

**STRUCTURE-PROPERTY RELATIONSHIPS OF: 1) NOVEL
POLYURETHANE AND POLYUREA SEGMENTED COPOLYMERS AND
2) THE INFLUENCE OF SELECTED SOLUTION CASTING VARIABLES
ON THE SOLID STATE STRUCTURE OF SYNTHETIC POLYPEPTIDE
FILMS BASED ON GLUTAMATE CHEMISTRY**

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ABSTRACT

The foundational studies of this dissertation concern the characterization of segmented polyurethanes and polyureas synthesized without the use of chain extenders—molecules that are typically used to promote a microphase separated morphology that gives these materials their useful characteristics. Polyurethanes in which a single asymmetric diisocyanate comprising the whole of the hard segment were found to display poor microphase separation. Conversely, polyurethanes in which a single symmetric diisocyanate composed the hard segment were found to display good microphase separation. The more efficient packing of the symmetric hard segments also led to an increase in hard segment connectivity and hence higher values of storage moduli in these systems. When hydroxyl-terminated diisocyanates were replaced with amine-terminated diisocyanates, polyureas were formed. Here too, diisocyanate symmetry was found to play a key role with symmetric diisocyanates leading to better microphase separation. In addition, the polyurea materials displayed broader service temperature windows than their polyurethane counterparts as the relatively stronger bidentate hydrogen bonding replaced monodentate hydrogen bonding in these materials. A thread-like, microphase separated morphology was visually confirmed using atomic force microscopy. Other techniques such as ambient temperature tensile testing, and wide and small angle x-ray scattering were employed to confirm the presence of the microphase separated structure.

The investigation into the effects of diisocyanate chemistry and its symmetry was broadened to incorporate non-chain extended polyurethane materials with different soft segment molecular weights, as well as polyurethanes that did contain chain extenders. Once again the effect of using symmetric versus asymmetric diisocyanates was evident in the structure–property behavior of these systems, with symmetric diisocyanates forming materials that displayed better microphase separation and more connectivity of their hard domains.

Lastly, in a departure from the segmented copolymer area, a study was conducted into the influence of casting variables on the solid-state structure of synthetic polypeptide films based on glutamate chemistry. The effect of solvent evaporation was determined to play a key role in the morphology of these polypeptide films. Measured small angle light scattering patterns were compared to computer calculated patterns to reveal information about the structure, shape, and length scale of the polypeptide structure.

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LIST OF ACRONYMS, TRADE NAMES, AND VARIABLES

χ	Flory-Huggins interaction parameter
AFM	Atomic Force Microscopy
BD	1,4-Butane diol
CE	Chain Extender
CHDI	<i>Trans</i> -cyclohexyl diisocyanate
DMF	N,N-Dimethyl Formamide
DMA	Dynamic Mechanical Analysis
DMAc	N,N-Dimethylacetamide
DSC	Differential Scanning Calorimetry
Dytek A	Trade name for DuPont's 2-methyl-1,5-diaminopentane
E'	Storage modulus
E''	Loss modulus
EDA	Ethylenediamine
EG	Ethylene glycol
f	Volume fraction of a block in diblock copolymers
FA	Formic acid
FT-IR	Fourier Transform Infrared Spectroscopy
HDI	Hexamethylene diisocyanate
HMDI	Hydrogenated 4,4'-diphenylmethane diisocyanate
HS	Hard segment(s)
H_V	Small angle light scattering performed with the radiation polarized vertically and the analyzer oriented horizontally
IPA	Isopropanol
LCST	Lower critical solution temperature
M_c	Critical molecular weight between chain entanglements
MDI	4,4'-diphenylmethane diisocyanate
MH	Mechanical hysteresis
MW	Molecular weight
MWD	Molecular weight distribution
N	Overall degree of polymerization of a copolymer chain
<i>m</i> PDI	<i>meta</i> -Phenylene diisocyanate or 1,3-Phenylene diisocyanate
ODT	Order–Disorder Transition
PBLG	Poly (γ -benzyl L-glutamate)
PDMS	Polydimethylsiloxane
PELG	Poly (γ -ethyl L-glutamate)
PMDG	Poly- γ -methyl-D-glutamate
PMLG	Poly (γ -methyl L-glutamate)
PnHxLG	Poly (γ -N-hexyl L-glutamate)
<i>p</i> PDI	<i>para</i> -phenylene diisocyanate or 1,4-phenylene diisocyanate
PPO	Poly(propylene oxide)
PTMO	Poly(tetramethylene oxide)
PU	Polyurethane(s)
PUr	Polyurea(s)
PUU	Polyurethaneurea(s)

RU	Repeat unit
SALS	Small Angle Light Scattering
SAXS	Small Angle X-ray Scattering
SBS	Poly(styrene-butadiene-styrene)
SEM	Scanning Electron Microscopy
SIS	Poly(styrene-isoprene-styrene)
SR	Stress relaxation or Set-point ratio
SS	Soft segment(s)
$\tan \delta$	Loss tangent
TCE	1,1,2,2-tetrachloroethane
TDI	Toluene diisocyanate
T_g	Glass transition temperature
THF	Tetrahydrofuran
T_m	Melting temperature
TMA	Thermo Mechanical Analysis
TPE	Thermoplastic elastomer(s)
TPU	Thermoplastic polyurethane(s)
UCST	Upper critical solution temperature
WAXS	Wide Angle X-ray Scattering
V_V	Small angle light scattering performed with the radiation polarized vertically and the analyzer oriented vertically

PREFACE

This preface is meant to provide the reader with an understanding of the overall structure of this work and to give a short description of the chapters that follow. Many of the chapters are based on manuscripts prepared for publication and therefore also contain background information and discussion of the literature pertinent to the work covered in each. This dissertation is divided into seven chapters dealing with segmented copolymers, the areas of polyurethanes and polyureas, and synthetic polypeptides.

The first chapter provides a review of the literature in the area of block and segmented copolymers. Topics that are highlighted and discussed at length include: the chemistry of these materials, the physics and significance of hydrogen bonding, and the significance and importance of microphase separation. Within those general topics, the focus is placed on reviews of work done on polyurethanes and polyureas in particular as the majority of work described in subsequent chapters was done on those materials. Studies that have special significance or influence to *this* work are discussed in greater detail. The five chapters that immediately follow the literature review cover work done in the fields of segmented polyurethanes and polyureas. An overview of each chapter follows.

Chapter 2 details the importance of hydrogen bonding and diisocyanate chemistry on the structure–property characteristics of segmented polyurethane and polyurea materials synthesized without the use of chain extender (CE) molecules. By omitting the CEs, the hard segment of the segmented copolymers are constituted by only a single diisocyanate molecule. Materials with this characteristic are referred to as ‘single-segment’ materials hereafter. The chapter also focuses on two specific segmented copolymer samples constructed with a *ca.* 1000 g/mol MW polytetramethylene oxide (PTMO) soft segment (SS). The first material contains a *para*-phenylene diisocyanate (*p*PDI) hard segment (HS); the second uses *meta*-phenylene diisocyanate (*m*PDI) as the HS. All materials discussed in this chapter have hard segment contents of 12.7–14.1%. Using these two diisocyanates which differ only in their symmetry, allows for the exploration of how this simple but important structural change impacts (1) the packing ability of the hard segments, (2) the subsequent influence on the materials’ thermal stability, and (3) the thermo-mechanical properties of these materials. In addition, a change from hydroxyl-terminated soft segment (which produces monodentate hydrogen bonding in the urethane—U—samples) to an amine-capped soft segment (which introduces bidentate hydrogen bonding in the ureas—Ur)

allows for the study of the effects of hydrogen bonding on the structure–property behavior of these materials. Also discussed are two blends made from the *p*PDI-based urethane and *m*PDI-based urethane; the first material was synthesized by adding each diisocyanate to the reaction vessel during polymer formation, the second material is a blend of the *p*PDI–U and *m*PDI–U segmented polymers. To complete the study, a number of different analytical techniques were used to determine if the materials were crystalline, amorphous, or microphase-separated. Techniques included: Dynamic Mechanical Analysis (DMA), Small Angle X-ray Scattering (SAXS), Atomic Force Microscopy (AFM), Wide Angle X-ray Scattering (WAXS), and Differential Scanning Calorimetry (DSC) and ambient temperature mechanical tensile testing.

Chapter 3 addresses many of the same issues as chapter 2, such as the impact of hydrogen bonding and diisocyanate chemistry, but introduces five new diisocyanates to the synthesis of the PTMO based polyurethanes and polyureas, namely: *trans*-1,4-diisocyanatocyclohexane (CHDI), an 80/20 mixture of 2,4- and 2,6-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), 4,4'-methylenediphenyl diisocyanate (MDI), and 4,4'-dicyclohexylmethane diisocyanate (H-DMI). The use of different diisocyanate chemistries provides a fuller understanding of the effects on the structure–property behavior of these non-chain extended materials with hard segment contents lower than 21 wt%. Again the full range of analytical techniques mentioned earlier was used to fully understand the morphologies of these materials and to understand their structure–property relationships.

Chapter 4 focuses on how a change in the soft segment molecular weight $\langle M_n \rangle$ of a PTMO-based polyurethane affects the structure–property behavior of the non-chain extended materials. For this study, three monodisperse hard segment polyurethanes were produced by reacting hydroxyl terminated PTMO with a select diisocyanate, either *p*PDI, HDI, or CHDI. Here, the diisocyanates are reacted in a one-step process with 2,000 g/mol PTMO glycol SS instead of 1,000 g/mol PTMO glycol. The resulting materials were subjected to the same analytical techniques used in previous chapters. The increase in SS molecular weight is shown to also affect the T_m of the semicrystalline SS. This, in conjunction with the decrease in HS content, influences both the structure and properties of the resulting material. The higher SS $\langle M_n \rangle$ leads to the presence of crystalline SS at ambient temperature. In addition, the changes imposed by the decreased HS content on the percolation and connectivity of the hard phase throughout the soft phase and its effect on ambient temperature mechanical properties is discussed.

Chapter 5 details the characterization of new PTMO-based polyurethanes that are chain extended with 1,4-butane diol (BDO). Discussion in this chapter focuses on samples that were synthesized to study the effect of increased SS and HS contents on a material's morphology and structure–property characteristics. Materials containing identical SS (PTMO) and diisocyanate (*p*PDI) were reacted with BDO to produce samples with either 14 or 20 wt% HS content. The single segment materials discussed in the previous chapters rarely contained HS contents above 14 wt%. In addition, two series of samples with constant HS contents (either 14 wt% or 20 wt%) were produced by simultaneously varying both the SS and HS molecular weights. This variation allowed for the exploration of how common chain extender technology affects a sample's morphology and structure–property relationships.

Chapter 6 addresses the synthesis and characterization of novel segmented polyurethaneurea copolymers which *have* been chain extended. This chapter is essentially a reprint of a paper published in the journal *Polymer* (though table and figure numbers have been updated to fit the format of this dissertation) [1]. The materials used in this study were synthesized using a poly(ethylene-butylene) glycol based SS, using either H-MDI or HDI as the diisocyanate, and either ethylene diamine (EDA) or 2-methyl-1,5-diaminopentane (DY) as the chain extender. A range of characterization techniques was employed and DMA, AFM, and SAXS established the presence of a microphase-separated structure in which hard microdomains are dispersed throughout a soft segment matrix. WAXS and DSC imply that the materials are amorphous at ambient temperature. Samples were also made with a combination of H-MDI and DY, and have hard segment contents in the range of 16–23 wt%. Ambient temperature mechanical testing of these materials show near-linear mechanical deformation behavior in excess of 600% elongation. They also show very high levels of recoverability though their hysteresis is also considerable. The materials were also determined to be melt processable.

Finally, chapter 7 detours from the area of segmented copolymers altogether, though it still focuses on the determination of structure–property relationships, here in synthetic polypeptide materials. Specifically, this chapter addresses the formation and solid state morphological characterization of solution cast homopolymer synthetic polypeptide films based on glutamate chemistry. Films of either poly- γ -benzyl-L-glutamate (PBLG), poly- γ -ethyl-L-glutamate (PELG), and poly- γ -methyl-L-glutamate (PMLG) were cast from three different solvents: 1,1,2,2-tetrachloroethane (TCE), formic acid (FA) and chloroform. The type of solvent

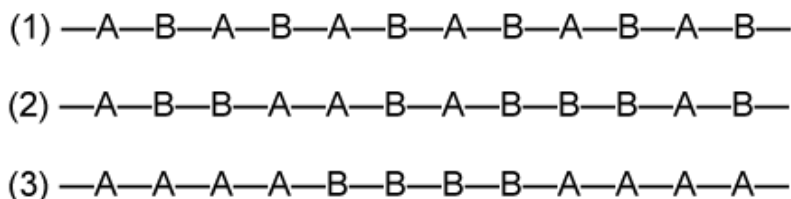
and its evaporation rate were controlled to an extent that allowed a study of the effects that each had on the solid state morphology of the resulting films. Of primary importance in this study was the Small Angle Light Scattering (SALS) theory and technique which are discussed in detail in the chapter as it was used both to determine sample morphology and to predict expected scattering patterns under different radial conditions not tested (e.g. scattering rods of different lengths, different angles of scattering, different sample to film distances etc.). Other important methods of characterization included AFM and WAXS as well as two techniques not mentioned previously, namely, Polarized Optical Microscopy (POM) and Scanning Electron Microscopy (SEM). The combination of these methods and a computer simulation based on well-known scattering theory aided in the determination of film microstructure and molecular orientation.

1. LITERATURE REVIEW

As indicated in the previous section, this chapter will address the field of segmented copolymers in some depth. Therefore the reader may find it useful to review some of the fundamentals of block copolymers and phase (and microphase) separation and how the materials addressed within this dissertation relate to others in the realm of polymer science. A brief overview will be provided here but more extensive discussions can be found in the literature [2, 3]. This chapter is not meant to be exhaustive as the individual chapters that follow also contain relevant background information and references to the literature that are pertinent to their individual subjects. The details of this section are broken down into the following subtopics:

- Some of the fundamental principles governing classic block copolymers possessing no specific interactions and their microphase separation behavior.
- A general description of the field of segmented copolymers possessing specific interactions such as hydrogen bonding.
- The chemical nature of microphase separation in segmented copolymers.
- The chemistry of segmented polyurethane and polyurea copolymers.
- A synopsis of the main techniques used in the study of structure–property relationships in segmented copolymers
- Key studies related to the motivation behind the current research work.

Polymers can be classified in a number of ways; one of the most basic is the division of materials into two groups, homopolymers and copolymers (the latter which contain a subset of materials known as block and segmented copolymers). A material is deemed a homopolymer when only one type of repeating unit (RU) is used to form the polymer chain, and as a copolymer if two or more different repeat units are used to create the chain. Employing just two repeat units, represented here as A and B respectively, copolymers with very different structures can be formed. If the units are chemically linked in an alternating fashion, as in Scheme 1.1(1) an “alternating copolymer” is formed. If the RUs are not alternated sequentially but rather are randomly joined, then the resulting polymer is termed a “random copolymer”. An example of RUs joined randomly is shown in Scheme 1.1(2)



Scheme 1.1. Alternating (1), random (2), and block (3) copolymer arrangements of repeat units 'A' and 'B'.

If instead of either of these two arrangements, RUs are grouped together into reasonably long segments or blocks of similar species, a “block copolymer” is formed as shown in Scheme 1.1(3). Importantly, generally an individual block usually contains far more repeat units than is shown above (blocks lengths in classic block copolymers are typically 10,000–100,000 g/mol). Only a few units are shown here for the sake of simplicity.

1.1. GENERAL BACKGROUND ON CLASSIC BLOCK COPOLYMERS POSSESING NO SPECIFIC INTERACTIONS AND THEIR PHASE SEPARATION CHARACTERISTICS

As shown in the last scheme, block copolymers are composed of long sequences (blocks) of similar repeat units covalently bonded to chemically dissimilar sequences formed from a different repeat unit. Block copolymers are currently produced in three main categories: diblock copolymers often referred to as AB block copolymers (here A and B indicate an entire block instead of single repeat units), triblock copolymers of the ABA type and multiblock copolymers of the $(AB)_n$ type. Other types of block copolymers do exist such as ABC types, which are constructed from three different types of repeating units, star block copolymers, and graft copolymers (such as high-impact polystyrene) [4-6]; however, these are beyond the scope of this review. Common examples of ABA triblock copolymers are poly(styrene-butadiene-styrene) (SBS) used in footwear and poly(styrene-isoprene-styrene) (SIS) used in adhesives. The backbone chain of a triblock copolymer is composed of three distinct blocks. In SBS for example, the first block is polystyrene (S), the second polybutadiene (B) and the third is a second polystyrene block. Diblock and triblock copolymers are graphically represented in Figure 1.1.

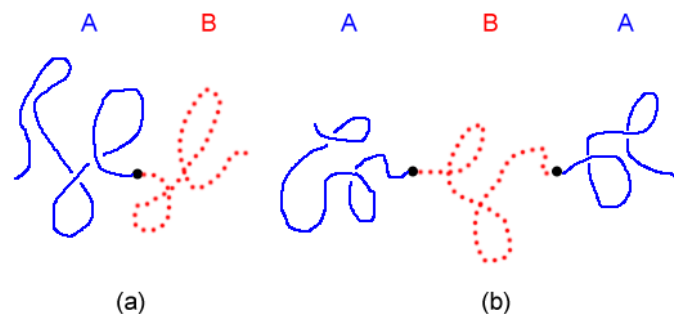


Figure 1.1. Representation of AB diblock (a) and ABA triblock (b) copolymers.

Historically, linear di- or tri-block copolymers have most typically been synthesized via anionic polymerization, though living free radical polymerization can also be used. With anionic polymerization, these materials can have very narrow block and total molecular polydispersities ($\langle M_w \rangle / \langle M_n \rangle$), often 1.1 or lower. The individual blocks often range in molecular weight from 10,000—100,000 g/mol. Because block copolymers are synthesized with chemically different monomers, one might be tempted to believe that they display properties similar to those of polymer blends in which different homopolymers are mixed to form a new material. However, the properties are typically very different due to the different morphological/microphase separated structures formed in block copolymers possessing chemically incompatible but covalently attached components.

Whenever two materials are blended, the ultimate structure and properties depend on the level at which mixing takes place (microscopic or macroscopic) and the level of chemical interaction between the mixing species. In polymer blends more specifically, the ultimate structure of the material depends on the miscibility and phase separation characteristics of the polymers that are blended. A miscible blend results when the blended components form a material that has a homogenous structure down to the molecular level and no phase separation exists. Immiscible blends are formed when phase separation occurs, often due to chemical interaction between the blended components. When two polymers are mixed, the most common result is a system in which almost total macrophase separation exists due to the lower entropy of mixing of the different polymer chains in the macrophase separated state compared to the mixed state [7, 8]. This macrophase separation results in a material with a structure composed of distinct regions which have high contents of either polymer “A” or polymer “B”. However, some polymer blends *can* display complete miscibility of their components although this behavior is

the exception rather than the rule. The most important thermodynamic relationship governing the behavior of polymer blends is the Gibbs free energy of mixing:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (\text{Equation 1.1})$$

where ΔG_m is the free energy of mixing, ΔH_m is the enthalpy of mixing and ΔS_m is the entropy of mixing. For mixing to occur, two conditions must be satisfied for (Equation 1.1). First, the term ΔG_m must be less than zero. Second, the second derivative with respect to volume fraction must be larger than 0 for complete miscibility. For high molecular weight components, the $T\Delta S_m$ term is very small and thus at higher temperatures these blends often become immiscible and phase separate. This is known as the lower critical solution temperature (LCST) behavior. An example of this behavior is witnessed when mixing polycarbonate and polystyrene. Lower molecular weight blends are often miscible at higher temperatures and phase separate at lower temperatures. This results in what is known as an upper critical solution temperature (UCST) behavior [8-10]. Diagrams of these phenomena are presented in Figure 1.2. Two well-known theories that address the miscibility of polymer blends were developed to determine the thermodynamic basis for the behavior by Flory [11, 12] and by Sanchez [13-15]. These theories are not easily applied in cases where specific interactions such as hydrogen bonding occur (the case where it does occur will be discussed in more detail in section 1.3). Rather, they apply when the chemically immiscible materials exhibit only weak or non-specific interactions between chains (e.g. Van der Waals).

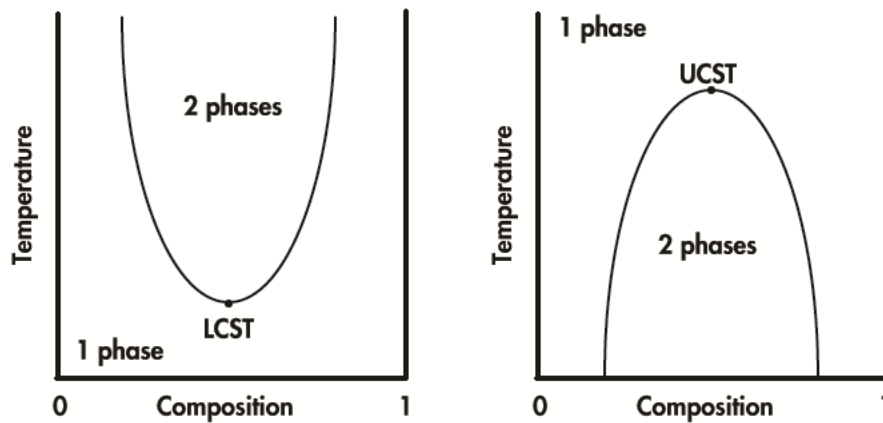


Figure 1.2. Simplified phase diagrams of a polymer blends showing LCST and UCST behavior.

