.
A.10. Differential Scanning Calorimeter (DSC) Results.

Figure A.21. DSC plot for PBA (sample mass=17.6 mg).

Figure A.22. DSC plot for AP5 (sample mass=11.1 mg).
Figure A.23. DSC plot for AP10 (sample mass=9.9 mg).

Figure A.24. DSC plot for AP15 (sample mass=11.3 mg).
Figure A.25. DSC plot for AA6 (sample mass=9.3 mg).

Figure A.26. DSC plot for AA10 (sample mass=12.8 mg).
Figure A.27. DSC plot for AA21 (sample mass=8.3 mg).

Figure A.28. DSC plot for CEA5 (sample mass=8.7 mg).
Figure A.29. DSC plot for CEA12 (sample mass=8.9 mg).

Figure A.30. DSC plot for UPy1 (sample mass=9.3 mg).
Figure A.31. DSC plot for UPy2 (sample mass= 8.8 mg).

Figure A.32. DSC plot for UPy5 (sample mass=10.2 mg).
Figure A.33. DSC plot for AA5-X (sample mass=10.5 mg).

Figure A.34. DSC plot for AP5-X (sample mass=11.3 mg).
Figure A.35. DSC plot for CEA5-X (sample mass=10.1 mg).

Figure A.36. DSC plot for AA21-X (sample mass= 10.2 mg).
Figure A.37. DSC plot for UPy2-X (sample size = 10.1 mg).
A.11. References


Appendix B: Supplemental Documents for Chapter 4


Figure B.1 Poly(hydroxyethyl methacrylate) (polyHEMA) linear homopolymer synthesis scheme and $^1$H-NMR spectrum in dms0-d6.
Figure B.2 Poly(hydroxyethyl methacrylate)-co-UPy linear synthesis scheme and $^1$H-NMR spectrum in dmoso-d6.
B.2. Differential Scanning Calorimetry (DSC) Summary

Figure B.3. DSC plot for dry HG-U0 (sample size = 6.6 mg).

Figure B.4. DSC plot for dry HG-U2 (sample size = 8.5 mg).
Figure B.5. DSC plot for dry HG-U6 (sample size = 5.9 mg).

Figure B.6. DSC plot for dry HG-U10 (sample size = 7.2 mg).
Figure B.7. DSC heating scans for hydrated HG-U0. A. -50 – 20°C (sample size = 10.2 mg). Endotherm attributed to melting of water frozen upon cooling; B. 0 – 75°C (sample size = 14.2 mg). Note: heating to higher temperatures resulted in irreproducible artifacts attributed to distortion of the hermetically sealed DSC pan.
Figure B.8. DSC heating scans for hydrated HG-U6. A. -50 – 20°C (sample size = 9.2 mg). Endotherm attributed to melting of water frozen upon cooling; B. 0 – 75°C (sample size = 12.2 mg). Note: heating to higher temperatures resulted in irreproducible artifacts attributed to distortion of the hermetically sealed DSC pan.
Appendix C: Supplemental Documents for Chapter 5

C.1. Computer Programs

Note: Programs written in IGOR PRO for Windows v. 6.1.2.1, Wavemetrics Inc, Lake Oswego, OR

Program Used to Predict Time-dependent Material Behavior

```plaintext
#pragma rtGlobals=1 // Use modern global access method.
//**********************************************************************
Function CalcLambda()
// declare local variables
variable deltaTime, finalTime, nDim, timeStepper, rateConst, setStrain, stress_constant
variable nu1, nu2, load
// declare waves, that have been defined outside
wave lambda, expTime, delayIntegral, permComp, deltaComp, productWave, strain, reversible,
Creep_Compliance, perm_plus_delta

//**********************************************************************
deltaTime =1 // timestep [seconds]
finalTime = 2000 // seconds
rateConst =.02// sec^-1
setStrain = 1.00 //annealed strain prior to unloading
nu1 = 4.5  // covalent strand density [mol of cov strands / m^3]
nu2 =28.0// reversible strand density [mol of rev strands / m^3]
load = .3
stress_constant=8.3//units in kPa
//**********************************************************************
nDim = finalTime / deltaTime
Redimension/N=(nDim+1) lambda
Redimension/N=(nDim+1) expTime
Redimension/N=(nDim+1) delayIntegral
Redimension/N=(nDim+1) permComp
Redimension/N=(nDim+1) deltaComp
```
Redimension/N=(nDim+1) strain
Redimension/N=(nDim+1) reversible
Redimension/N=(nDim+1) Creep_Compliance
Redimension/N=(nDim+1) productWave
Redimension/N=(nDim+1) perm_plus_delta