Just as the physical properties of polymer blends are dependent on their phase separation behavior, so too are the physical properties of most block copolymers, though the length scale of the separation is different due to block length and the chemical linkages (covalent bonds) found across the phase boundary in block copolymers. Indeed, the majority of the important properties of block copolymers that make them so attractive as a class of materials such as thermoplastic elastomeric properties, elasticity, and surfactant applications depend on *microphase* rather than *macrophase* separation as found in blends [3, 7]. It should be noted that this is generally true, but not always. Blends can achieve a microphase separated structure if they can obtain a spinodal structure and then be quenched below T_g of at least one or both components to achieve two microphase separated phases.

As in macrophase separation, microphase separation is principally driven by the chemical incompatibility between the blocks that make up block copolymer molecules, measured with the term ΔH_{mix} . In the simplest AB block copolymers, the dissimilarity is between the A and B blocks. In these cases, the ΔS_m per unit volume of dissimilar blocks is small and varies inversely with molecular weight. Therefore, small chemical and structural differences between blocks are usually sufficient to produce excess free energy contributions that lead to microphase separation. The Flory–Huggins interaction parameter, χ , associated with the two blocks is used to describe the non-ideal part of the free energy of mixing of components A and B and describes the cost of free-energy per monomer of contacts between A and B:

$$\chi_{AB} = (Z/k_B T)[\varepsilon_{AB} - (1/2)(\varepsilon_{AA} + \varepsilon_{BB})] \quad (\text{Equation 1.2})$$

Here Z is the number of nearest neighbor monomers to a configuration cell and ε_{AB} is the interaction energy per monomer between repeat units A and B respectively. Accordingly, a positive χ value implies a net repulsion between A and B. In a system lacking specific interactions such as hydrogen bonding or ionic interactions, the χ value is small but positive and the system tends towards microphase separation. Conversely, a negative χ value derives from a net attraction between A and B units and results in a drive towards mixing. Also note that the classic Flory–Huggins χ parameter varies inversely with temperature. Hence, increasing the temperature of the system decreases the χ value and drives the system towards mixing.

Just as in polymer blends, the chemical incompatibility of the blocks is the principal driving force causing them to separate, but because the blocks cannot physically separate to the

extent that they do in non-bonded materials, a *microphase*-separated structure develops. For diblock materials lacking specific secondary interactions, the microphase separation is controlled by a number of factors including the temperature and Flory interaction parameter. In addition, the molecular structure is characterized by two parameters: the total degree of polymerization (Block A + Block B), N , and the volume fraction of the respective blocks, f_A and f_B (where $f_A = N_A/N$). For a symmetric diblock material, $f_A = f_B = 1/2$. At low temperatures (indicating a large χ_{AB}) microphase separation takes place with the microdomains forming lamella. Equating the elastic energies per polymer chain in the ordered lamellar phase with those in the disordered phase leads to the determination of the order–disorder transition (ODT) where $\chi_{AB}N = 10.4$. This well-known result indicates that in systems of symmetric diblock copolymers—with high molecular weight (high N) or strongly incompatible blocks (high χ_{AB}) such that $\chi_{AB}N > 10.5$ —microphase separation occurs as lamellar phases, whereas smaller copolymers with more chemically compatible blocks ($\chi_{AB}N < 10.5$) show no microphase separation. A schematic of the thermally reversible ordering process is shown in Figure 1.3.

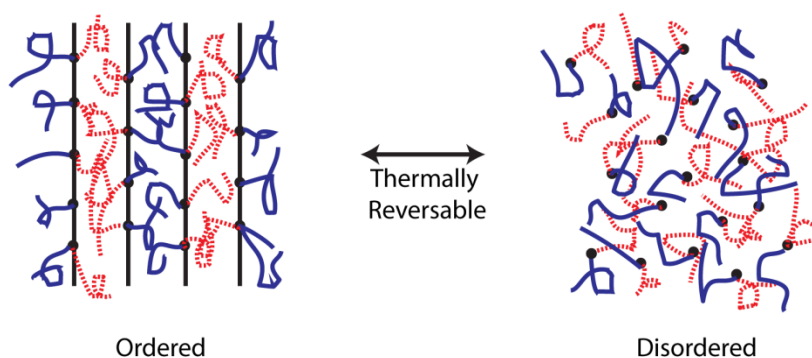


Figure 1.3. Schematic drawing of an ordered and disordered state in diblock copolymers with high molecular weight or strongly incompatible blocks.

Dissimilar blocks segregate into separate domains (regions which are highly enriched with blocks of the same type) often to the point that the domains are essentially pure in one component except very near the interface. The covalent bonds between blocks are located within the interface of the phase-separated domains. It should be noted that the transition between the domains is not as sharp as drawn in Figure 1.3, and that transition zone has a finite thickness that has led to the use of the term “interphase” to describe the region.

As opposed to the comparatively simple phase diagram found for polymer blends (Figure 1.2), more complex phase diagrams such as the one presented in Figure 1.4 are typically found for microphase-separated block copolymers. Here, a representative phase diagram is shown for a diblock system labeled as blocks A and B with narrow block distributions. The phase boundaries in Figure 1.4 are drawn as a function of the volume fraction of component A.

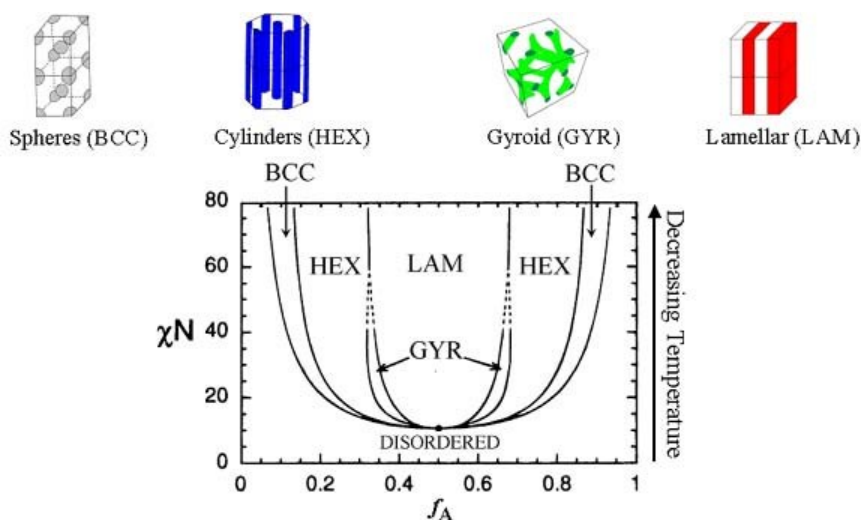


Figure 1.4. Schematics of phase morphology and representative phase diagram for block copolymers with narrow block molecular weight distributions [16].

As the volume fraction of component A increases, the shape of the phase it composes changes as well. At low fractions of block A, the A phase separates into spherical domains dispersed throughout a matrix of B as depicted in the upper left-most graphic in Figure 1.4. As the volume fraction of A blocks in the copolymer is increased to 0.5, the shape of the A domains change from spheres to cylinders, to the gyroid phase and eventually lamellae. When f_A increases beyond 0.5, phase inversion occurs and the A component becomes the majority phase while the B component of the copolymer becomes the minority phase. The material is then characterized as having domains of component B dispersed in a matrix of component A. Phase shape continues to be based on the product of χN and the volume fraction of each component, A and B. Having looked at the defining characteristics of block copolymers and their phase separation behavior, we will now focus on the corresponding topics in segmented copolymers which are more pertinent to the materials that will be discussed later in this dissertation.

1.2. GENERAL BACKGROUND OF SEGMENTED COPOLYMERS THAT POSSESS SPECIFIC INTERACTIONS WITH A CONCENTRATION ON POLYURETHANES AND POLYUREAS

Segmented copolymers and block copolymers share the defining attribute that they are able to microphase separate under appropriate conditions. However, they differ in a number of important ways. First, segmented copolymers are more typically synthesized via the step-growth polymerization technique and therefore achieve an overall molecular weight distribution of *ca.* 2. This is in great contrast to the more narrow molecular weight distributions found in anionically polymerized linear amorphous block copolymers, which are often less than 1.1. Also, individual segments have molecular weights on the order of 400–6,000 g/mol, often far below the 10,000–100,000 g/mol block weights of traditional block copolymers. Hence, the size or length scales of the microphase separated structures are likely to be much smaller than for the previously discussed block copolymers. Other issues that impact the microphase separation of segmented copolymers are hard segment packing and the distribution of segment lengths. As this dissertation is primarily concerned with work done on segmented copolymers, the bulk of this review will focus on those materials and will delve into more detail on some of the concepts already discussed (e.g. copolymer chemistry, microphase separation, specific vs. non-specific interactions, etc.). These topics were given only a cursory review thus far. They each will be discussed at more length in the following sections.

The general class of polymers called polyurethanes was originally synthesized in 1937 by Otto Bayer and coworkers while working at I.G. Farbenindustrie in Germany [3, 17, 18]. Now over 70 years old, this specific area and its breadth of applications has grown tremendously, consisting of many concentrations and containing many materials with a myriad of uses and forms. Polyurethanes are currently synthesized as plastics and elastomers in both cellular form (such as foams) and in solid form and are used in a wide variety of applications. Commercial products include those utilizing soft materials such as the flexible foam seating in office chairs and automobiles (polyurethane-ureas), foams for carpet backings, packing foams and many more. Thermoplastic and elastomeric fibers are used widely in the clothing industry. Other businesses use stiffer urethanes such as the footwear industry for use in shoe soles, and the automotive industry for use in car bumpers and body panels. Even stiffer urethanes are used in

paints, clear coatings, structural foams, refrigeration insulation, electronic equipment housings and many more areas [3, 19]. The range of uses for these materials is virtually endless and can be seen in Figure 1.5.

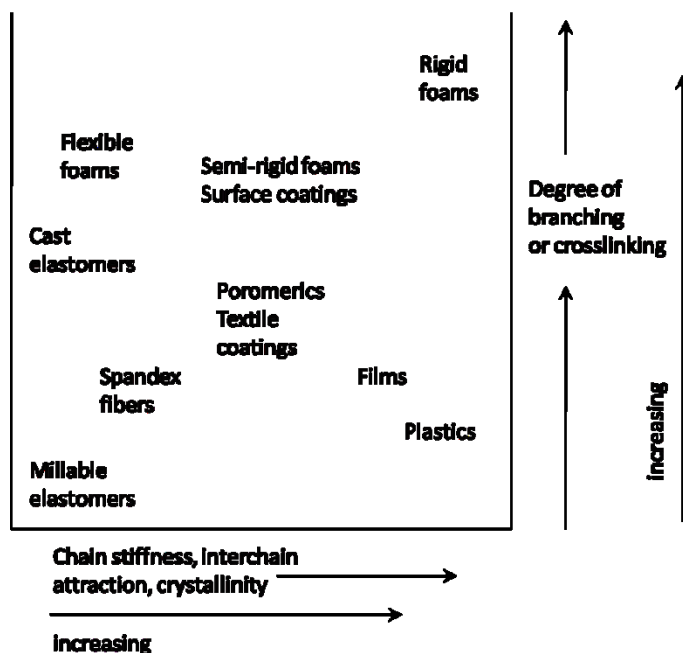


Figure 1.5. Range of structure–property relationships in polyurethanes.

Polyurethanes and polyureas distinguish themselves from other synthetic materials in that they can be formulated in such a way that an entire range of material properties, from soft flexible foams to rigid inflexible coatings can be engineered to have properties anywhere in between these two extremes.

The thermoplastic urethanes and ureas (TPUs) discussed here, as well as solution processed materials that are not (such as Spandex) are a subcategory of a class of copolymers known as thermoplastic elastomers (TPEs). TPEs are macromolecular systems that behave as rubber, elastic materials, but lack the chemical, covalent crosslinks responsible for the network structure of conventional rubbers [20]. First introduced in the late 1950s by Goodrich under the trade name Estane[®], TPUs are similar to the familiar block copolymers discussed earlier in the introduction (such as the SBS triblock copolymers) in that they form a microphase separated structure. The TPU chains, with their chemically incompatible hard and soft phases, are responsible for the useful physical behavior of these materials at their use temperatures. Generally the polymer chains are composed of two types of segments, soft segments (SS) and

hard segments (HS) which microphase separate into soft and hard phases respectively. The designation “SS” arises because the temperature at which the copolymer is used is *above the SS* T_g of these segments (or T_m if the SS is crystalline), rendering these segments soft at the use temperature. The HSs are so described because at the copolymer’s use temperature, the hard domains that they comprise are glassy or crystalline due to the fact that the use temperature of the copolymer is below the T_g or T_m of the hard block. Just as the SSs can often associate to form a soft phase, the hard blocks can often associate into morphologically distinct domains to form a hard phase. A more in-depth discussion of HS chemistry and morphology will be presented later in this chapter.

With the commercial introduction of TPUs in the 1960s [17, 21], the field garnered more intense interest in the academic community. Beginning with the work of Schollenberger on linear ester-based materials [22, 23], TPUs were shown to be extremely elastic at high extension ratios without undergoing a vulcanization process. What followed constituted the first argument for the existence of physical or virtual crosslinks formed by the interaction of the distinct hard domains. These physical crosslinks were also theorized to aid in the recoverability of the materials. The key difference between the physical crosslinks proposed by Schollenberger and the covalent crosslinks found in vulcanized rubber products is their ability to be reprocessed by melt or solution methods. The covalent bonds in the vulcanized products do not disassociate at elevated temperatures; hence the chains are unable to achieve the mobility necessary to be reformed into new shapes or products. Instead, the covalent bonds restrict movement of chains, even at high temperatures, and these bonds hold together until the material ultimately degrades at those elevated temperatures. Conversely, TPUs can be melt extruded, solution processed, reprocessed and recycled whereas the covalently bonded network structure of the vulcanized rubbers cannot.

Following the early discovery of polyurethanes, Bayer produced polyurethaneureas products and noted that the addition of water in the reaction step and the removal of CO_2 was found to produce materials with good elastomeric properties. In those studies it was determined that the water molecules served to introduce urea linkages along the length of the macromolecule and served as a chain extender. From there, it was a small but important change to use a hydroxyl capped polyester molecule and a low molecular weight diol or diamine as the CE in place of water for urethane and urea respectively. Following the early work by Bayer, DuPont began producing elastomeric materials with the introduction of a commercial fiber in the 1950s. Now

known as Lycra[®], the material was constructed with diphenylmethane-4,4' diisocyanate, a long diol as the SS, and was extended using a diamine (e.g. ethylene diamine) CE. Lycra[®] is actually a polyurethaneurea as it contains both urethane linkages, connecting the soft and hard segments, and urea linkages within the HSs themselves. The urea linkages prevent the melt reprocessability of fibers and therefore the material cannot be classically defined as a TPE. However, it is notable as DuPont's first entry into the new field of elastomeric fibrous materials. The issue of reprocessability was later resolved by substituting a diol-terminated CE for the amine-terminated CE used previously. This effectively replaced the urea linkages in the HS with urethane linkages.

As we are now beginning to address the properties of segmented copolymers, it is crucial to first understand the chemistry of these materials.

1.3. CHEMISTRY OF SEGMENTED POLYURETHANE AND POLYUREA COPOLYMERS

Polyurethanes and polyureas are conventionally based on the reaction of polyisocyanates with either hydroxyl containing polyols (to form polyurethanes) or amine terminated polyols (to form polyureas) [2]. Industrially, only a few basic isocyanates are used in conjunction with a broader range of polyether or polyester polyols that can have different functionalities and different molecular weights (though they generally range from 600–6,000 g/mol). Likewise, the isocyanates themselves can have unique functionalities, polarities, symmetries etc. Knowing this, it is the synthesis step in the production of polyurethanes and polyureas that is particularly important. Precise control of the reacting groups can be exercised during this crucial step which allows for the tailoring of the end product's properties to a specific application's needs. In particular, control may be exercised over the following parameters during synthesis: chemical composition, molecular weight and molecular weight distribution of the reacting components (and final products as well), functionality of the reactants, and the potential of promoting crystallinity of either the soft or hard segments that make up the final segmented copolymer.

The synthesis of polyurethanes is a relatively straightforward process which can be completed in one step (the “one-shot method”) or two steps (the “prepolymer method”). In the one step process, the hydroxyl terminated polyol is mixed with a chosen polyisocyanate to form

a polyurethane with properties governed by the chemistries of the reacting species (including the chain extender) and the predetermined molar ratios of the species to be reacted. When controlling the reaction conditions to minimize side reactions, the use of difunctional species results in a linear polyurethane. The result is an end-capped polymer chain consisting of both hard and soft segments.

In the more commonly used two-step “prepolymer” process for making a linear polyurethane elastomer, most typically a polyester or polyether diol is reacted with a large excess of diisocyanate to form a prepolymer (Figure 1.6). The prepolymer is then further reacted with diol chain extender to form the final linear polyurethane.

Polyureas can also be formed using the one step method by utilizing an amine terminated polyol instead of a hydroxyl terminated polyol, with the resulting material containing urea linkages instead of urethane linkages. The prepolymer method may also be used to produce polyureas, in this case the chain extension stage is carried out with a diamine chain extender.

Lastly, a linear polyurethaneurea may be produced with the prepolymer method by reacting a hydroxyl terminated diol with diisocyanate to form the prepolymer, and then reacting with diamine chain extender in the chain extension step. Alternatively, one could react an amine terminated diol with diisocyanate to form the prepolymer, and then carry out the subsequent chain extension step with a diol.

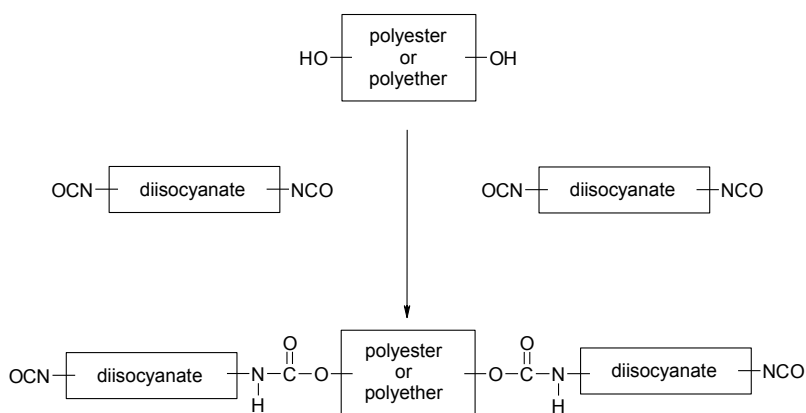


Figure 1.6. “Prepolymer” process for the synthesis of linear polyurethanes.

Figure 1.7 shows the basic reactions between isocyanates and hydroxyl terminated groups and amine terminated groups that form the urethane and urea linkages respectively. Generally, any group containing active hydrogens can react with isocyanates [17, 24, 25]. As mentioned

earlier, the most common isocyanate reactions (and the reactions most relevant to this body of work) form urethane and urea linkages. However, it should be noted that other reactions can occur and are useful to generate materials not used in this study. For instance, the reaction of isocyanate with water forms the unstable species carbamic acid (Figure 1.8). Its decomposition generates carbon dioxide which can then be used to form a flexible polyurethaneurea foam product with urea linkages.

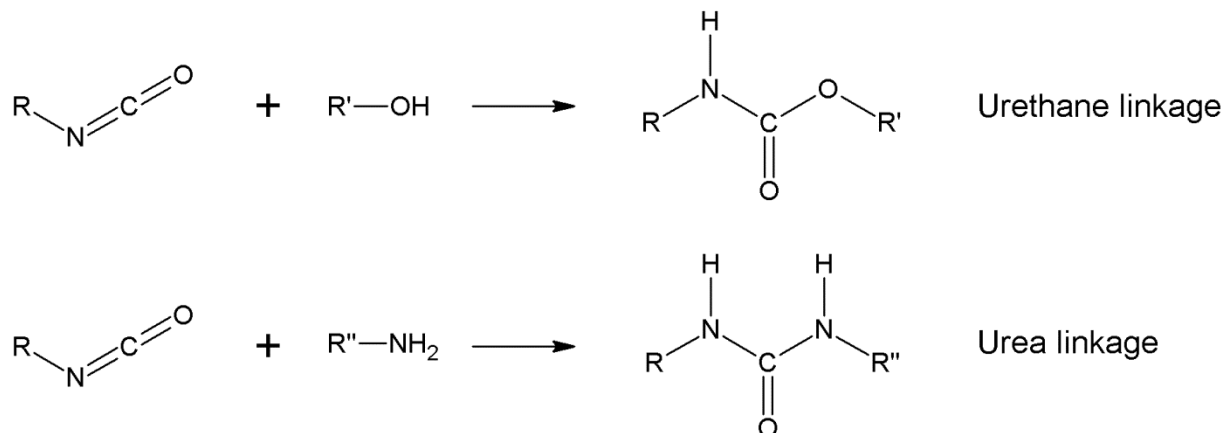


Figure 1.7. Basic reactions to form urethane and urea linkages.

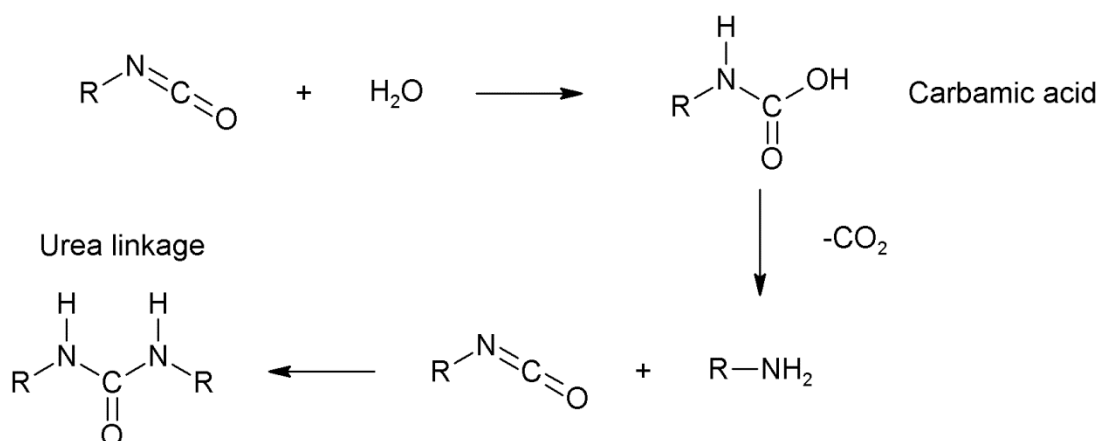


Figure 1.8. Formation of urea linkage via the decomposition of carbamic acid.

Two other linkages can also form if the active hydrogen reacts with the remaining protons of the urethane or urea groups. Shown in Figure 1.9, these reactions allow for crosslinking and branching. When the desired end product is a linear material, as in this study,

such side reactions are minimized by reacting in solution and by controlling the reaction conditions of the process [3, 19, 24, 25].

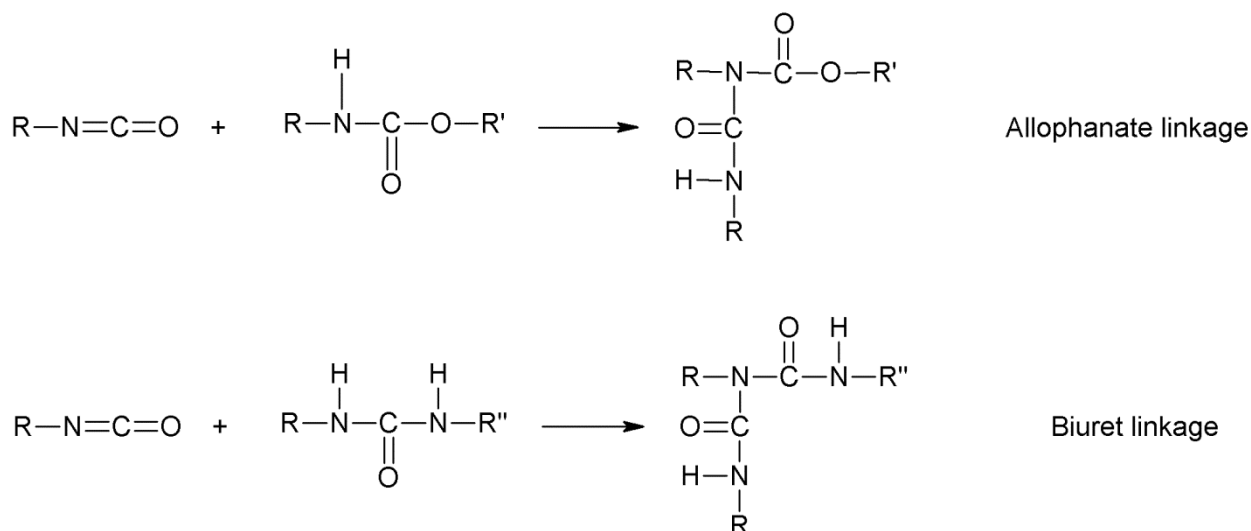


Figure 1.9. Formation scheme of allophanate and biuret linkages.

As we are discussing the details of one- and two-step reactions used to form polyurethanes and polyureas, it might be useful to examine a theoretical comparison of each. Just such a comparison was made by Peebles beginning in 1974 [26, 27]. In that study he determined that when using the same basic starting materials, choosing a two-step reaction produced a polymer with a somewhat narrower distribution of HS lengths than would be produced via the one step reaction route. More pertinent to this study, in 1982 Abouzahr and Wilkes looked specifically at the effect of real one- or two-step reactions on polyether and polyester based polyurethanes [28]. Their study investigated polyurethanes based on PTMO and polytetramethylene adipate SSs, and HSs constructed of MDI and BDO. Their results supported the earlier work by Peebles, showing that the one-step reaction product based on the polyester polytetramethylene adipate had somewhat poorer mechanical properties than the two-step reaction product. The poorer properties of the one-step product were explained on the basis of a greater distribution of HS length which provided for more mixing of the polyester SS and urethane HS. Poorer phase separation led to less desirable mechanical properties. Of more relevance to this study are the results based on polyether PTMO (which will be the primary SS used throughout this work representing the author's own research). In this case it was found that the one-step reaction also formed polyurethanes with poorer mechanical properties than the two-

step method, but showed that the drop in mechanical properties was much less dramatic than in the polyester case. This was attributed to the lower interaction between the polyether SS and the polyurethane HS when compared to the polyester SS and the polyurethane HS. Hence, better phase separation resulted with the polyether-based material and the resultant material displayed better mechanical properties than the less phase-separated product.

Having now looked at the possible urethane and urea products of an isocyanate and its reactions with active hydrogen containing compounds, we turn our attention to a more in depth look at the reacting species used to synthesize polyurethanes and polyureas. A wide variety of diol and diamine terminated polyesters or polyethers can be used as the soft segment in the production of polyurethanes or polyureas. The author's studies presented in chapters 2–5 will be concerned primarily with a polyether polytetramethylene oxide (PTMO) soft segment. However, there are many others that are of commercial importance such as polydimethylsiloxane (PDMS), and polyethers such as polyethylene oxide (PEO), polypropylene oxide (PPO), and random copolymers of propylene oxide and ethylene oxide.

As mentioned before, diol or diamine capped SSs are reacted with a diisocyanate to form linear polyurethanes or polyureas. There are a wide variety of aromatic or aliphatic diisocyanates to choose from depending on the desired thermal and mechanical properties of the final material. Among the most commonly used aliphatic diisocyanates are 1,6-hexamethylene diisocyanate (HDI), hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), and the cycloaliphatic isophorone diisocyanate. These diisocyanates are often used due to their greater UV stability when compared to aromatics. 1,4 trans-cyclohexyl diisocyanate (CHDI) is used less frequently due to its cost, toxicity, and volatile organic compounds (VOCs). Aromatic diisocyanates include para-phenylene diisocyanate (*p*PDI), meta-phenylene diisocyanate (*m*PDI), 4,4'-diphenylmethane diisocyanate (MDI), and an 80/20 mixture of 2,4- and 2,6-toluene diisocyanate (TDI). Such aromatic species are generally chosen because they are more reactive than the aliphatics and as such, the latter often require the need for catalysts during the chemical reaction. As we will see, another very critical aspect of the structure of diisocyanates is their symmetry. Linear symmetric structures such as *p*PDI, HDI, and 1,4 trans-CHDI may promote HS crystallization (thereby increasing the cohesiveness of the hard domains) and lead to better microphase separation, increased modulus, hardness, and tear strength. Symmetric diisocyanates may also broaden the service temperature window of their respective TPUs by extending the

useful temperature range of these materials to higher temperatures. (A more in-depth discussion of the concept of a material's service temperature window will be presented in the section discussing microphase separation.) Alternatively, asymmetric structures in the HS such as those produced with the isomeric mix of 2,4- and 2,6-TDI have the opposite effect. That is, they may produce materials with more poorly packed HS domains since there is less cohesiveness of these domains. Both symmetric and asymmetric diisocyanates will be used throughout the author's own work as the effect of diisocyanate chemistry and its symmetry on the structure–property behavior of segmented polyurethanes and polyureas is one of the key focal points of this work.

The previous discussion of the symmetry of diisocyanates did not greatly take into account the effect of chain extenders, but it is important to understand their role in structure–property relationships of typical commercially available TPEs. Polyurethanes and polyureas produced from one-step reactions without the use of CE molecules in general do not typically have sufficient mechanical properties to make them useful for commercial applications, particularly at lower HS contents. Many mechanical properties are governed by the hard phase in microphase separated materials. Without CEs, the hard phase is composed of only the diisocyanate species used in the one-step reaction. However, the introduction of a CE molecule which can also react with the diisocyanate and any excess diisocyanate present, forms a HS composed of both species. The longer and stiffer HS enhances microphase separation, adding strength and stiffness to the material which makes them viable products for commercial applications; hence, almost all commercial products are chain extended. The most common CE molecules used are ethylenediamine (EDA) and 1,4-butanediol (BD) to form polyureas and polyurethanes respectively. When reacted with an isocyanate capped prepolymer, the second reaction step with EDA produces a material with urea linkages between the prepolymer and CE. When BD is used instead of EDA, the result is a material with urethane linkages connecting the prepolymer and CE [3, 7, 19, 24, 29].

Now, with a better understanding of the synthesis routes to form linear polyurethanes and polyureas, we turn our attention to the microphase separation characteristics of these materials since it is the microphase separation that gives these materials their useful properties.

1.4. THE CHEMICAL NATURE OF MICROPHASE SEPARATION IN SEGMENTED COPOLYMERS

As addressed earlier, the phenomenon of microphase separation can occur in block copolymers when component blocks are sufficiently chemically incompatible as dictated by the equilibrium thermodynamics of the system and the time frame is sufficient for the equilibrium state to be attained. Polymer blends of homopolymers may macrophase separate with the individual polymers forming regions relatively pure in one species. The macrophase separation occurs because of the insolubility of the blended polymers. As the individual polymers are not covalently linked to the other chemically incompatible species, they separate into large scale regions rich in each polymer species. However, with segmented copolymers, the chemically incompatible blocks are covalently linked, hence, individual blocks cannot separate on the same length scale as blends. However, due to the smaller lengths of segments in segmented copolymers than the blocks found in block copolymers (where the size of the component blocks greatly increases the size of the regions), the size of the microphase regions are smaller as well.

As also addressed earlier, microphase separation of block copolymers is generally a well understood phenomenon when specific interactions such as hydrogen bonding and ionic forces do not occur between constituent blocks. As stated earlier, in such materials, microphase separation is governed by the parameters, χN , f_A and f_B . Recall that χ is the well-known Flory Huggins parameter and is temperature dependent, N is the degree of polymerization and f_A and f_B are the volume fractions of components A and B respectively. Well-known theories include the random phase approximation theory developed by Leibler [30] and the narrow interphase based self-consistent theory of Helfand [31].

The parameter χN , while successful in predicting microphase separation behavior in various block copolymer systems, fails to translate easily into the prediction of microphase separation of segmented copolymers for a variety of reasons. The difficulty is due to the specific interactions present in these systems [32, 33] such as hydrogen bonding or the introduction of ionic species into segmented copolymers. Other issues besides occurrence of specific interactions also cause difficulties for the theories developed for block copolymers. Among these are the crystallization of the SS and/or HS (though this can pose a problem in block materials as well), the variation of the free-energy of monomer contacts along the length of the macromolecule

chain (a variable assumed to be constant along the chain length for the homopolymer blended systems), and the increased polydispersity of the segmented copolymers due to the step-growth polymerization. In an attempt to relate microphase separation in segmented copolymers to a quantifiable parameter, in this case χ , Camberlin and Pacault made a systematic study of the effect of SS on phase separation. They first constructed four polyurethane samples with different SSs, but identical HS chemistries (MDI chain extended with BD) and *ca.* 30 wt% HS. With known chemistries, they used the four known SS solubility parameters, δ , and calculated δ for each HS using group contributions [34]. Using the values of δ s of the samples, the authors then calculated χ values for each of their four materials and attempted to relate them to the microphase separation of their samples. They also measured the specific heat capacities of the samples with DSC, and tried to correlate the critical interaction parameter for the system to the degree of microphase separation. Although they were unable to find a correlation between the two, their work marked the first attempt to relate the microphase separation of segmented polyurethane copolymers to a quantifiable thermodynamic variable.

The difficulty in explaining the cause and ultimate extent of microphase separation with traditional block copolymer thermodynamics has not prevented investigations into the thermodynamic underpinnings of the process. A good deal of work has been done in this area, much of it directed towards understanding the miscibility of different species and the investigation of the value of δ of different blocks [35-38]. With lower molecular weight materials, mixing occurs when the solubility parameters of the components to be mixed are roughly equal [39, 40].

As discussed before, this approach has limitations when applied to segmented copolymers due to the specific interactions such as hydrogen bonding and permanent dipole interactions. One way to try to incorporate all these contributions was first developed by Hansen using a three-dimensional solubility parameter [41] though even this approach has some difficulties associated with it. To calculate the three-dimensional solubility parameter, one needs to first calculate the cohesive energy density, not an easy task for polymer samples [8, 39, 40] though there are indirect ways of measuring or estimating the solubility parameter [41-44]. Hansen proposed a three-dimensional solubility parameter theory in which hydrogen bonding, permanent dipole interactions and van der Waals forces could be directly related to the Flory–

Huggins interaction parameter, χ [41]. According to the theory, the overall solubility parameter was defined to be:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (\text{Equation 1.3})$$

where δ_d , δ_p , and δ_h , correspond to permanent dipole interactions, van der Waals forces, and hydrogen bonding respectively. The Flory–Huggins interaction parameter is related to the solubility parameter by:

$$\chi = \frac{\bar{v}(\delta_1 - \delta_2)^2}{RT} \quad (\text{Equation 1.4})$$

where δ_1 and δ_2 are the solubility parameters of species 1 and 2, $\bar{v}$ is the molar segmental volume of the polymer segment, R is the universal gas constant and T is the temperature in Kelvin. Hence, the parameter χ is dimensionless. This parameter provides the link between hydrogen bonding and microphase separation of block and segmented copolymers.

Measurements have been made to determine the values of the different δ s for a number of different species and calculations based on the group contribution method suggest that for urethanes, the δ_h contribution to the three dimensional solubility parameter is ~68% while the contribution for ureas is ~75% [45, 46]. It was also determined that the overall solubility parameter δ for ureas is higher than those of urethanes. This reinforces the conclusions of Yilg r that hydrogen bonding in ureas is stronger than in urethanes.

A key study of hydrogen bonding in PUs was made by Harrell and coworkers [47]. Model PUs were made with PTMO soft segments and monodisperse HSs containing one, two, three, or four repeat units. They prevented the HS from containing –NH groups by confining the nitrogen atoms to a piperazine ring. Lacking the –NH groups, the materials did not exhibit any hydrogen bonding. Samuels and Wilkes performed a structure–property investigation on these model materials and determined that the PU structure was still well microphase separated despite the lack of hydrogen bonding [48]. The lack of hydrogen bonding did not prevent the HS from forming a very spherulitic (crystalline) superstructure however, and therefore they did display many of the classical physical properties of microphase separated PUs including storage moduli, tensile strengths and elongation at break comparable to the more conventional ester or ether based polyurethanes that do contain hydrogen bonding.

Clearly, microphase separation is an important process that promotes the elastomeric properties of polyurethanes and polyureas, as well as the triblock SBS systems. The studies of Harrell should not, however, be viewed as minimizing the importance of hydrogen bonding in real world applications. The model PUs he studied contained monodisperse HSs and crystallizable HSs which are not typically found in most segmented polyurethane commercial products, particularly where the HS does not crystallize.

One of the pioneering efforts in the investigation of microphase separation for segmented polyurethanes was done by Cooper and Tobolsky in 1966 [49]. They showed that the storage modulus plateau of polyester TPUs measured with dynamic mechanical analysis (DMA) were strikingly similar to those of triblock copolymers such as SBS, a well-researched block copolymer of the time. As an explanation for the behavior, they offered the argument that SS and HS separation caused physical cross-links to form from the different segments. In making this declaration, they were the first to verify the role that physical cross-links play in the mechanical properties of TPUs, though the concept of a “virtual” cross-link was first introduced by Schollenberger [23]. From this insight, a great deal of work was initiated which attempted to understand the nature of the SSs and HSs in TPUs in hopes that control over these variables would lead to better control over the extent of physical cross-linking and hence, influence over mechanical and thermal properties of final materials.

As stated earlier, a great deal of control over the SS and HS (diisocyanate and CE) can be exercised during the synthesis step. In particular, the polarity of the segments, their symmetry, molecular weights and chemical linkages can be tailored to provide the desired mechanical and thermal properties of the segmented copolymer. Clearly the chemistry of these systems is vitally important and was discussed in the previous section.

It has been established that a microphase separated structure is necessary for good thermal and mechanical properties in segmented copolymer systems in order for them to be commercially viable. A key variable that promotes that structure and is responsible for these properties is the nature of the hydrogen bonding mentioned previously. Therefore it is vital to understand the chemical nature of hydrogen bonding and its effect on the phase separated structure.

1.5. THE CHEMICAL NATURE OF HYDROGEN BONDING

As mentioned earlier, many polyurethanes and polyureas have the potential to form hydrogen bonds. Hydrogen bonding is an attractive force between a lone pair of electrons of an electronegative atom (N, O, or F) and a hydrogen atom that is attached directly to an N, O, or F. When an electronegative O is hydrogen bonded to a single H atom, this is termed monodentate hydrogen bonding. When an electronegative O is hydrogen bonded to *two* H atoms, this is termed bidentate hydrogen bonding. Looking at the typical polyurethane and polyurea backbone structure, one sees that the potential for H-bonding exists between the hydrogen atom or proton of a urethane group and the oxygen atom of a carbonyl group or another nearby urethane linkage Figure 1.10. Hydrogen bonding can also arise between the urethane (or urea) group and the ether or ester group of the SS.

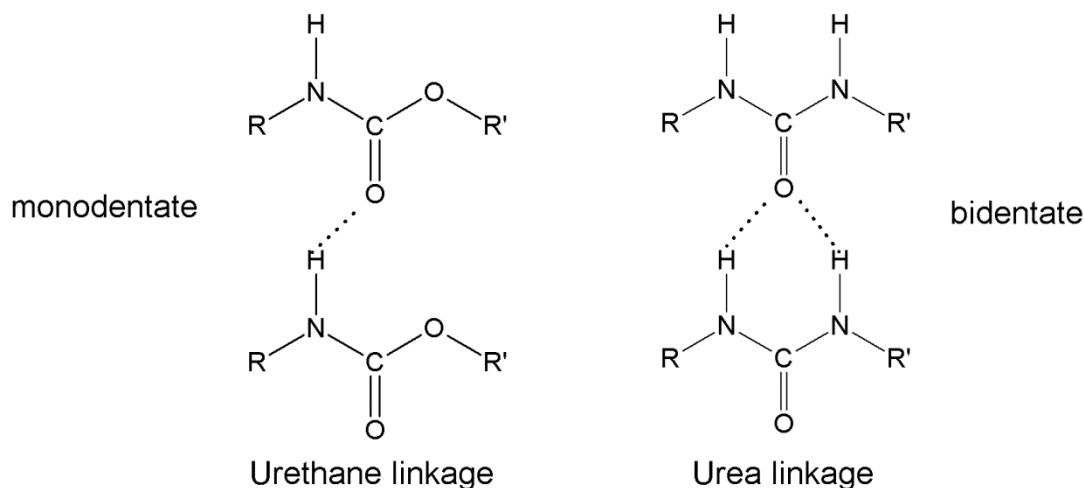


Figure 1.10. Hydrogen bonding schemes for polyurethanes and polyureas.

The strength of the hydrogen bonding in polyurethanes and polyureas has a direct effect on the final properties of these materials. Bidentate hydrogen bonding is stronger than monodentate hydrogen bonding as determined by semi-empirical quantum mechanical calculations performed by Yilgör et al. [50]. His calculations based on the density functional theory show that urea-ether hydrogen bond interaction energy is 19.2 kJ/mol (and occur in pairs), as compared to the lower urethane-urethane 18.4 kJ/mol interaction energy. Urethane-ether or urea-ether (or the respective ester counterparts) hydrogen bonding interactions are also possible.