// initialize vectors to clear any prior memory
for (timeStepper=0 ; timeStepper <= nDim; timeStepper+=1)
    lambda[timeStepper] =0
    expTime[timeStepper]=0
    delayIntegral[timeStepper]=0
    permComp[timeStepper]=0
    deltaComp[timeStepper]=0
    strain[timeStepper]=0
    reversible[timeStepper]=0
    Creep_Compliance[timeStepper]=0
    productWave[timeStepper]=0
    perm_plus_delta[timeStepper]=0
endfor

FillExpTimeArray(nDim, deltaTime)

// solve for the initial condition
lambda[0]=SolveInitialStateOfEase(nu1, nu2, setStrain, load)
for (timeStepper=1 ; timeStepper <= nDim; timeStepper+=1)
    SolveStateOfEase(nu1,nu2,timeStepper, rateConst, setStrain, deltaTime, load, stress_constant)
endfor

End

//******************************************************************************
Function  SolveStateOfEase(nu1, nu2, timeStepper, rateConst, setStrain, deltaTime, load, stress_constant)

variable nu1, nu2, timeStepper, rateConst, setStrain, deltaTime, load, stress_constant
variable timeSpan, x, x_plus_dx, x_new, tol, RHS, RHS_new, deriv
wave lambda, delayIntegral, strain,Creep_Compliance

timeSpan = timeStepper*deltaTime
tol = 0.00001

// lambda[timeStepper] = lambda[timeStepper-1]*1.0

x = lambda[timeStepper-1]*1.0
RHS = EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime, load)

// if root is small enough, use that lambda t, if not enter a loop
if (abs(RHS)>tol)
    do  
        // calculate derivative
        x_plus_dx = x * 1.0001
        RHS_new = EvalRHS(x_plus_dx, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, 
            deltaTime, load)
        deriv = (RHS_new - RHS) / ( x_plus_dx - x)
        // use NR method
        x_new = x - RHS / deriv
        x = x_new
        RHS = EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime, load)
    while (RHS>tol)
    endif

lambda[timeStepper]=x
strain[timeStepper]=lambda[timeStepper]-1
Creep_Compliance[timeStepper]=strain[timeStepper] / stress_constant
End

//**********************************************************************
Function CalcDelayIntegral (deltaTime, timeStepper, rateConst, nu2)
variable deltaTime, timeStepper, rateConst, nu2
wave lambda, delayIntegral, productWave
variable tau, tau_index, riemannSum
variable FirstTerm, SecondTerm, product
// "timeStepper" * deltaTime is experimental time
riemannSum=0
for (tau_index=1 ; tau_index <= timeStepper; tau_index+=1)
    tau = tau_index * deltaTime
    // low value (wrt tau)
    FirstTerm = exp(-rateConst*(tau_index*deltaTime-deltaTime))
    SecondTerm = (lambda[timeStepper] / lambda[timeStepper-tau_index])^2-
lambda[timeStepper-tau_index]/lambda[timeStepper]
    product = SecondTerm * FirstTerm
    // high value (wrt tau)
    FirstTerm = exp(-rateConst*(tau))
    SecondTerm = (lambda[timeStepper] / lambda[timeStepper-tau_index+1])^2-
lambda[timeStepper-tau_index+1]/lambda[timeStepper]
    product += SecondTerm * FirstTerm
    riemannSum += product /2
if (timeStepper==45)
    productWave[tau_index]=product
endif