In order to investigate hydrogen bonding in these materials, Fourier transform infrared spectroscopy (FT-IR) is a very important and most frequently used technique [51-58] because it can often quantify the size, extent and strength of hydrogen bonding in polyurethanes and polyureas as a function of backbone chemistry [54, 57]. The magnitude of the frequency shifts in the peak positions of the C=O stretching absorption region ($1600\text{--}1800\text{ cm}^{-1}$) and the N-H stretching absorption region ($3200\text{--}3400\text{ cm}^{-1}$) are most often monitored. Thermal transitions of PUs such as the SS T_g have been monitored via hydrogen bonding by following the N-H absorption as a function of temperature [52, 55].

The FT-IR technique has been used to track the real-time development of hydrogen bonding by monitoring the shift in the urethane carbonyl group's absorption to lower wavenumbers as hydrogen bonding occurs [36, 55, 59-68]. Hydrogen bonding has also been monitored during the heating and cooling of polyureas and polyurethaneureas. For example, Ning and coworkers showed that the strength and degree of monodentate hydrogen bonding in polyurethanes decreases with increasing temperature [64]. Polyurethaneureas do not display as large a drop in storage modulus with increasing temperature as the bidentate bonding in these materials is stronger than monodentate bonding found in polyurethanes. As a result, the value of storage modulus often remains high until the material thermally degrades [69]. A great deal of information is available detailing the hydrogen bonding effects in polyurethanes, polyureas and polyurethane ureas [17, 36, 55, 59, 62-68, 70-72].

1.6. KEY WORK RELATED TO THE MOTIVATION BEHIND THIS DISSERTATION

In 1987, Barikani and Hepburn published a series of papers detailing the thermal properties of a series of linear segmented polyurethanes. A series of these materials were constructed (using the prepolymer method) with a 2000 g/mol polycaprolactone SS, and a hard segment composed of BD and a diisocyanate of either CHDI, *p*PDI, MDI, HMDI, or an 80/20 mixture of 2,4- and 2,6-TDI. The molar ratio of SS/diisocyanate/CE used was 1/2.6/1. Each of these materials was studied using DMA and a reproduction of their results is presented in Figure 1.11 (red arrows added by me for guidance).

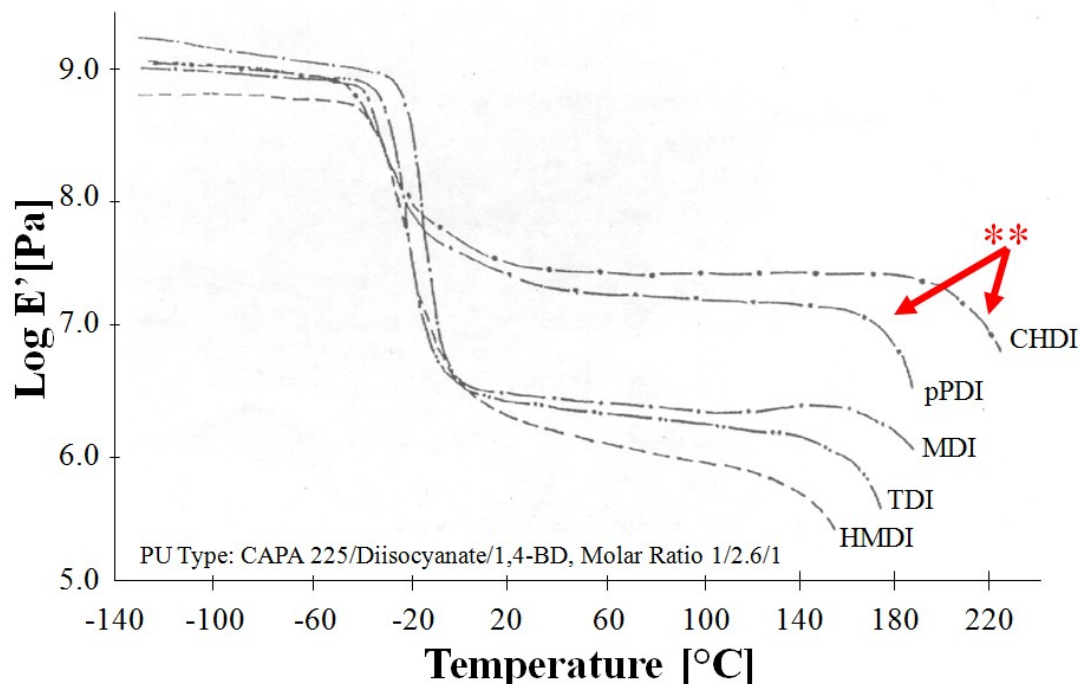
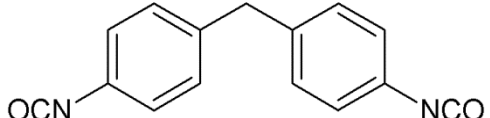
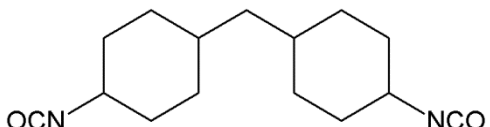
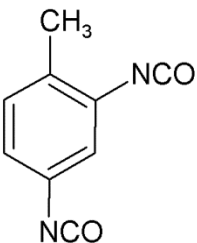
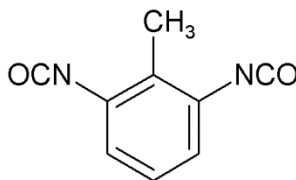


Figure 1.11. DMA results of Barikani and Hepburn for a series of polyurethanes based on polycaprolactone and a series of different diisocyanates. Materials were all chain extended with BD [73].

Interestingly, the authors made no comment on the large difference in storage modulus for the CHDI- and *p*PDI-based materials (indicated with arrows) as compared to the other materials (MDI-, TDI, and HMDI-based). Their focus was on the upper use temperature of their samples and the effect of diisocyanate on the location of the final sample softening in stiffness. However, a difference in storage modulus over the service temperature window clearly exists between the pair of CHDI- and *p*PDI-based polyurethanes (*ca.* 10^7 Pa) and the MDI-, HMDI-, and TDI-based polyurethanes (*ca.* 10^6 Pa). The obvious difference between these two groups of materials is that the former are composed of symmetric diisocyanates whereas the latter are all composed of asymmetric, non-linear or symmetric (but kinked) diisocyanates (see Table 1.1).

Table 1.1. Diisocyanate structures used by Barikani and Hepburn.

Diisocyanate	Structure
(<i>p</i> PDI) para-phenylene diisocyanate	
(CHDI) 1,4 trans-cyclohexyl diisocyanate	
(MDI) 4,4'-diphenylmethane diisocyanate	
(HMDI) hydrogenated 4,4'-diphenylmethane diisocyanate	
(TDI) 2,4-, 2,6-toluene diisocyanate	 2,4  2,6

A deeper investigation of the chemistry of diisocyanates and their symmetry on the structure–property effects on polyurethanes and polyureas was therefore warranted. The polyurethanes synthesized by Barikani and Hepburn had hard segment contents ranging from 20–28%. At the same time, it is well known that the structure–property relationships of certain biological systems are strongly influenced by hydrogen bonding and crystallization, e.g. polynucleic acids, proteins, cellulose, lipids etc. These materials are obviously not chain extended. With this in mind, it was hypothesized that non-chain extended polyurethanes and polyureas might also be produced that could display microphase separation. In addition, without the use of CEs, the effect of the chemistry and symmetry of the diisocyanate molecules could be more directly determined. Indeed, the bulk of this dissertation will deal with the characterization

of non-chain extended polyurethane and polyurea materials based on a PTMO soft segment and a single diisocyanate as the hard segment. We will see that, indeed, these materials often displayed good microphase separation (even with relatively low HS contents of *ca.* 14%) and that diisocyanate chemistry and symmetry play a pronounced role in the mechanical and thermal properties of these materials.

In addition to the single-segment materials, BD chain extended materials will also be investigated to determine not only if the behavior measured by Barikani and Hepburn could be reproduced with regard to the effect of diisocyanate chemistry and symmetry on the storage moduli of these materials, but also to determine what effect the introduction of chain extenders would have on the symmetric systems that were not previously chain extended. These materials were constructed to have HS content as low as *ca.* 7 wt% .

1.7. EXPERIMENTAL METHODS

A number of experimental techniques are available today that are particularly valuable to help characterize segmented polyurethanes and polyureas. This brief descriptive review will focus on two methods in particular that are of importance in the individual studies that follow. A plethora of other measurement and characterization methods are available (and many others have been used), however this discussion will be limited to those that were most frequently used. The first method is that of Dynamic Mechanical Analysis (DMA) which can provide insight into the mechanical properties of polymeric materials and is also sensitive to transitions that polymers undergo during heating, during frequency scans and due to changes in moisture environment. When applied to segmented copolymers, it can also provide information regarding the presence of microphase separation. Atomic Force Microscopy (AFM) can often elucidate the morphology and structure of segmented copolymers and can provide visual evidence of the same.

1.7.1. DYNAMIC MECHANICAL ANALYSIS

In DMA studies, a polymeric sample is deformed cyclically and its small-strain linear viscoelastic behavior is recorded while changing temperature [74-76]. Because the sample is being subjected to a sinusoidal stress or strain rather than a constant stress or strain, it is more convenient and perhaps more intuitive to use the complex Young's modulus to describe stress-strain behavior as it reflects the inherent viscoelastic nature of polymer systems where there is a time lag between the application of a stress and its subsequent strain response. The complex Young's modulus is defined as:

$$E^* = E' + iE'' \quad (\text{Equation 1.5})$$

where E' is the storage modulus and E'' is the loss modulus. The storage modulus is a measure of the energy stored elastically during deformation and the loss modulus is a measure of the energy converted to heat during cyclic deformation. The time between the application of the sinusoidal stress and the resultant strain is defined as the phase angle δ (Figure 1.12). The ratio of loss modulus to storage modulus is given by the tangent of the phase angle describing the material's behavior. That is, the loss tangent is defined as:

$$\tan \delta = E''/E' \quad (\text{Equation 1.6})$$

Therefore, the stiffness of a material and its damping properties can be completely described with any two of these three quantities. The loss modulus and loss tangent are indicative of a material's ability to dissipate heat during deformation and therefore peaks in $\tan \delta$ plots are often referred to as damping peaks.

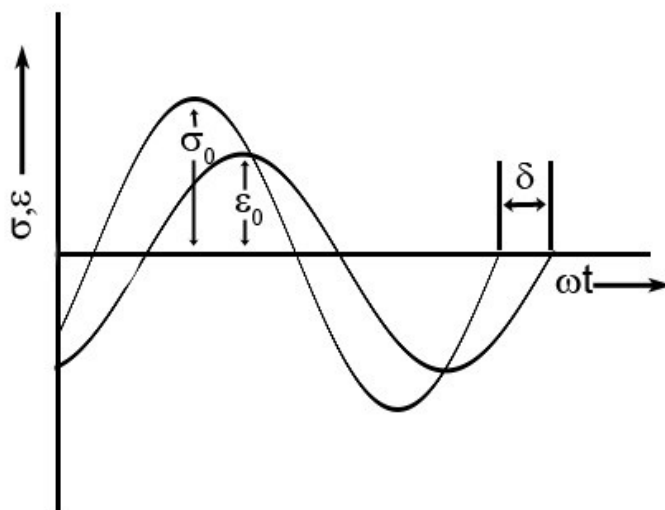


Figure 1.12. Sinusoidal oscillation and response of a linear viscoelastic material.

As mentioned earlier, DMA is a technique that can provide valuable information and insight into thermal transitions of polymeric materials. In segmented copolymers that display good microphase separation, DMA is used to detect soft segment glass transition temperature, the melting temperature of soft segment domains if the soft phase can crystalline, the glass transition temperature and/or the melting temperature of hard segment domains. The location of these transitions and their magnitudes can be useful in determining the morphology of the materials being studied and in particular, can give information about the microphase separation in the segmented systems. An example of the results provided by DMA was shown previously in Figure 1.11. Details of the test conditions used in the investigations that follow are explicitly stated for each study.

All of the DMA studies completed in this work were done in temperature sweep mode, where the frequency of the deformation was 1 Hz and the temperature was increased at a rate of 2 °C/min. However, the instrument can also be operated in frequency sweep mode where the temperature of the test is held constant while the frequency of the cyclic deformation is varied. In this mode, peaks in $\tan \delta$ and E'' with respect to frequency can be associated with the T_g and with secondary transition.

1.7.2. ATOMIC FORCE MICROSCOPY

The characterization technique that provides information about microphase separation most directly is AFM. This technique gives the most direct visual information compared to any other method for this scale length of polyurethanes and polyureas. The Atomic Force Microscope was invented in 1985 by Binnig, Quate and Gerber to overcome the basic limitation of Scanning Tunneling Microscopy (STM) that it can only image conductive or semiconductive surfaces. In contrast, the AFM can image almost any type of surface, be it ceramic, metallic, polymeric, composite or in some cases even living biological surfaces [77-79].

AFMs work using a detection system in which a laser is focused on the end of a cantilever beam. Attached to the end of the cantilever is an AFM tip, usually made from silicon or silicon nitride and having a tip radius a few to tens of nanometers. The back of the cantilever is a reflective surface such that the incident laser reflects off the cantilever and hits a position sensitive detector. A schematic setup of the beam deflection system is provided in Figure 1.13.

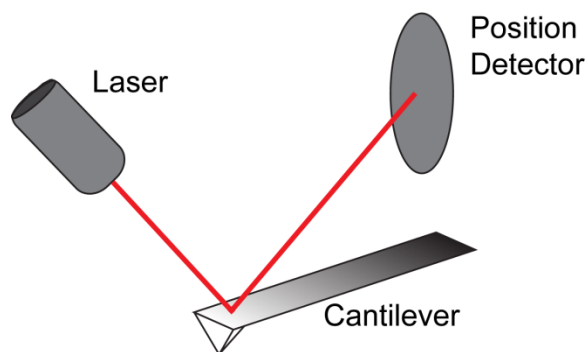


Figure 1.13. Beam deflection system used in atomic force microscopy.

AFM is based on the accurate measurements of forces between the AFM tip and the surface of the sample being measured. This force is not measured directly, but rather, it is calculated by measuring the deflection of the cantilever as it probes the surface. The cantilever obeys Hooke's Law, that is:

$$F = -kz \quad (\text{Equation 1.7})$$

where F is the force being calculated, k is the known stiffness of the lever, and z is the measured deflection of the cantilever. The force versus z -distance curve is presented in Figure 1.14. When the probe is in contact with the surface of the sample, repulsive forces are generated to push the

tip away from the surface. As the sample-to-tip distance increases to small values just above the surface, attractive forces pull the tip back towards the surface of the sample. At still larger distances from the sample surface, there is no deflection of the cantilever as the force between sample and tip approaches zero.

The microscope can be operated in a variety of modes but the one most pertinent to this study is alternatively known as “dynamic force”, “intermittent contact”, or most commonly “tapping-mode AFM”. In this mode, a stiff cantilever is oscillated close to the sample surface such that part of its oscillation takes it into the repulsive contact zone, where the tip intermittently touches or “taps” the surface. Tapping mode is often used to increase lateral resolution on soft samples. Because of the water contamination layer on the surface of samples, stiff cantilevers are used to prevent the tips from becoming “stuck” in this layer.

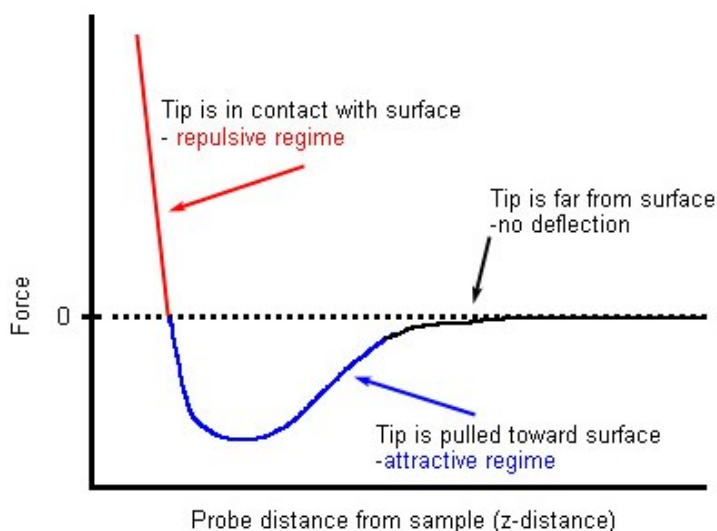


Figure 1.14. Force versus z-distance curve which governs AFM.

In addition to the measurement of topography or differences in height in the sample using tapping mode, the phase imaging mode is often run concurrently. The phase imaging mode measures the phase shift of the motion of the oscillating cantilever relative to its driving signal. This shift in phase can be correlated to specific material properties that effect the tip/sample interaction, particularly it can be used to differentiate areas on a sample with such differing properties as friction, adhesion, viscoelasticity, and stiffness. As we will see later in this

dissertation, the ability to differentiate between stiff and soft areas will be vitally important to measuring microphase separation of segmented polyurethanes and polyureas.

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. Some samples, however, necessitated the use of a much higher free air amplitude of *ca.* 8.0 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4–0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz.

2. ROLE OF CHAIN SYMMETRY AND HYDROGEN BONDING IN SEGMENTED COPOLYMERS WITH MONODISPERSE HARD SEGMENTS

2.1. INTRODUCTION

Linear segmented copolymers consist of alternating hard and soft segments along their backbone. Their ability to develop microphase separation is one of their most defining features because such a morphology imparts many useful properties for practical applications [3, 7, 17, 19, 24]. Under appropriate conditions for microphase separation, and when the relative hard segment (HS) volume or weight fraction of the copolymer is low, the HSs generally are postulated to segregate into isolated microdomains that are randomly dispersed in the continuous matrix of the soft segment (SS) phase [3, 7, 17, 19, 31]. It is well established that the appropriate conditions for microphase separation of block copolymers e.g. SBS (which have weaker secondary bonding than segmented copolymers with specific interaction such as hydrogen bonding) are determined by the parameters χN and f for a specific chemistry, where χ is the Flory–Huggins interaction parameter, N the overall degree of polymerization, and f the volume fraction of a block or segment. This approach, however, is not easily applicable to the types of segmented copolymers addressed in this study. As the HS content is increased, the long range connectivity of the HSs is also expected to increase, which in turn may be expected to promote a percolation of the hard phase through the soft matrix. The hard domains act as physical cross-link sites and reinforce the soft matrix thereby enabling the copolymer to display controlled useful structural properties in its ‘service window’, where in for block and segmented copolymers, the service window is defined by the region in the storage modulus (E')–temperature space within which the value of E' is relatively temperature insensitive. In addition, this region lies above the SS T_g (or T_m , if it can crystallize) and below the softening point of the copolymer’s hard phase or the copolymer’s degradation temperature. More specifically, this upper temperature limit could come from one of three mechanisms: 1) the hard phase softens due to a HS T_g , 2) the hard phase melts due to a crystalline HS at T_m , or 3) the material degrades at high temperatures prior to softening. Materials that are most desirable in commercial applications tend to have little if any change in E' across the breadth of this service temperature

window, and therefore the region is often referred to as a plateau region. In addition to the copolymer's HS content, the extent of the HS percolation and the potential crystallizability of the hard phase have been found to greatly influence the mechanical and thermal response of the material. In segmented copolymers resulting from isocyanate, namely polyurethanes, polyureas and polyurethaneureas, the cohesiveness of the hard domains is further enhanced by the ability of the HS to establish a hydrogen bonded network, particularly within the HS phase.

The step-growth copolymers mentioned previously in the literature review, of which polyurethanes are extensively used commercially, are generally synthesized by a two-step route, commonly referred to as the “prepolymer” method. In the first step, a prepolymer is made by end-capping a difunctional oligomer, typically in the presence of excess diisocyanate. In the second step, the HSs are formed by reacting the prepolymer mixture with stoichiometric amounts of difunctional chain extender. Over the years consensus has developed amongst practitioners in the field (based on the need for a high molecular weight of the final polymer) that lengthening the HS, which of course also increases the HS content, is necessary to produce segmented copolymers that display useful structural properties in their service window. Therefore, few reports in the literature have addressed segmented copolymers that are non-chain extended. The most noteworthy of those that do is the report by Tyagi et al. [37] (also from this lab) on polydimethylsiloxane based polyurea copolymers. In their report however, a percolated hard phase, such as could be produced by hard segment crystallinity or hydrogen bonding, was not observed visually or reconfirmed by any other method irrespective of the hard segment content (6–22 wt%) investigated. Segmented copolymers in which crystallizable HSs of monodisperse uniform length are synthesized before condensing them with a selected SS generally require multi-step synthesis and are expensive to produce. Therefore, they have also received limited attention.

As is well documented, crystallization and hydrogen bonding are two factors that strongly influence the morphology and properties of natural polymers, such as poly(nucleic acids) (e.g. DNA, RNA), proteins (e.g. spider silk), and cellulose [80-82]. Inspired by such observations for bio-based polymeric materials, it was hypothesized that a proper selection of the type of hydrogen bonding and the level of segment symmetry could potentially produce, without chain extension, segmented polyurethane and polyurea copolymers that would still display strong microphase separation. Furthermore, the hope was to demonstrate that the service window

behavior might be sufficient or even comparable to the traditional chain extended systems, particularly for materials that possessed urea linkages as these can promote strong bidentate hydrogen bonding. To confirm the hypothesis, copolymers were synthesized using a one-step procedure where equimolar amounts of a selected diisocyanate were reacted with dihydroxy or diamine terminated poly(tetramethylene oxide) (PTMO) oligomer of $\langle M_n \rangle$ 975 and 1100 g/mol thereby promoting either segmented polyurethane or polyurea segmented copolymers, respectively. The resulting segmented copolymers contained PTMO as the SS and a uniform length (monodisperse) HS based upon a single diisocyanate molecule. The diisocyanates: *para*-phenylene diisocyanate (*p*PDI), *meta*-phenylene diisocyanate (*m*PDI), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), diphenyl methane diisocyanate (MDI), Hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), and 1,4 cyclohexyl diisocyanate (CHDI) were utilized to fully examine the role played by the level of HS symmetry. Only those segmented polyurethane and polyurea copolymers based on *p*PDI and *m*PDI are addressed in this chapter. Materials based on the remainder of the diisocyanates are discussed in subsequent chapters. The dihydroxy and diamine terminated PTMO allowed us to synthesize analogous polyurethanes and polyureas, respectively. The synthesis strategy presented in Figure 2.1 resulted in copolymers with *ca.* 14 wt% HS content.

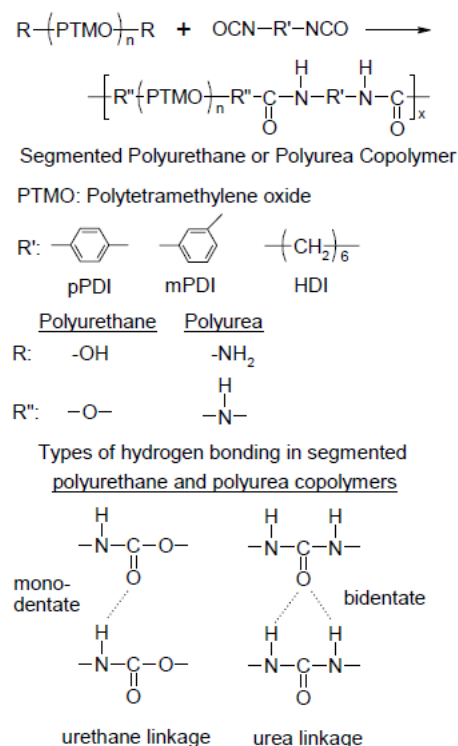


Figure 2.1. Reaction scheme for the synthesis of segmented polyurethane and polyurea copolymers consisting of HS based only on a single diisocyanate. The -OH and -NH₂ terminated PTMO have <M_n> of 975 and 1100 g/mol respectively. Monodentate and bidentate hydrogen bonding schemes are also shown.

2.2. EXPERIMENTAL

2.2.1. MATERIALS

1,4-Phenylene diisocyanate (*p*PDI) and 1,3-phenylene diisocyanate (*m*PDI) and were purchased from Aldrich. The diisocyanate *m*PDI was used as received, while *p*PDI was sublimed at 70 °C. Purities of diisocyanates were better than 99.5%. α,ω-Aminopropyl terminated poly(tetramethylene oxide) (PTMO) with <M_n> 1100 g/mol was purchased from Aldrich. Poly(tetramethylene oxide) glycol, with <M_n> 975 g/mol was kindly provided by DuPont. Reagent grade dimethylformamide (DMF) was purchased from Aldrich and used as received.

2.2.2. POLYMER SYNTHESIS

All polymer synthesis performed for this study was carried out in our lab by Prof. Iskender Yilgor while on sabbatical from Koc University. Polymerizations were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. All copolymers were prepared by reacting equimolar amounts of the selected diisocyanates and PTMO oligomers. No chain extenders were utilized. Segmented polyurea copolymers were prepared at room temperature in DMF at a concentration of about 20 wt% solids, by dropwise addition of PTMO solution onto the diisocyanate solution, under strong agitation. Polyurethanes were prepared in DMF at 60 °C. Completion of reactions was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 cm⁻¹ with an FTIR spectrophotometer.

Polymer films *ca.* 1 mm thick were obtained by pouring the solutions into Teflon molds. The molds were covered with a glass Petri dish to slow down the solvent evaporation and placed in an oven maintained at 60 °C. After evaporation of the solvent, the molds were placed in a vacuum oven at 60 °C for complete drying, which was monitored gravimetrically. The resulting films were then removed from the Teflon molds and stored under vacuum at room temperature until needed for testing. Portions of these films were also compression molded in order to check their melt processability and to compare their solid-state behavior with that of their solution cast analog.

2.3. EXPERIMENTAL TECHNIQUES

2.3.1. ATOMIC FORCE MICROSCOPY (AFM)

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. Some samples, however, necessitated the use of a

much higher free air amplitude of *ca.* 8.0 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4–0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz. The free air and mold surfaces were noted for each film sample and care was taken to scan the free air surface of each so that the surfaces were not influenced by or contaminated with Teflon from the molding containers themselves.

2.3.2. DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed on a Seiko DMS 210 tensile module with an attached auto-cooler for precise temperature control. Rectangular samples measuring 10 mm in length and 4.5–6.5 mm in width were cut from the cast films. Under a dry nitrogen atmosphere, the films were deformed using a 1 Hz frequency. The temperature was increased from -150 to 300 °C at a rate of 2 °C/min. Typically the test was halted before reaching this upper temperature due to excessive sample softening. Soft segment glass transition temperatures reported by the DMA methodology were denoted as the location of the peak in the $\tan \delta$ vs. temperature plots.

2.3.3. TENSILE TESTING

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. A bench-top die was used to cut dogbone samples with an overall length of *ca.* 25 mm and the width of the grip section of *ca.* 10 mm. The reduced section measured 2.91 mm $\times$ 10 mm (width $\times$ gage length). These dogbones were then tested to failure at a crosshead speed of 25 mm/min and their load vs. displacement values recorded. Three samples were measured and their results were averaged to determine modulus, yield strength, and strain-at-break for each of the five materials. In addition to testing the materials to failure, hysteresis measurements were also made on select materials. For this test, the dogbone shaped samples were stretched to 800% strain at a crosshead speed of 25 mm/min and then immediately returned to its initial position of 0% strain at the same rate.

Samples were then immediately redrawn for a second loading. This loading–unloading cycle was repeated twice more to produce a three-cycle hysteresis test

2.3.4. WIDE ANGLE X-RAY SCATTERING (WAXS)

Photographic flat WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu–K α radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was determined (using an NaCl diffraction pattern) as 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an evacuated sample chamber. X-ray exposures lasted four hours. Sample thickness ranged from 12–14 mils.

2.3.5. SMALL ANGLE X-RAY SCATTERING (SAXS)

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu–K α doublet, with an average wavelength of $\lambda = 1.54 \text{ \AA}$. The camera used 200 μm , 100 μm and 300 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector, located approximately 65 cm from the sample. After azimuthal averaging, the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source at the Argonne National Laboratory, as a secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s , where $s = 2\sin(\theta)/\lambda$, and 2θ is the scattering angle [83, 84].

2.3.6. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC was used to determine potential melting behavior of the segmented copolymers and was also used as a second method for determining SS glass transition temperatures. DSC experiments were conducted on a Seiko DSC 220C with an attached auto-cooler for precise temperature control. Samples weighing 10–15 mg were heated in a nitrogen atmosphere from -150 to 200 °C at 10 °C/min, quenched to -150 °C at 10 °C/min, and reheated to 200 °C at 10 °C/min.

2.4. RESULTS AND DISCUSSION

The temperature dependent storage modulus (E') and $\tan \delta$ responses of *p*PDI and *m*PDI based segmented copolymers and their polyurea counterparts are presented in Figure 2.2. The DMA was conducted on films cast from 20 wt% solutions in DMF. The four samples are identified by the nomenclature: soft segment–diisocyanate–copolymer type. The copolymer type is denoted with “U” for polyurethane or “Ur” for polyurea.

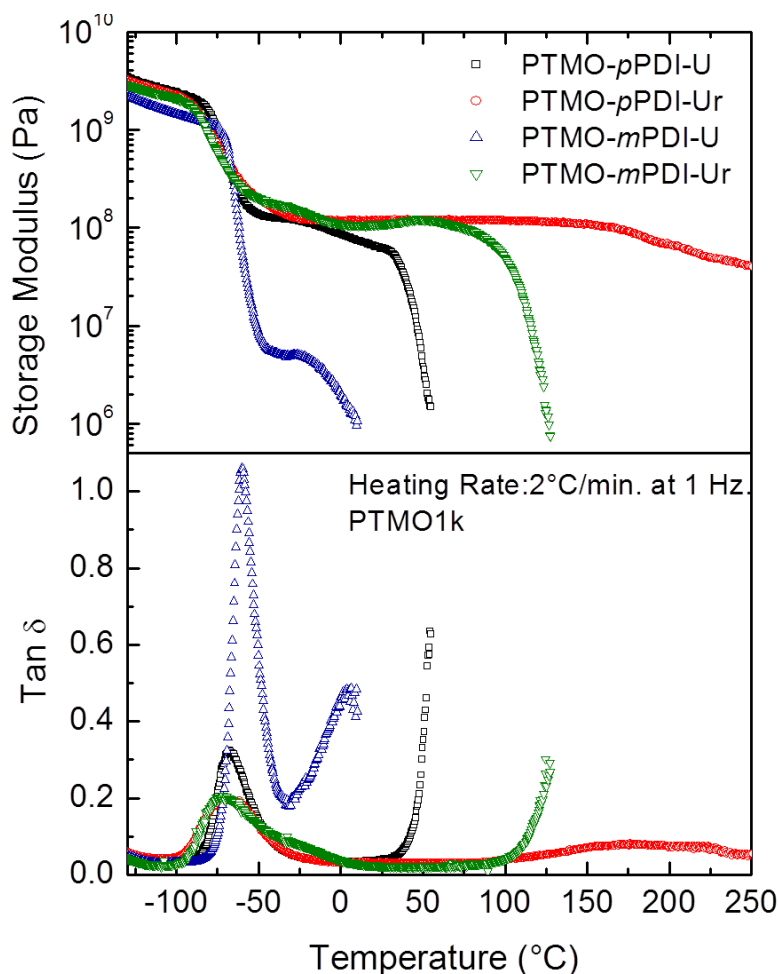


Figure 2.2. Dynamic mechanical analysis behavior of copolymer films cast from 20 wt% solution in DMF. The tests were conducted under a nitrogen blanket by quenching the samples from ambient temperature to -130 °C and thereafter heating them at 2 °C/min using a frequency of 1 Hz.

Focusing first on E' below the SS glass transition temperature, which occurs between -75 °C and -60 °C, all four samples behave as rigid solids and have E' values above 10⁹ Pa as would be expected. Following the T_g is a rubbery plateau whose breadth, average plateau modulus value, and temperature sensitivity depend upon the level of HS symmetry and the type of hydrogen bonding network within the hard phase. The rubbery plateau of PTMO-*p*PDI-U, although narrow and temperature insensitive, displays an average E' value of 10⁸ Pa. Such high E' values above the SS T_g are more commonly exhibited by conventional chain extended polyurethanes with a distinctly higher HS content relative to the much lower 14 wt% present in these non-chain extended segmented copolymers. The high average E' value in the

plateau strongly implies the presence of long-range connectivity of the HS and the percolation of the hard phase through the soft matrix. The tensile behavior of PTMO-*p*PDI-U (Figure 2.3), in fact, provides indirect support for this argument.

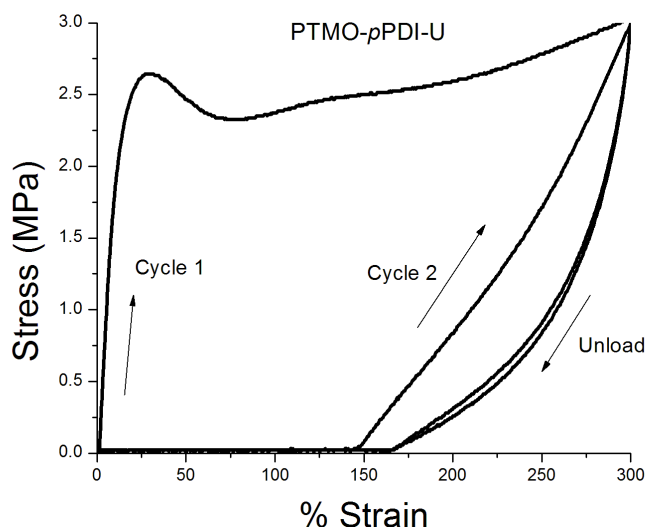


Figure 2.3. Mechanical hysteresis behavior of the sample PTMO-*p*PDI-U. The test was conducted at a crosshead speed of 25 mm/min on a dogbone shaped sample having a gauge length of 10 mm. The second cycle was initiated immediately upon the completion of the first.

When stretched uniaxially to 300 % strain at ambient temperature, this sample visibly necks and displays a yield point, which is strongly indicative of the break-up of a percolated hard phase. Consequently, when the applied load is released, the sample exhibits large permanent set (at that moment) as well as mechanical hysteresis. During the subsequent cyclic deformations, which begin immediately following the first, the sample displays typical elastomeric behavior due to the inability of the microstructure to fully “heal” before another deformation cycle is initiated. The observed elastomeric behavior further strengthens the argument that the material displays good microphase separation because a material with SS-HS mixing certainly would not be expected to display good recovery following additional deformations at this temperature.

Tapping mode atomic force microscopy (AFM) can be used to obtain direct visual confirmation of the HS phase morphology. It should first be noted that the tapping strength used can dramatically affect the quality of AFM images. A demonstration of this can be seen in (Figure 2.4). Here, one area of a *p*PDI-U film sample was imaged multiple times and the set-

point ratio was lowered in a stepwise fashion between scans. Better contrast between the hard phases (light regions) and soft phases (dark regions) was obtained as the set-point ratio (SR) was lowered to 0.60. On the basis of this result, all future scans were made with SR=0.60 to provide an equal basis for comparison of AFM images.

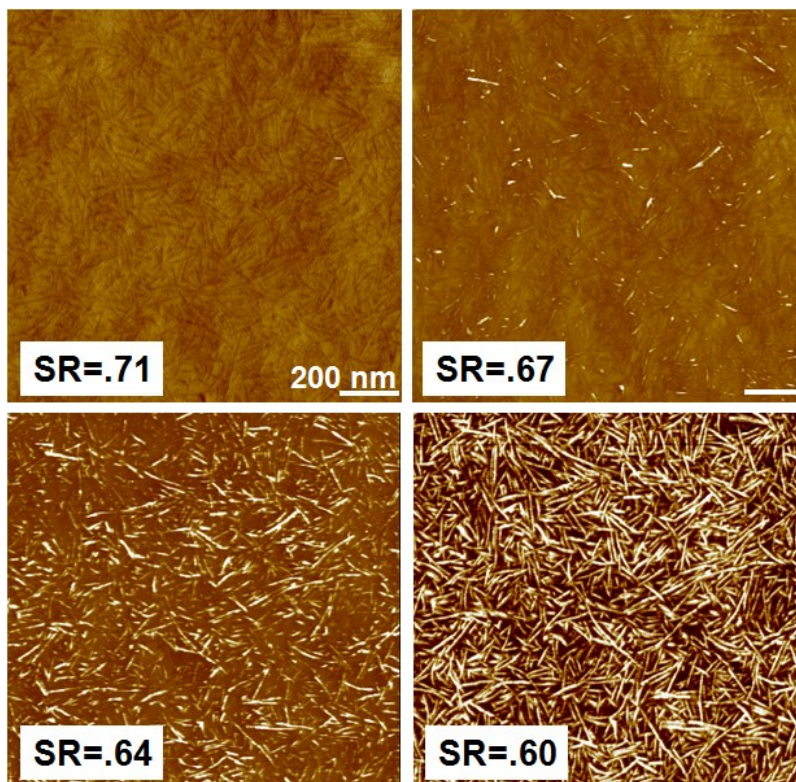


Figure 2.4. AFM phase image of *p*PDI-U (14% HS) showing the effect of various tapping strengths (labeled as set point ratios, SR) on the contrast in the final image. All scale bars are 200 nm.

The *p*PDI-U material's phase image (Figure 2.5A) clearly suggests a well-defined percolated HS phase that has developed in the form of ribbon-like hard domains of high aspect ratio. These ribbons show no preferred orientation (though they tend to look as if they lie in the film plane as a result of the casting process) and appear continuous throughout the SS phase, the latter of which dominates the composition.

In addition to the HS connectivity visually observed with AFM, crystallization of the symmetric *p*PDI-based HS phase may also cause the average value of E' in the rubbery plateau to be further enhanced.

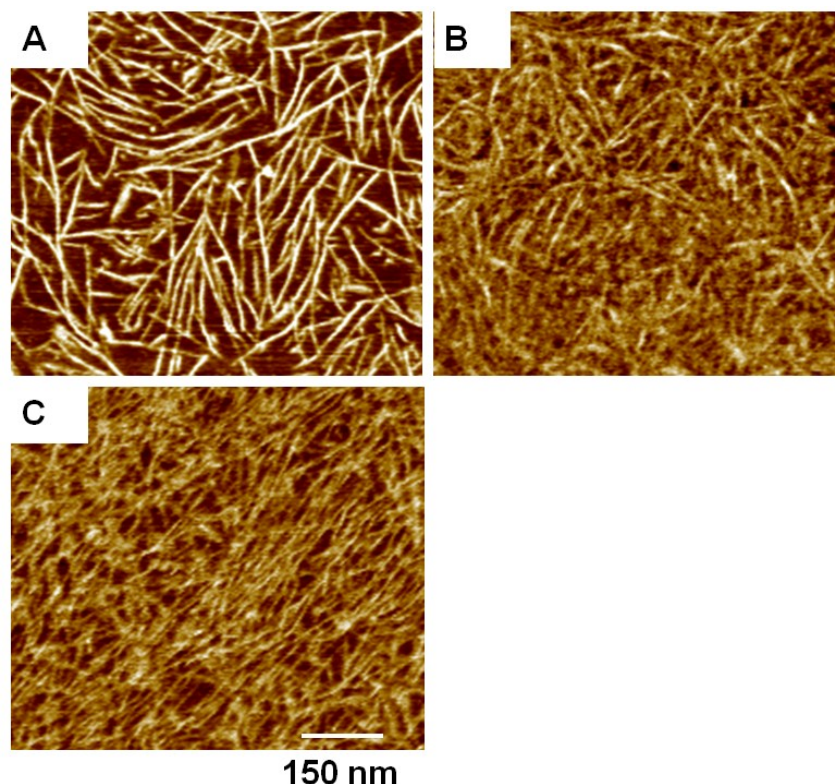


Figure 2.5. Ambient temperature tapping-mode atomic force microscopy phase images of segmented copolymer films cast from 20 wt% solution in DMF. (A) PTMO-*p*PDI-U; (B) PTMO-*p*PDI-Ur; and (C) PTMO-*m*PDI-Ur. The above images were captured at a set point ratio of 0.6. Note: The imaging tip in tapping mode AFM probes not just the free surface of a given sample but also the region a few nanometers underneath the free surface.

The crystallization of the HS phase was confirmed by WAXS (Figure 2.6) as well as DSC (Figure 2.7). Recall that the DMA results showed the SS T_g at $-68\text{ }^{\circ}\text{C}$. As this pattern was taken at ambient temperature, the diffraction ring recorded is not from a crystalline SS and therefore must be due to a crystalline HS. The azimuthally independent reflection recorded corresponds to a d-spacing of $4.1\text{ }\text{\AA}$. One reason the diffraction ring may not be particularly sharp is believed to be due to small crystal size broadening, which occurs when the scattering crystal is so small that there is not enough constructive interference from the diffracting planes to get sharp diffraction lines. According to the Laue diffraction function, broadening can occur whenever the number of unit cells in the scattering body (N_l) is less than *ca.* 100 [85]. Other potential sources of broadening such as large crystals with defects have been ruled out as these are typically associated with long chain-folded spherulitic crystals not present in the materials used in this study. Since the crystallizable HS found in these materials is only a single

diisocyanate molecule in length, defects across the thickness of the crystals, such as dislocations, will not occur.