delayIntegral[timeStepper] = riemannSum * rateConst * nu2 * deltaTime

Function EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime, load)
    variable x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime, load
    wave delayIntegral, permComp, deltaComp, lambda, reversible, perm_plus_delta
    variable root

    lambda[timestep]=x

    CalcDelayIntegral(deltaTime, timeStepper, rateConst, nu2)
    root = nu1 * (x^2 - 1/x)
    permComp[timeStepper] = root

    root += nu2 * exp(-rateConst * timeSpan) *(( ( x / setStrain)^2 - (setStrain / x) )
    deltaComp[timeStepper] = nu2 * exp(-rateConst * timeSpan) *(( ( x / setStrain)^2 - (setStrain/ x) )

    root += delayIntegral[timeStepper]
    reversible[timeStepper]=deltaComp[timeStepper]+delayIntegral[timeStepper]+delayIntegral[timeStepper]
    perm_plus_delta[timeStepper]=permComp[timeStepper]+deltaComp[timeStepper]
    root+=load

    Return root
End

Function SolveInitialStateOfEase(nu1, nu2, setStrain, load)
    variable nu1, nu2, setStrain, load
    variable x, x_plus_dx, x_new, tol, RHS, RHS_new, deriv

    tol = 0.00001

    x = setStrain*0.9
    RHS = EvalRHS_init(nu1, nu2, setStrain, x, load)

    // if root is small enough, use that lambda t, if not enter a loop
if (abs(RHS)>tol)
    do
// calculate derivative for NR
    x_plus_dx = x * 1.0001
    RHS_new = EvalRHS_init(nu1, nu2, setStrain, x_plus_dx, load)
    deriv = (RHS_new - RHS) / ( x_plus_dx - x)
// use NR method
    x_new = x - RHS / deriv
    x = x_new
    RHS = EvalRHS_init(nu1, nu2, setStrain, x, load)
    while (abs(RHS)>tol)
    endif
    return x
End

//**********************************************************************
Function EvalRHS_init(nu1, nu2, setStrain, x, load)
    variable nu1, nu2, setStrain, x, load
    variable root
    root = nu1 * ( x^2 - 1 / x)
    root += nu2 * ( (x/setStrain)^2 - 1 / (x/setStrain) )
    root += load
    Return root
End

//**********************************************************************
Function FillExpTimeArray(nDim, deltaTime)
    variable nDim, deltaTime
    wave expTime
    variable i
    for (i=0 ; i <= nDim; i+=1)
        expTime[i] = i * deltaTime
    endfor
End

//**********************************************************************
Program Used to Predict Dynamic Mechanical Behavior

#include rtGlobals=1  // Use modern global access method.

//**********************************************************************
//change load as a function of time and obtain lambda as a function of time

Function CalcLambda()

  // declare local variables
  variable deltaTime, finalTime, nDim, timeStepper, rateConst, setStrain, stress_constant
  variable nu1, nu2, omega, max_load_loc, V_PeakLoc, min_lambda_loc, delta, max_load_value,
  V_PeakVal, min_lambda_value, tan_delta, storage_mod, loss_mod
  // declare waves, that have been defined outside
  wave lambda, expTime, delayIntegral, permComp, deltaComp, productWave, strain, reversible,
  Creep_Compliance, load, freq_time

  //******************************************************
  omega=0.02*(2*pi)//sec-1
deltaTime =pi/(omega*1000)// timestep [seconds]
finalTime = 2*pi/omega // seconds
rateConst =0.2// sec^-1
setStrain = 1.00 //annealed strain prior to unloading
nu1 = 73  // covalent strand density [mol of cov strands / m^3]
u2 =57// reversible strand density [mol of rev strands / m^3]
//load = 0
stress_constant=8.3//units in kPa
//Note: Temperature = 60degC