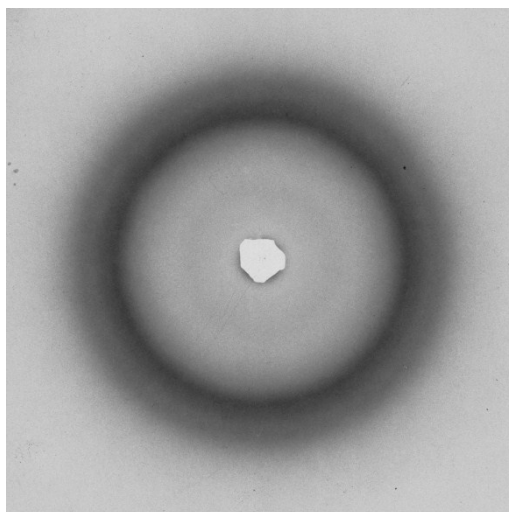


Figure 2.6. Ambient temperature 2D WAXS pattern of PTMO-*p*PDI-U (14 wt%).

It should also be noted that in addition to the small crystal size effects, the scattered “crystalline” intensity of the x-rays may be quite low due to the amount of crystalline hard phase present in the sample. Recall that the *p*PDI-U sample has a hard segment content of 14 wt%. Even if 100% of the HSs were packed into a crystalline lattice, only 14% of the material in the film sample would be capable of diffracting x-rays. Furthermore, considering that the number of crystalline HSs is likely lower than 100%, the diffraction pattern is not expected to be very strong.

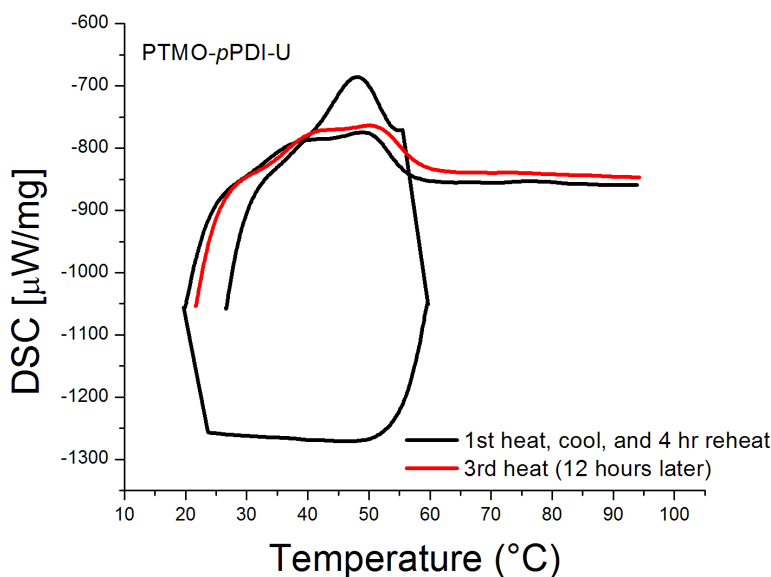


Figure 2.7. DSC results for solvent cast PTMO-*p*PDI-U heated from ambient temperature to 100 °C at 10 °C/min, quenched to 20 °C, and reheated at the same rate 12 hours later.

An endothermic peak was also noted in the DSC heating scan of PTMO-*p*PDI-U centered at 48 °C and corresponds to the melting transition of the *p*PDI based HS phase. For contrast, it might be stated that the melting point of pure *p*PDI is 94 °C although *p*PDI molecules in a pure sample are very different than those found in these segmented copolymers with a semicrystalline HS structure. That is, the HS in the polymer is covalently bonded to PTMO SSs, the H atoms from the SS diol precursor are now part of the HS (in the urethane linkage) and the diisocyanate's -NCO groups are rearranged into the urethane bond configuration.

When the urethane linkages are replaced with urea linkages to form PTMO-*p*PDI-Ur, the monodentate hydrogen bonded network is replaced by the stronger bidentate network and the upper limit of the rubbery plateau extends to considerably higher temperatures due to the stronger forces holding the hard phase together. In addition, it also exhibits a Young's modulus of 75 MPa and a tensile strength of 26 MPa, which are respectively a factor of three and two higher than its polyurethane counterpart, PTMO-*p*PDI-U. Similar to its polyurethane analog, the polyurea, PTMO-*p*PDI-Ur also exhibits neck formation and a yield point in its uniaxial stress-strain response at ambient temperature. Another important advantage conferred by the low HS content in PTMO-*p*PDI-Ur is that the copolymer can be melt processed (by compression molding cut up pieces of solvent cast film at 210 °C) with no visible degradation or chemical

cross-linking to generate a transparent homogeneous film that possesses comparable physical property behavior and morphology to the solution-cast sample. Tensile tests were conducted on the PTMO-*p*PDI-U sample before and after compression molding. The original and remolded samples exhibited comparable Young's modulus, tensile strength, and elongation at break, thereby suggesting that the degradation or chemical cross-linking upon compression molding was minimal, if it occurred at all.

An understanding of the influence of the HS symmetry on the E' response can be gained by comparing PTMO-*p*PDI-U with PTMO-*m*PDI-U. In the latter copolymer, the SS glass transition results in a precipitous drop in the value of E' (recall Figure 2.2). A very narrow rubbery plateau extends thereafter and its average plateau modulus is over an order of magnitude lower than that of PTMO-*p*PDI-U. Such an inferior service window response of the PTMO-*m*PDI-U can be attributed to the absence of symmetry in the *m*PDI-based HS which hinders the efficiency of the HS packing and hence the lack of their long-range connectivity. No hard phase crystallinity was observed in this sample by either WAXS or DSC. In fact, the solution cast film of PTMO-*m*PDI-U is considerably tacky at ambient temperature whereas that of PTMO-*p*PDI-U is non-tacky. This observation further confirms the importance of HS symmetry in enabling the packing, phase separation and long-range connectivity of a hard phase in copolymers having low HS content. Substitution of the monodentate hydrogen bond network in PTMO-*m*PDI-U with its bidentate counterpart in the segmented polyurea PTMO-*m*PDI-Ur raises the average ambient temperature plateau modulus of the copolymer nearly up to the level of the symmetric *p*PDI-based samples. DSC and WAXS analysis discussed earlier showed that the hard phase of this sample was also able to crystallize. Moreover, its rubbery plateau, while lower in magnitude than the polyurethane PTMO-*p*PDI-U, is much broader. Such behavior indicates that in addition to HS symmetry and possible crystallinity, the nature of the hydrogen bonded network within the hard phase distinctly influences HS long-range connectivity (see below). Not surprisingly, PTMO-*p*PDI-Ur, which has both bidentate hydrogen bonding and a symmetric HS, exhibits the most enhanced service window response amongst the series addressed in Figure 2.1.

As implied above, the HS structure, its symmetry and the type of hydrogen bonding it promotes strongly influences the potential crystallizability and cohesiveness of the hard domains formed. This fact is further evident from the $\tan \delta$ response (Figure 2.2). Here we note that with the exception of PTMO-*m*PDI-U, the peak value of $\tan \delta$ is maintained between 0.2–0.3,

whereas that of the remaining sample is above 1.0. While at first the higher $\tan \delta$ value of the sample might be thought to imply better microphase separation, this is not the case based on the obvious clear sharp microphase separated AFM images of the other three materials to be discussed shortly. Takayanagi first reported on the expected $\tan \delta$ behavior for materials as measured via DMA by constructing phenomenological models. The models were arranged such that the stress response behavior of the materials acted as though the hard and soft components were loaded in parallel or series with one another as well as combinations of the two. That work showed that when the materials are uniaxially measured by DMA, the response could be modeled appropriately based on the particular arrangement of the phases with respect to one another. That is, the model hard and soft phases were arranged such that the uniaxial load was applied with the phases acting in parallel to one another, orthogonal to one another and combinations of the two. Thus, the $\tan \delta$ behavior noted in the *pPDI* and *mPDI* systems discussed here may not be as straight forward as implied. Without a clearer understanding of how the hard and soft microphases share the applied stress, the $\tan \delta$ response alone should not be utilized as the sole measurement to predict the film's *morphologies*. Restated, the PTMO-*mPDI*-U material's elevated $\tan \delta$ is not a good predictor of the material's morphology, i.e. the material does not show well-defined microphase separation. Indeed, WAXS, SAXS, and DSC data, not shown here, directly support the AFM results. Furthermore, one observes that PTMO-*mPDI*-U exhibits a very short rubbery plateau and then undergoes viscous flow below room temperature, thereby suggesting that it has relatively little microphase separation or if it does, that the HS phase is not cohesive enough to enable an extended rubbery plateau before the HS softens and flow occurs. In addition, SAXS (measured at ambient temperature) and DSC also did not indicate any microphase separation. On the other hand the cause of the surprisingly depressed $\tan \delta$ peak of the three samples that display sharp microphase separation is due to the strong restrictions placed on the mobility of the SS phase by the rigid percolated HS that are covalently bonded to the relatively low MW (*ca.* 1000 g/mol) SS. At first this might not be intuitive, but in view of the discussion of the Takayanagi models, it appears to be supported. The conclusion that the materials are microphase separation is further buttressed by the predictions of several fiber-reinforced composite models, in particular those of Cox, Cristensen and Pan [86]. Calculations of ambient temperature modulus values for PTMO-*pPDI*-U (assuming a 2D or 3D

random arrangement of hard fibers in a soft matrix) closely matched those values measured via DMA [87].

As indicated above, tapping-mode AFM was also utilized to confirm the hypothesis regarding the presence of a percolated HS phase in some of the segmented copolymers (Figure 2.5). As noted above, the sample PTMO-*p*PDI-U (Figure 2.5A) exhibits long ribbon-like bright regions that are the hard domains. Furthermore, while the AFM cannot be said to show conclusively that the films do not show distinct branch points connecting the hard ribbon-like HS elements, it would be justifiable to state that there is little to no sign of branching by the HS ribbon phase. The average width of these ribbons determined by AFM is *ca.* 30 Å. Such a morphology strongly suggests that the HSs, which consist of only a single diisocyanate-derived moiety, may be expected to pack in a near perpendicular arrangement to the long axis of the ribbons. The width of the ribbons as seen in the AFM is likely broadened due in part to PTMO segments as they are covalently bonded to the HSs and therefore have restrictions placed on their mobility. This mobility limitation is likely detected by the AFM and thus the hard phase ribbons probed may appear to be thicker due to measuring both the hard phase and a portion of the PTMO soft segment. Aneja and Wilkes have also noted similar packing in PTMO-based polyurethanes with uniform crystallizable HS length and general hard segment packing in other polyurethanes [88]. The hard domains in PTMO-*p*PDI-U are semicrystalline (see earlier discussion) and their connectivity is facilitated by the HS's ability to establish a hydrogen bonded network; such connectivity in turn results in the percolation of the HS through the soft matrix. In fact, the calculated molecular length of the HS, which includes the two urethane linkages and the link between them, in PTMO-*p*PDI-U is only *ca.* 10 Å. Therefore, in this more rigid interfacial region the portions of the included SS also appear bright in the phase image. The general morphology of the segmented polyurea PTMO-*p*PDI-Ur (Figure 2.5B) is similar to that of its polyurethane counterpart (Figure 2.5A), though based on the AFM and SAXS data (which will be discussed in the next chapter), the hard phase may in fact be packed in a different manner. This hypothesis is based on the “thinner” ribbon structure of the polyureas when imaged in the AFM as well as the smaller SAXS spacings measured. An explanation for different packing characteristics of the polyurethanes and polyureas is not yet determined.

In our earlier discussion we noted that the segmented copolymer PTMO-*m*PDI-U was tacky and its dynamic mechanical response suggested less microphase separation than in the

other samples within the series. This conclusion is supported by AFM because we did not observe the presence of hard and soft regions in the phase image of this sample and the sample was difficult to even try to measure due to its tackiness at ambient temperature. On the other hand, its polyurea counterpart, namely PTMO-*m*PDI-Ur (Figure 2.5C) clearly exhibits ribbon-like hard domains. *This implies that the more cohesive bidentate hydrogen bonding of the urea groups can overcome the decreased symmetry of the mPDI diisocyanate in promoting HS connectivity.*

In view of the differences exhibited by the PTMO-*p*PDI-U and PTMO-*m*PDI-U materials, one might question how materials that incorporated both diisocyanates would behave. To answer that question, two new polyurethanes were produced. The first material was made by introducing an equal molar fraction (and 50/50 weight fraction) mixture of *p*PDI and *m*PDI to the synthesis step at the same time, resulting in a material with each isocyanate placed randomly along the segmented copolymer backbone. This material was extremely soft and tacky at ambient temperature and was deemed not appropriate for further study. A second material was produced by equal weight blending of the earlier PTMO-*p*PDI-U and PTMO-*m*PDI-U segmented systems. Following solution casting of their blend, further analysis displayed a morphology and properties rather intermediate to its precursors. Figure 2.8 shows a DMA comparison of the segmented polymer blend of the PTMO-*p*PDI-U and PTMO-*m*PDI-U materials. The sample shows a high E' value at very low temperatures comparable to the *p*PDI material. It too undergoes a SS T_g between -60 °C and -75 °C. The service window plateau modulus discussed previously is an intermediate value between that of the PTMO-*p*PDI-U and PTMO-*m*PDI-U samples. There is a small drop in the E' value around -25 °C (likely due to the presence of *m*PDI) but the material does not soften substantially until about ambient temperatures (similar to the *p*PDI sample). The fact that it maintains a high modulus until *ca.* 25 °C may indicate a certain level of HS crystallinity and that is borne out by the WAXS pattern shown in Figure 2.9. Though not as distinct as that of the PTMO-*p*PDI-U, a diffraction ring is evident on the WAXS film. This too is an intermediate result compared to the two precursor materials, PTMO-*p*PDI-U showing a sharper diffraction ring and PTMO-*m*PDI-U showing only diffuse scattering.

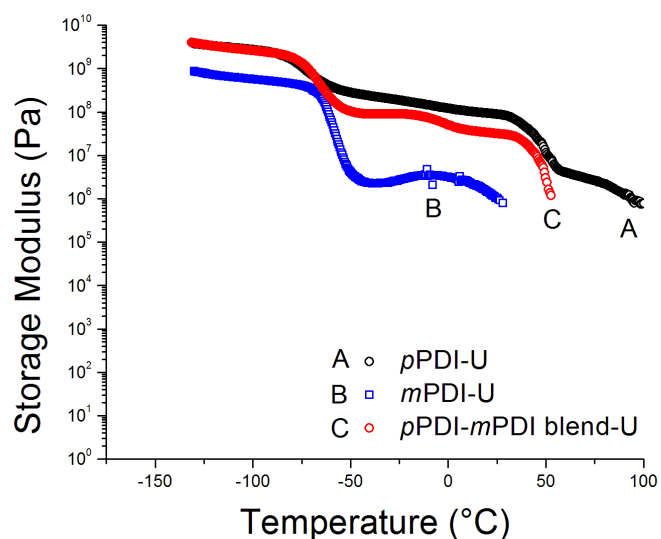


Figure 2.8. DMA comparison of A) *p*PDI, B) *m*PDI and C) *p*PDI/*m*PDI polymer blend urethanes.

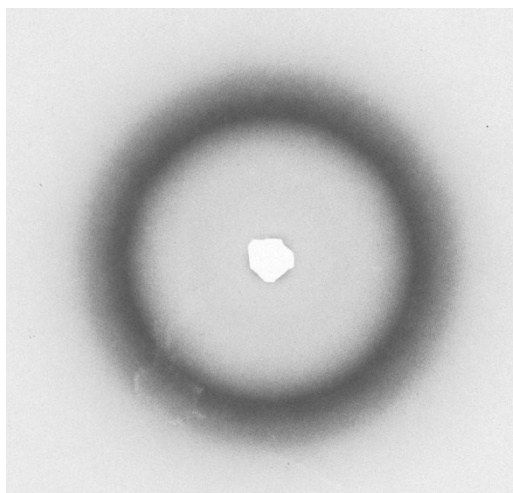


Figure 2.9. WAXS pattern of *p*PDI-*m*PDI-U segmented copolymer physical blend.

2.5. CONCLUSIONS

These results undermine the widely held belief that it is necessary to employ chain extension to produce segmented polyurea copolymers with useful structural properties. Polyurethane materials were also produced but their hard phase T_g 's would likely limit their use in applications with temperatures above ambient conditions. In particular, it has been

demonstrated that non-chain extended segmented urea copolymers in which the HS is based on only a single diisocyanate molecule may well exhibit properties, such as the breadth of the service window, the average plateau modulus, stiffness, tensile strength, and elongation at break that are similar to conventional chain extended segmented copolymers that possess distinctly higher HS content and length (via CEs). However, careful control of the HS symmetry and the nature of the hydrogen bonding are necessary to achieve such improved performance in non-chain extended systems. Thus, this chapter particularly, provides strong evidence for the controlling role played by the symmetry of the hard segment in morphology development in polyurethanes. It provides new direction for the production of thermoplastic segmented urea copolymers that display a considerable thermal range for their service window yet are solution- as well as melt-processable.

3. STRUCTURE-PROPERTY BEHAVIOR OF NEW SEGMENTED POLYURETHANES AND POLYUREAS WITHOUT USE OF CHAIN EXTENDERS

3.1. INTRODUCTION

The field of block and segmented copolymers is well established and has provided many examples of unique systems that have led to their commercialization—particularly as thermoplastic elastomers, TPE's [2-5]. Some of the most noteworthy systems are the anionically polymerized ABA tri-block materials—the initial ones were either based on styrene (S) and butadiene (B), or S and isoprene (I), which promoted the well-known and versatile TPEs often designated as SBS or SIS respectively. A wide compositional range of these and other chemically different tri- or multi-block anionically prepared systems have been well addressed in the literature along with other modifications based on architectural changes as well, such as those of the radial block type [2, 3].

Some of the well-known attributes of the anionic block copolymers are the high level of control for achieving narrow polydispersity of the respective blocks, as well as the total molecular weight of the tri-block copolymer itself. Furthermore, typically the former values often are in the range of several thousand at the low end to tens of thousands at the upper end. Considerable theoretical strides have also been made that well describe the type of equilibrium microphase separated morphologies and order-disorder thermal transition behavior that arise in these materials due to compositional variation. Detailed studies on the understanding of the level of block-block compatibility as accounted for by the well-known Flory Huggins Chi parameter have also been performed [6, 7, 30, 89-92]. As a result of the narrow block polydispersity, molecular weight, and block incompatibility, extremely long range order can be easily induced in these systems as has been verified by many researchers over the last two or more decades [2, 3, 25, 35, 93-97].

In contrast to the anionic block copolymers briefly described in the preceding paragraphs, the area of segmented copolymers, which also are very important industrially, are much less susceptible to precise theoretical descriptions with respect to the specification of a narrow range order-disorder thermal transition. Furthermore, the long-range order or microphase

morphological features in these systems are not as fully understood although certainly the occurrence of a microphase texture is well established and critical for their utilization [3, 4, 25, 91, 98]. Examples of such materials that are particularly pertinent for this report are the well-known thermoplastic polyurethanes, TPUs, as well as the common segmented urethane-urea of Lycra™ spandex. Lycra™ is presently processed from solution due to the considerable level of bidentate hydrogen bonding that occurs between the hard segments (HS) in this particular material [99-101]. Lack of a clear theoretical description of the observed microphase behavior in either of these systems is certainly due in part to the often much stronger localized hydrogen bonding that occurs as compared to the SBS- or SIS-like systems described above that lack specific interactions. General absence of long range order in segmented materials where one or both of the two segment types (hard and soft) are prepared by a step growth polymerization also generally arises due to a much more enhanced distribution of segment lengths when compared to the SBS systems. This latter issue has been well addressed by Frederickson [102] although there have been some indications of exceptions to his analysis [103-106]. Finally, another major difference is that the segment molecular weights are *typically much lower* than those of the anionically polymerized tri-block copolymers—in fact, usually the soft segment molecular weights are less than 3,000 g/mol. Furthermore, polarity often occurs in both the hard and soft segments giving rise to the potential solubility/miscibility of one segment within that of the other, particularly if the molecular weights of the respective segments are low. As a result, investigating the degree of segmental mixing has been a major focal point in many of the TPU systems [28, 49, 62, 100, 101, 107-110]. In fact, with specific regard to the segmented polyurethanes as well as urethane-ureas already mentioned, to minimize the formation of particularly short hard segments, chain extenders are conventionally used to lengthen the average hard segment size. For the case of TPUs, one of the most common chain extender is that of 1,4-butanediol while in segmented urethane-ureas as Lycra™ spandex, the chain extender is typically a low molecular weight diamine such as ethylenediamine (EDA). In fact, the author knows of no commercial TPU or urethane-urea segmented systems that are prepared without the use of chain extenders. At least one early study did, however, attempt to promote such non-chain extended materials that arose from joint work within our laboratory. In particular, segmented polydimethylsiloxane (PDMS) ureas, amides and imides were prepared by utilizing amine endcapped PDMS oligomers that were reacted with diisocyanates, diacids or dianhydrides,

respectively, but without any use of chain extender moieties. The basis of that work was the assumption that due to the very low solubility parameter of PDMS and extremely high polarity of urea, amide or imide groups it might well be possible to obtain a phase separated morphology with a “single molecule” hard segment [111, 112]. In addition, especially the PDMS–urea and PDMS–amide systems, due to their strong hydrogen bonding capacities, these systems might provide materials with reasonably good mechanical properties. Indeed, while direct visualization of microphase separation was not achieved microscopically, it was clearly verified by the techniques of DSC, DMA and SAXS thereby supporting the above supposition but it required that the PDMS soft segment molecular weight be at least 1,000 g/mol or higher or otherwise major hard/soft segmental mixing occurred [37]. However, while the low temperature T_g of PDMS typically defined the onset of the service window for elastomeric behavior, the upper end of this window where the hard segment phase undergoes softening generally begins distinctly below 100 °C. This result suggested that a single molecular hard segment (monodisperse) of this type prepared without chain extenders would not possess sufficient hard segment-hard segment cohesiveness to allow these materials to possess a sufficiently high softening point needed for practical applications. Since the publication of that work, little effort has been directed at similar “single molecule” hard segment studies based on a search of the literature. Recently work from our own laboratory again suggested that when one molecule from the asymmetric isomeric 80/20 mix of 2,4- and 2,6-toluene diisocyanate, TDI, was placed between two soft segments based on monols of either poly(propylene oxide) or a copolymer of ethylene and propylene oxide, each being of about 1,000 g/mol, no microphase separation was denoted at ambient conditions. Rather, only a low viscosity fluid was observed [113]. However, it was also illustrated that if the TDI “molecular” hard segment was further chain extended with water and additional TDI, as is commonly done in making flexible conventional slab stock polyurethane foams [114-118], not only did the resulting tri-segment system display strong microphase separation as denoted by SAXS and DSC measurements, but the tri-segments with as little as about 20 weight percent of hard segment as the “mid-segment” led to solidification of the material at ambient conditions! Since the average total molecular weight of the model tri-segment material was less than 3,000 g/mol, no significant chain entanglements were expected. Furthermore, the majority of the remaining 80% of the systems composition, by DSC, was represented by the two *terminal* soft segments that displayed a distinct T_g by DSC at about -60 °C [113]. Thus, for this system to

promote distinct solidification, it was proposed that this could only occur if the urethane-urea mid-segments were cohesively bonded into a microphase that was not particulate in nature but rather *must be percolated* throughout the matrix, thereby promoting the solidification process. Indeed, proof of this was well verified and even visually observed by use of AFM. An example taken from that study is reproduced in Figure 3.1. This study therefore distinctly illustrated how the short chain extended urethane-urea mid-segment could, at relatively low weight fraction, establish a wispy thread-like microphase morphological texture with a correlation length on the order of 100 Å. This correlation length or interdomain distance is similar to what is actually observed by SAXS in many conventional flexible slabstock foams based on poly(propylene oxide)glycol soft segments and TDI/H₂O hard segment systems [114-118]. (It might be pointed out for clarity to the reader that what is denoted conventionally as a polyurethane slabstock foam are typically poly(urethane urea) foams that possess a chemical (or covalent) crosslinked network as well as a microphase separated network due to the fact that the polypropylene oxide soft or elastomeric component is branched and possesses a hydroxyl functionality of about 3.) Again, a main point that resulted from this tri-segment study was not only could a percolated hard segment microphase be promoted in these unique model systems but if the hard segment was only a single TDI species, no microphase separation occurred at all. This suggested once again that chain extension may well be a necessity for promoting the necessary soft segment-hard segment incompatibility such that microphase separation would be induced. This did not seem surprising at the time in view of the fact that both the soft segment and hard segment possessed some polarity which favored some degree of mutual solubility at low hard segment molecular weights as was mentioned earlier.

In more recent studies [119, 120] it was also shown that the “softening”/disruption of the hydrogen bonding network in the hard segment phase of these chain extended tri-segment systems described above could be induced. This was done by either adding a small amount of a hydrogen bonding screening molecule as lithium chloride [119] or, by promoting some level of branching within the hard segment by replacing a portion of the TDI with a triisocyanate during chain extension [120, 121]. (It might be pointed out that it was realized that when branching of the hard segment is induced, the molecular structure is not strictly trisegmental in nature.) AFM and other related characterization methods clearly showed that either of these two means of modification led to disruption of the strong percolation of the hard segment phase discussed

earlier. These results, while possibly being anticipated, clearly underscored the importance of hydrogen bonding as well as packing capabilities as being critical for facilitating hard segment percolation. This information, in conjunction with other studies involving urethane and/or urea linkages in segmented systems, strongly suggested that the urea linkage which allows for bidentate hydrogen bonding would distinctly promote a greater cohesiveness between the hard segments as is also supported theoretically [50]. In summary, the information from various studies addressed in this introduction, suggested us to revisit the preparation of segmented polyurethanes and polyureas that utilize no chain extenders, but where symmetry of the chosen diisocyanate employed should be more carefully investigated. This report considers some of the results of this work and places principal emphasis on the portion of the study that addresses the structure-property behavior of the segmented polyurethanes and polyureas that we now have produced by this approach. Data for comparable both polyurethane and polyurea samples will be provided to illustrate the importance of the bidentate versus monodentate linkages of the respective urea and urethane linkages in greatly influencing the upper softening temperature of urea versus urethane systems prepared for a given diisocyanate.

We recently reported the synthesis and characterization of a series of polyurethane and polyurea materials made without the use of chain extenders [120, 121]. Those materials contained poly(tetramethylene oxide) (PTMO) as the soft segment (SS) and two different diisocyanates as the hard segment (HS): *para*-phenylene diisocyanate (*p*PDI) and *meta*-phenylene diisocyanate (*m*PDI). Those materials were shown to produce copolymers with useful structural properties despite the fact that the HS was comprised of a single diisocyanate molecule, due to the lack of chain extenders. Some of the properties exhibited by those materials were a broad service temperature window with a high storage modulus in the plateau region, high stiffness, tensile strength and in some cases high elongation at break. The use of *p*PDI and *m*PDI in particular allowed for the investigation of the role of diisocyanate symmetry on the properties of the resulting films. The synthesis of both polyurethanes and polyureas permitted the determination of the role hydrogen bonding plays on the ultimate morphology and structure-property relationships in those materials.

The current work expands on that previously done by introducing five new diisocyanates to the synthesis of single segment polyurethanes and polyureas: 1,4 trans-cyclohexyl diisocyanate (CHDI), hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), 4,4'-

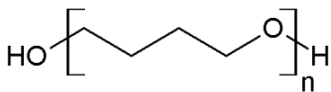
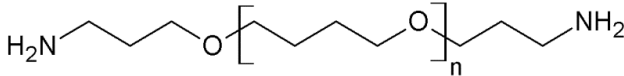
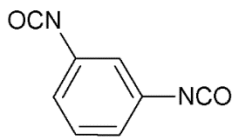
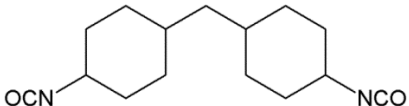
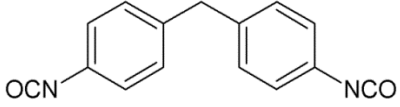
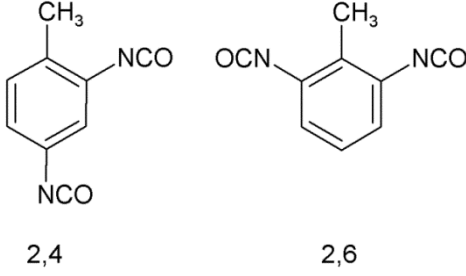
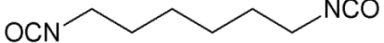
diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI). With each of these diisocyanates used as the single molecule comprising the HS, the role of aromaticity can be determined and the role of hydrogen bonding can be expanded upon.

3.2. EXPERIMENTAL SETUP

3.2.1. MATERIALS

1,4-phenylene diisocyanate (*p*PDI) and 1,3-phenylene diisocyanate (*m*PDI) and were purchased from Aldrich. *trans*-1,4-diisocyanatocyclohexane (CHDI) was purchased from DuPont. A mixture of 2,4- and 2,6-tolylene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HDI), 4,4'-diphenylmethane diisocyanate (MDI), Hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI) were kindly provided by Bayer. All diisocyanates, except *p*PDI were used as received, while *p*PDI was sublimed at 70 °C. Purities of diisocyanates were better than 99.5%. α,ω -Aminopropyl terminated poly(tetramethylene oxide) (PTMO) with $\langle M_n \rangle$ 1,100 g/mol was purchased from Aldrich. Poly(tetramethylene oxide)glycol, with $\langle M_n \rangle$ 975 g/mol was kindly provided by DuPont. Reagent grade tetrahydrofuran (THF), dimethylformamide (DMF) and isopropyl alcohol (IPA) were purchased from Aldrich and used as received. Table 3.1 provides the structural information for the materials utilized in this work.

Table 3.1: Chemical structural information for the materials used in this study.

Chemical Species	Abbreviation	Structure
poly(tetramethylene oxide)	PTMO	
α,ω -Aminopropyl terminated poly(tetramethylene oxide)	PTMO	
<i>para</i> -phenylene diisocyanate	<i>p</i> PDI	
<i>meta</i> -phenylene diisocyanate	<i>m</i> PDI	
1,4 trans-cyclohexyl diisocyanate	CHDI	
hydrogenated 4,4'-diphenylmethane diisocyanate	HMDI	
diphenyl methane diisocyanate	MDI	
toluene diisocyanate	TDI	
hexamethylene diisocyanate	HDI	

3.2.2. POLYMER SYNTHESIS

Polymerizations were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and PTMO oligomer. No chain extenders were utilized. Segmented polyurea copolymers were prepared at room temperature in DMF at a concentration of about 20 wt% solids, by the dropwise addition of PTMO solution into the diisocyanate solution, under strong agitation. Polyurethanes were prepared in DMF at 60 °C. Completion of reactions was determined by monitoring the disappearance of the isocyanate absorption peak at 2270 cm^{-1} by FTIR spectroscopy.

Polymer films *ca.* 1 mm thick were obtained by pouring the solutions into Teflon molds. The molds were covered with a glass Petri dish to slow down the solvent evaporation and placed in an oven maintained at 60 °C. After evaporation of the solvent, the molds were placed in a vacuum oven at 60 °C for complete drying, which was monitored gravimetrically. The resulting films were then removed from the Teflon molds and stored under vacuum at room temperature until needed for testing. Portions of some of these films were also cut into small pieces and then compression molded in order to check their melt processability and to compare their solid-state behavior with that of their solution cast analog.

The nomenclature used throughout the remaining text is presented for easy identification of each material. All materials discussed herein are based on a PTMO1k SS. Recall that the urethanes are actually based on a 975 g/mol PTMO soft segment whereas the ureas are based on an 1,100 g/mol soft segment. Because all samples have roughly the same $\langle M_n \rangle$ soft segment, the presence of PTMO is not indicated in the individual samples' names. Samples are indicated by the diisocyanate used during synthesis followed by a "U" or a "Ur", indicating that the sample is a polyurethane or polyurea respectively. Hence, the symbol *pPDI-U* is meant to indicate a polyurethane material based a PTMO1k SS and a *pPDI HS*.

3.3. EXPERIMENTAL TECHNIQUES

3.3.1. ATOMIC FORCE MICROSCOPY (AFM)

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. Some samples, however, necessitated the use of a much higher free air amplitude of *ca.* 8.0 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4 to 0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz.

3.3.2. DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed on a Seiko DMS 210 tensile module with an attached auto-cooler for precise temperature control. Rectangular samples measuring 10 mm in length and 4.5–6.5 mm in width were cut from the cast films. Under a dry nitrogen atmosphere, the films were deformed using a frequency of 1 Hz. The temperature was increased from -150 to 300 °C at a rate of 2 °C/min. Typically, the test was halted before reaching this upper temperature due to excessive sample softening. Soft segment glass transition temperatures reported by the DMA methodology were denoted as the location of the peak in the *tan δ* vs. temperature plots.

3.3.3. TENSILE TESTING

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. A bench-top die was used to cut dogbone samples with an overall length of *ca.* 25 mm and the width of the grip section of *ca.*

10 mm. The reduced section measured 2.91 mm $\times$ 10 mm (width $\times$ gage length). These dogbones were then tested to failure at a crosshead speed of 25 mm/min and their load vs. displacement values recorded. Three samples were measured and their results were averaged to determine modulus, yield strength, and strain-at-break for each of the five materials. In addition to testing the materials to failure, hysteresis measurements were also made on select materials. For this test, the dogbone shaped samples were stretched to 800% strain at a crosshead speed of 25 mm/min and then immediately returned to its initial position of 0% strain at the same rate. Samples were then immediately redrawn for a second loading. This loading–unloading cycle was repeated twice more to produce a three-cycle hysteresis test.

3.3.4. WIDE ANGLE X-RAY SCATTERING (WAXS)

Photographic flat WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu–K $_{\alpha}$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was set at 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an evacuated sample chamber. X-ray exposures lasted four hours. Sample thickness ranged from 12–14 mils.

3.3.5. SMALL ANGLE X-RAY SCATTERING (SAXS)

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu–K $_{\alpha}$ doublet, with an average wavelength of $\lambda = 1.54 \text{ \AA}$. The camera used 200 μm , 100 μm and 300 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector, located approximately 65 cm from the sample. After azimuthal averaging, the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source at the Argonne National Laboratory, as a

secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s , where $s = 2 \sin(\theta)/\lambda$, and 2θ is the scattering angle.

3.4. RESULTS AND DISCUSSION

3.4.1. DMA

The temperature dependent storage modulus (E') and $\tan \delta$ of all six solvent cast PTMO-based segmented polyurethane copolymers are presented in Figure 3.1. The figure specifically addresses the materials that incorporate: *p*PDI, *m*PDI, CHDI, MDI, HDI, and TDI respectively. The E' plots clearly reveal that the *m*PDI-U (14 wt% HS), and TDI-U (15 wt% HS) materials have T_g 's, around -60 °C with corresponding drops in E' from values typical of glassy solids ($\sim 10^9$ Pa) to lower values (less than 10^7 Pa) indicating a much softer material. This drop in E' is not consistent with a well microphase-separated material. In a microphase-separated material, the hard domains can act as physical crosslinks to the chains of the soft matrix, tending to restrict the mobility of those chains after the SS T_g and increasing the E' . As this is clearly not the case for either the *m*PDI-U or TDI-U sample, these materials are likely not microphase-separated, or if they are, there is little connectivity between the hard domains which results in low E' values.

The drop in E' at T_g for TDI-U is followed by a further decrease in E' over the next 50 °C, whereas the *m*PDI-U sample experiences a brief upturn in E' before it continues softening. In many polymer systems, there exists a region in the E' versus temperature curves characterized by a relatively flat, temperature-independent E' plateau. This plateau defines a material's "service window", a temperature range where the consistency of a material's mechanical properties may allow it to be utilized. Hence, the range of temperatures encompassed by the plateau, its flatness, and its breadth are very important. Therefore, close attention will be given to this feature of each material. In the case of *m*PDI-U and TDI-U, by the time each of these samples encounters ambient temperature they are too soft for measurement. The TDI-U material displayed an E' plateau that was neither very flat, nor broad as it spanned just 50 °C.

The *m*PDI-U material could not be said to display a plateau at all as it experienced the increase in E' upon heating before finally flowing at *ca.* 10 °C as well. Each of these materials was therefore soft and tacky at ambient temperature.

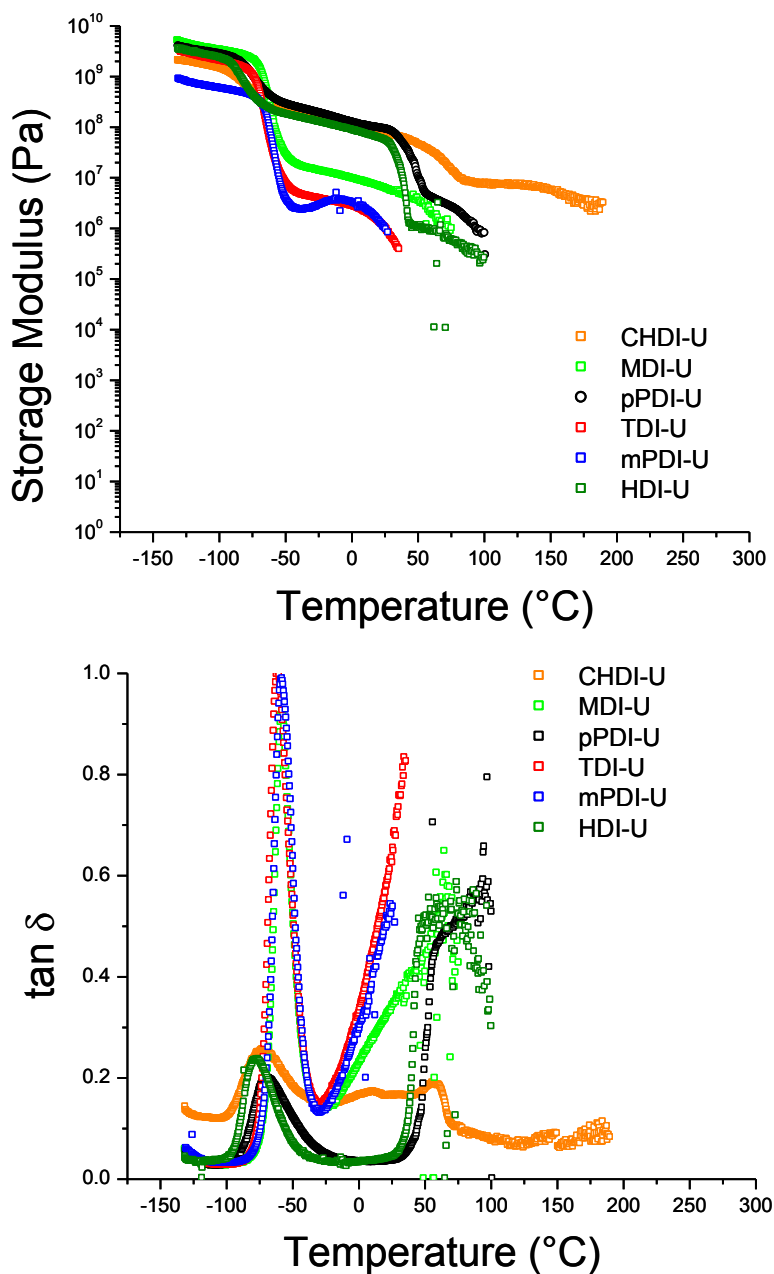


Figure 3.1. Temperature dependent storage modulus and $\tan \delta$ data for the polyurethanes used in this study.

It is essential to note that *m*PDI-U and TDI-U materials differ from the others most notably in that they utilize asymmetric diisocyanates. This accounts for the large drop in E' and the limited service window of these materials. The asymmetry of the diisocyanates hinders the ability of the hard segments to pack efficiently enough to induce a well-structured microphase-separated structure. The lack of a distinct microphase-separation results in materials of poor mechanical properties and limited service windows.

In the case of MDI-U (20 wt% HS), the T_g at *ca.* -57 °C also portends a drop in E' , from that of a glassy material ($\sim 10^9$ Pa) to a much softer one, ($\sim 2 \times 10^7$ Pa). Though the decrease is not as dramatic those of the TDI-U or *m*PDI-U materials, it is a significantly greater decrease, however, than occurs in the *p*PDI-U, CHDI-U, or HDI-U systems. This large drop in E' implies that microphase separation does not occur in the MDI-U sample, or that if it does, the level of connectivity between hard regions is low. If microphase separation does take place (which could account for the higher E' compared to TDI-U and *m*PDI), it is counterbalanced by a fair degree of mixing which lowers the value of E' to an intermediate value just above those well mixed systems. So while the diisocyanate used is symmetric (though it should be noted it is non-linear), that fact alone is not enough to ensure that the material will form a well-defined microphase-separated morphology. One other crucial difference exists between the behavior of MDI-U and the two other polyurethanes discussed thus far; the MDI-U has a much broader service window than either TDI-U or *m*PDI-U. The MDI-U sample has an upper end plateau temperature of 54 °C meaning that its service window is about twice that of the *m*PDI-U and TDI-U materials. So while the symmetric diisocyanate does not lead to well-ordered microphase separation, it does extend the upper temperature range of the material.

The remaining polyurethanes, *p*PDI-U (14 wt% HS), CHDI-U (15 wt% HS) and HDI-U (15 wt% HS) are all examples of materials synthesized using highly symmetric diisocyanates and they behave very differently upon heating than the previous three materials. The first difference in the DMA traces of these three materials occurs at T_g . More specifically, the temperature of the transition is lower in these samples, occurring below -70 °C in each case. This lower T_g is the first indication that these materials are more highly microphase separated PTMO1k-based polyurethanes. Recall that the three systems that did not show evidence of a well-defined microphase separated structure had T_g 's at temperatures greater than -60 °C. In addition to the lower T_g 's, the *p*PDI-U, CHDI-U and HDI-U samples experience a much less severe drop in E'

at this transition. Here the rubbery plateau region begins at E' values in excess of 10^8 Pa as compared to the sub- 10^7 Pa values witnessed before. This is a difference of roughly two orders of magnitude though the weight percentage of hard segment in all of these materials is 14–15%. This startling disparity indicates that there is a corresponding difference in morphology in these two sets of materials, due to the distinct microphase-separated structure for those materials with higher E' plateau values. Hence, the T_g 's measured at values lower than -70 °C are in fact SS T_g 's as these materials are microphase separated into hard domains dispersed throughout a soft segment matrix. After passing through the SS T_g , each material displays a plateau until softening at temperatures at or above *ca.* 30 °C. Again, these are much broader service windows than those of either the *m*PDI–U or TDI–U materials.