  //******************************************************
nDim = finalTime / deltaTime
Redimension/N=(nDim+1) lambda
Redimension/N=(nDim+1) expTime
Redimension/N=(nDim+1) delayIntegral
Redimension/N=(nDim+1) permComp
Redimension/N=(nDim+1) deltaComp
Redimension/N=(nDim+1) strain
Redimension/N=(nDim+1) reversible
Redimension/N=(nDim+1) Creep_Compliance
Redimension/N=(nDim+1) load
Redimension/N=(nDim+1) productWave
Redimension/N=(nDim+1) freq_time

  // initialize vectors to clear any prior memory
for (timeStepper=0 ; timeStepper <= nDim; timeStepper+=1)
lambda[timeStepper] = 0
expTime[timeStepper] = 0
delayIntegral[timeStepper] = 0
permComp[timeStepper] = 0
deltaComp[timeStepper] = 0
strain[timeStepper] = 0
reversible[timeStepper] = 0
load[timeStepper] = 0
Creep_Compliance[timeStepper] = 0
productWave[timeStepper] = 0
freq_time[timeStepper] = 0
endFor

FillExpTimeArray(nDim, deltaTime)

// solve for the initial condition
lambda[0] = SolveInitialStateOfEase(nu1, nu2, setStrain)

for (timeStepper = 1 ; timeStepper <= nDim; timeStepper += 1)
  load[timeStepper] = sin(deltaTime*timeStepper*omega)
  freq_time[timeStepper] = (timeStepper*deltaTime*omega)
  SolveStateOfEase(nu1, nu2, timeStepper, rateConst, setStrain, deltaTime, stress_constant)
endfor

//Find peaks

// look for positive load peak value and return x
FindPeak/M = load
max_load_loc = (V_PeakLoc)* (deltaTime)* (omega)
max_load_value = V_PeakVal

FindPeak/N lambda
min_lambda_loc = V_PeakLoc*deltaTime*omega
min_lambda_value = 1-(V_PeakVal)
delta = abs((max_load_loc)-(min_lambda_loc))
tan_delta = tan(delta)
storage_mod = 8.314*(60+273)*(max_load_value/min_lambda_value)*cos(delta)
// 60degC temperature taken into account
loss_mod = 8.314*(60+273)*(max_load_value/min_lambda_value)*sin(delta)
// 60degC temperature taken into account
End

/******************************************************************************
Function SolveStateOfEase(nu1, nu2, timeStepper, rateConst, setStrain, deltaTime, stress_constant)
*******************************************************************************/

variable nu1, nu2, timeStepper, rateConst, setStrain, deltaTime, stress_constant
variable timeSpan, x, x_plus_dx, x_new, tol, RHS, RHS_new, deriv
wave lambda, delayIntegral, strain, Creep_Compliance, load

timeSpan = timeStepper*deltaTime
tol = 0.0000001

// lambda[timeStepper] = lambda[timeStepper-1]*1.0

x = lambda[timeStepper-1]*1.0
RHS = EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime)

// if root is small enough, use that lambda t, if not enter a loop
if (abs(RHS)>tol)
do
  // calculate derivative
  x_plus_dx = x * 1.0001
  RHS_new = EvalRHS(x_plus_dx, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime)
  deriv = (RHS_new - RHS) / ( x_plus_dx - x)
  // use NR method
  x_new = x - RHS / deriv
  x = x_new
  RHS = EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime)
while (RHS>tol)
endif

lambda[timeStepper]=x
strain[timeStepper]=lambda[timeStepper]-1
Creep_Compliance[timeStepper]=strain[timeStepper] / stress_constant
End

//*******************************************************************************
Function CalcDelayIntegral (deltaTime, timeStepper, rateConst, nu2)

variable deltaTime, timeStepper, rateConst, nu2
wave lambda, delayIntegral, productWave
variable tau, tau_index, riemannSum
variable FirstTerm, SecondTerm, product
// "timeStepper" * deltaTime is experimental time

riemannSum=0
for (tau_index=1 ; tau_index <= timeStepper; tau_index+=1)
  tau = tau_index * deltaTime
  // low value (wrt tau)
  FirstTerm = exp(-rateConst*(tau_index*deltaTime-deltaTime))
SecondTerm = (lambda[timeStepper] / lambda[timeStepper-tau_index])^2 -
lambda[timeStepper-tau_index]/lambda[timeStepper]
product = SecondTerm * FirstTerm

// high value (wrt tau)
FirstTerm = exp(-rateConst*(tau))
SecondTerm =(lambda[timeStepper] / lambda[timeStepper-tau_index+1])^2 -
lambda[timeStepper-tau_index+1]/lambda[timeStepper]
product += SecondTerm * FirstTerm

riemannSum += product /2

if (timeStepper==45)
productWave[tau_index]=product
endif

endfor

delayIntegral[timeStepper] = riemannSum * rateConst * nu2 * deltaTime
End

/*******************************************************************************
Function  EvalRHS(x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime)
variable x, rateConst, nu1, nu2, setStrain, timeSpan, timeStepper, deltaTime
wave delayIntegral, permComp, deltaComp, lambda, reversible, load
variable root

lambda[timestepper]=x
CalcDelayIntegral(deltaTime, timeStepper, rateConst, nu2)
root = nu1 * (x^2 - 1/x)
permComp[timeStepper] = root
root += nu2 * exp(-rateConst * timeSpan) *(( x / setStrain)^2 - (setStrain / x) )
deltaComp[timeStepper] = nu2 * exp(-rateConst * timeSpan) *(( x / setStrain)^2 - (setStrain/ x) )
root += delayIntegral[timeStepper]
reversible[timeStepper]=deltaComp[timeStepper]+delayIntegral[timeStepper]
root+==load[timeStepper]

    Return root
End

*******************************************************************************
Function  SolveInitialStateOfEase(nu1, nu2, setStrain)
variable nu1, nu2, setStrain
variable x, x_plus_dx, x_new, tol, RHS, RHS_new, deriv
wave load
tol = 0.0000001
x = setStrain*0.9
RHS = EvalRHS_init(nu1, nu2, setStrain, x)

// if root is small enough, use that lambda t, if not enter a loop
if (abs(RHS)>tol)
do
  // calculate derivative for NR
  x_plus_dx = x * 1.0001
  RHS_new = EvalRHS_init(nu1, nu2, setStrain, x_plus_dx)
  deriv = (RHS_new - RHS) / (x_plus_dx - x)
  // use NR method
  x_new = x - RHS / deriv
  x = x_new
  RHS = EvalRHS_init(nu1, nu2, setStrain, x)
  while (abs(RHS)>tol)
  endif

return x
End

//********************************************************************************
Function EvalRHS_init (nu1, nu2, setStrain, x)
  variable nu1, nu2, setStrain, x
  variable root
  wave load
  root = nu1 * (x^2 - 1 / x)
  root += nu2 * ((x/setStrain)^2 - 1 / (x/setStrain))
  root += load[0]
  Return root
End

//********************************************************************************
Function FillExpTimeArray(nDim, deltaTime)
  variable nDim, deltaTime
  wave expTime
  variable i

  for (i=0 ; i <= nDim; i+=1)
    expTime[i] = i * deltaTime
  endfor
End

//********************************************************************************
Appendix D: Supplemental Documents for Chapter 6


Figure D.1. Diels-Alder adduct bearing aminoethanol linkage synthesis scheme and $^1$H-NMR spectrum in dmso-d6.
Figure D.2. Deprotected Diels-Alder product synthesis scheme and $^1$H-NMR spectrum in dmsod$_6$. 
Figure D.3. Diels-Alder diol synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 
Figure D.4. Diels-Alder diacrylate #1 synthesis scheme and 1H-NMR spectrum in CDCl₃.

Note LC-MS provided molecular weight = 347.
Figure D.5. Diels-Alder diacrylate #2 synthesis scheme and $^1$H-NMR spectrum in CDCl$_3$. 