As a group, the *p*PDI–U, CHDI–U and HDI–U materials behave very differently in the DMA than the *m*PDI–U and TDI–U group of materials, while the MDI–U sample exhibited intermediate behavior. As previously mentioned, the major dissimilarity in the structures of the diisocyanates in these two groups is their symmetries. Broadly, it is apparent that the increased symmetry of the former group allows for more efficient packing of the HS and leads to a microphase-separated structure with hard domains dispersed throughout a SS matrix. The effect is seen in a more direct way by comparing *p*PDI–U with *m*PDI–U. These diisocyanates are based on the same chemistry, differing *only* in their symmetry. Based on all of the preceding arguments, the effect of diisocyanate symmetry is profound. The change from an asymmetric (*m*PDI) to a symmetric (*p*PDI) moiety is enough to impact the phase-separation behavior of the materials. The microphase-separation of the *p*PDI–U can only be due to the better packing of the HS.

The HMDI–U material was not discussed in the previous sections. At ambient temperatures, the material was too soft and tacky to be tested with the DMA. HMDI, like MDI, is a non-linear “kinked” symmetric diisocyanate. HMDI also introduces symmetry differences due to chair and boat conformations of its cyclohexane ring. This is further evidence that the symmetry of the diisocyanate alone cannot predict the microphase-separated morphology nor the corresponding mechanical properties that result from that structure.

Before moving on to the polyureas, it is important to reflect on the earlier discussion of monodentate versus bidentate hydrogen bonding. Recall that the six materials presented thus far can only contain monodentate hydrogen bonding between monodisperse hard segments because

the PTMO SS is connected to the diisocyanate HS with urethane linkages. As we will see below, the introduction of bidentate hydrogen bonding in the polyureas can drastically alter the mechanical properties of these materials.

Figure 3.2 shows the DMA traces of the seven corresponding polyurea materials: *p*PDI-Ur, *m*PDI-Ur, MDI-Ur, CHDI-Ur, HDI-Ur, TDI-Ur, and HMDI-Ur. The sole difference in the materials listed in Figure 3.1A,B and Figure 3.2A,B is the chemical linkage between hard and soft segments (urea vs. urethane). Specifically, the polyureas offer the opportunity for bidentate hydrogen bonding in contrast to the monodentate bonding which occurs in the polyurethanes.

In general, the T_g 's of the polyureas do not vary radically from those measured in the polyurethanes though there are some exceptions, notably for the TDI-, *m*PDI-, and MDI-based systems. Recall that these materials showed distinctly lower E' values after T_g in the urethane materials. Table 3.2 is provided as a compilation of the pertinent E' values and thermal transitions measured with the DMA for all of the materials used in this study. The transitions of the polyureas begin at *ca.* -70 °C or lower in most cases. A T_g in this range is the first indication that a polyurea is likely to display a microphase-separated structure. A striking disparity in the DMA traces of polyurethanes and polyureas occurs in the rubbery plateau region following the glass transition. Both the magnitude and the breadth of the plateaus are distinctly greater in the polyurea systems compared to the polyurethanes. Other than the HMDI-Ur material, the other six polyureas show remarkably flat plateaus with E' values of *ca.* 10^8 Pa. In addition, the rubbery plateaus of TDI-Ur, *m*PDI-Ur, MDI-Ur, and HDI-Ur have upper temperature limits around 100 °C. In the case of *p*PDI-Ur and CHDI-Ur the values do not begin to soften until *ca.* 200 °C.

Table 3.2. Temperature dependent storage modulus behavior of single segment copolymers.

Sample	SS T_g [°C] from $\tan \delta$ peak in DMA	Service Window		Storage modulus at plateau extremes	
		Lower Plateau Temperature [°C]	Upper Softening Temperature [°C]	E' at Lower Limit [Pa]	E' at Upper Limit [Pa]
<i>p</i> PDI-U	-69	-59	31	8.60×10^8	7.90×10^7
<i>p</i> PDI-Ur	-64	-34	250	1.50×10^8	3.60×10^7
TDI-U	-61	-45	8	4.90×10^6	2.00×10^6
TDI-Ur	-75	-54	123	8.80×10^7	1.40×10^7
<i>m</i> PDI-U	-58	no plateau	N/A	N/A	N/A
<i>m</i> PDI-Ur	-72	-59	92	2.80×10^8	9.00×10^7
HMDI-U	-68	not tested	N/A	N/A	N/A
HMDI-Ur	-70	-51	69	1.30×10^8	6.50×10^6
MDI-U	-57	-43	54	7.30×10^8	6.50×10^6
MDI-Ur	-67	-21	114	7.80×10^7	7.60×10^7
HDI-U	-76	-70	28	2.80×10^8	5.50×10^7
HDI-Ur	-68	-22	107	1.00×10^8	6.30×10^7
CHDI-U	-72	-62	56	3.20×10^8	3.80×10^7
CHDI-Ur	-72	-22	215	7.60×10^7	5.80×10^7

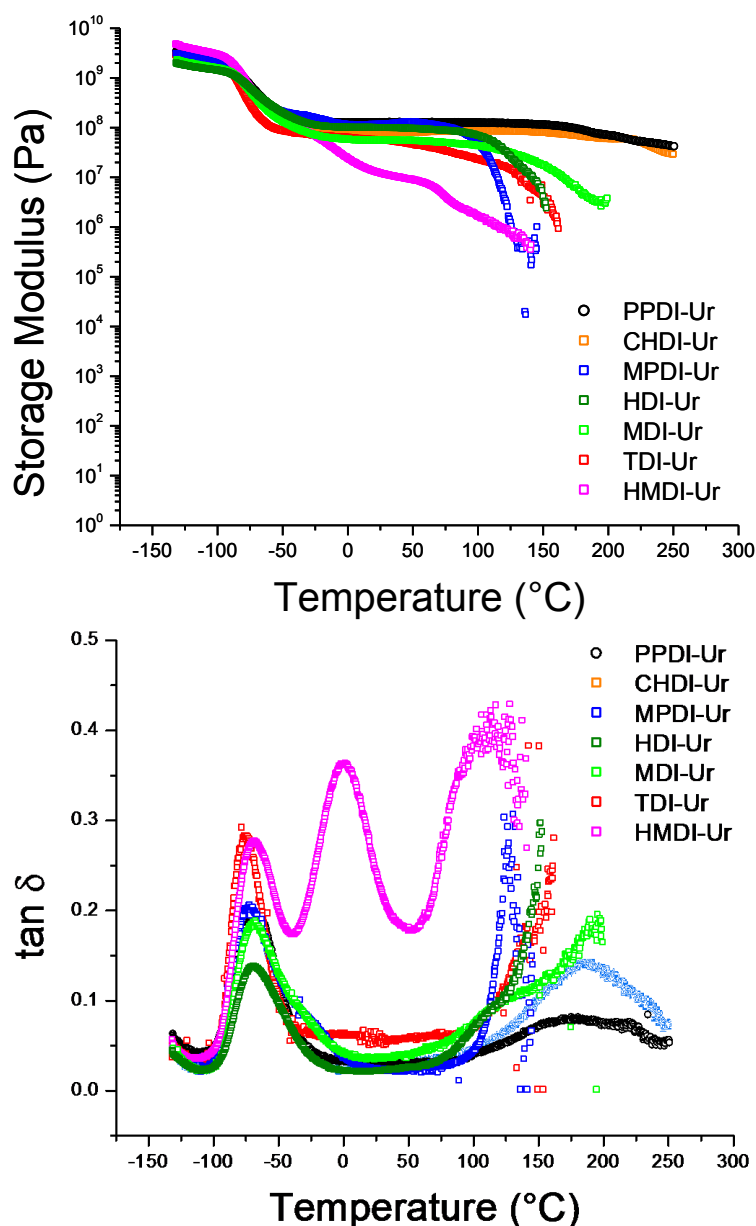


Figure 3.2. Temperature dependent storage modulus data for the polyureas used in this study.

These represent increases over the polyurethane values by 80 to 220 °C! Concentrating only on the two pPDI systems, urethane and urea, brings the effect of the bidentate bonding into sharper focus. When the material was synthesized with urethane linkages that allowed for only monodentate hydrogen bonding between HS, the upper service window temperature was 31 °C. With the change to urea linkages in the chain backbone, bidentate hydrogen bonding is available and the result is a drastically increased upper service temperature. The polyurea material

maintains a flat plateau until 150 °C and declines slowly upon further heating. Again, this is the direct result of the bidentate hydrogen bonding and the same trend can be seen for each of the diisocyanates used in this study. The effect of bidentate bonding is indeed dramatic. Just as in the polyurethane materials, the increase in the upper softening temperature indicates that the material retains its cohesive ordered nature to higher temperatures.

Interestingly, the polyureas materials which showed the greatest increase in E' were those made with the asymmetric diisocyanates, *m*PDI and TDI. Their polyurethane forms were extremely soft and tacky films at room temperature. The introduction of bidentate hydrogen bonding has enhanced the E' value in the rubbery plateau by roughly two orders of magnitude and has also extended the upper temperature softening point to about 100 °C, certainly to the point that the materials could have technological importance.

Based on the high E' values measured with DMA, many of the polyurethanes and polyureas are likely to be microphase separated. It was also hypothesized that the hard microphase was well percolated throughout a soft microphase matrix and served to strengthen the material by acting as physical crosslinks for the SS that compose the soft microphase. Other techniques such as AFM and SAXS are available which can support those hypotheses.

3.4.2. AFM

The microphase-separated structure of many of the materials discussed was visually verified by the use of AFM. As argued during the discussion of DMA results, the fact that these low hard segment weight content materials have such broad rubbery plateaus is one indication that there is a well percolated microphase structure in many of these films. Without that interconnectedness, films with such low HS contents could not display such high and broad E' plateaus. The AFM phase images shown in Figure 3.4 lend support to that argument. When taken in conjunction with the results in Figure 3.1, the ambient temperature AFM images of samples with narrow rubbery plateaus did not show an interconnected microphase-separated structure. Images are not shown for *m*PDI-U and TDI-U due to the small difference in stiffness in the sample. A large difference in stiffness between hard and soft phases is necessary to produce good AFM images. Because these materials are apparently not well microphase-separated at ambient

temperature, there are no hard and soft phases to provide that contrast. The four images in Figure 3.4 are of materials with broad E' plateaus as measured with the DMA. Each of the *p*PDI-U, HDI-U and CHDI-U images shows clear evidence of a well percolated microphase-separated structure. Here the lighter portions of the picture represent a harder region of the film and the darker regions indicate a softer region. Hence, the lighter stranded regions represent the microphase-separated hard phase consisting of a collection of hard segments while the darker regions represent the soft segment matrix. The monodentate and bidentate hydrogen bonding schemes that control the microphase separation also dictate that the short hard segments stack in such a way that their length is orthogonal to the long axis of the large strands seen in the AFM scan. This supposition was confirmed by computer simulations performed by David Cox, a professor of Chemical Engineering at Virginia Tech. The molecular simulation based on density functional theory (DFT) showed that two randomly oriented hard segments of *p*PDI-Ur would align such that the suggested bidentate bonding scheme occurs Figure 3.3 [122].

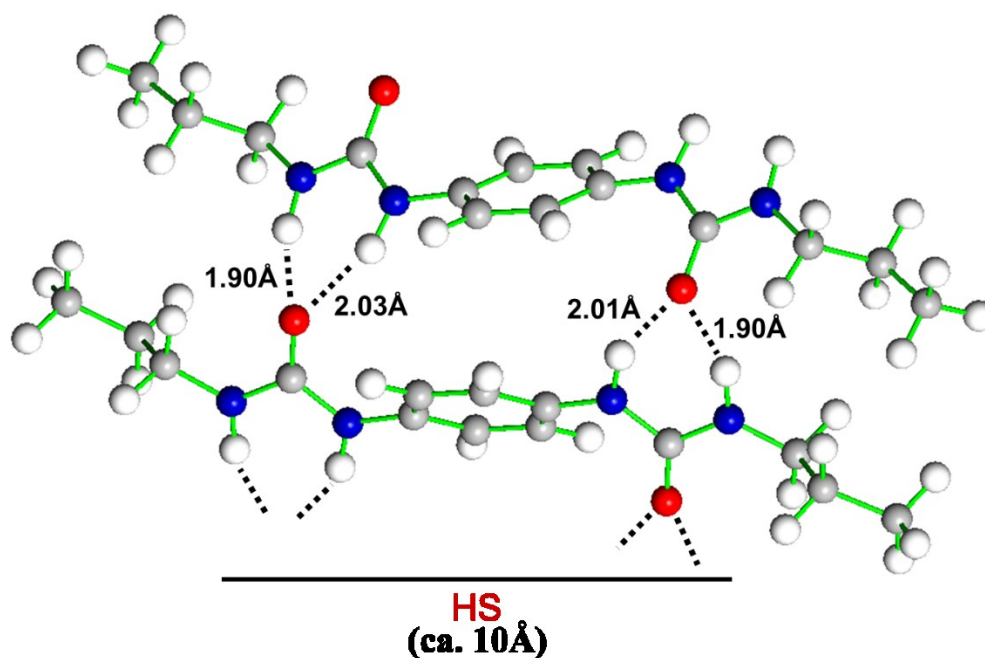


Figure 3.3. Bidentate hydrogen bonding modeled using *p*PDI polyurea hard segments.

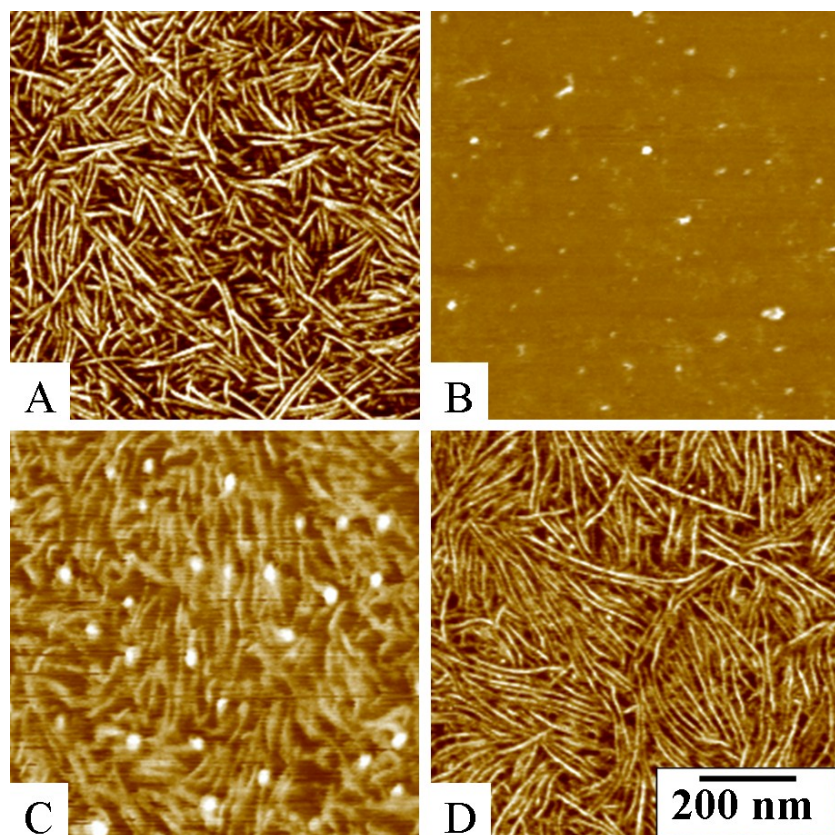


Figure 3.4. AFM phase images of several polyurethane samples displaying different levels of microphase separation: (A) *p*PDI-U; (B) MDI-U; (C) HDI-U; (D) CHDI-U.

Note that the MDI-U sample did not produce any clear visual evidence of a microphase-separated structure despite the broad service window measured with DMA. Recall however that this sample was much softer at ambient temperature than the other broad service window polyurethanes. The softness of the sample at the AFM imaging temperature certainly contributed to the lack of stiffness contrast for this image.

The introduction of bidentate hydrogen bonding both raised and broadened the service window of the polyurea materials when measured with DMA. As with the polyurethanes this was attributed to an interconnected, microphase-separated structure. Figure 3.5 shows AFM phase images of select polyureas.

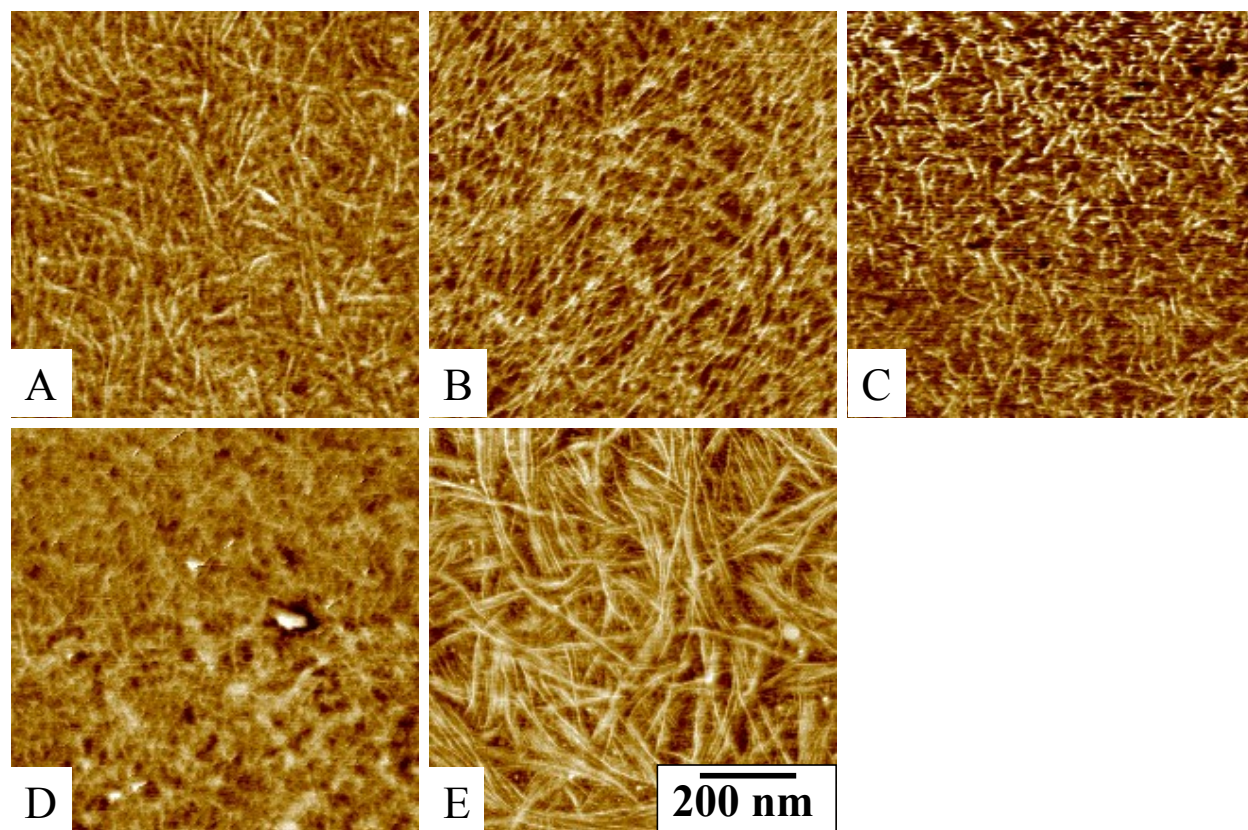


Figure 3.5. AFM phase images of single segment polyureas displaying different levels of microphase separation: (A) *p*PDI-Ur; (B) *m*PDI-Ur; (C) HMDI-Ur; (D) MDI-Ur; (E) HDI-Ur.

Particular attention should be given to the *m*PDI-Ur image. Its polyurethane counterpart was a soft and tacky material at ambient conditions that displayed a narrow service window with a low storage modulus in the DMA. That material was not expected to have a microphase-separated structure and no evidence of structure was seen in the AFM image of the material. But the polyurea gives very different results with AFM just as it did in the DMA. Now, microphase separation is expected for reasons mentioned earlier and confirmation of that structure was obtained with the AFM (Figure 3.5B).

Also of note is the HMDI-Ur image (Figure 3.5C). Because of the bidentate bonding in the polyurea material, this sample shows a microphase-separated structure whereas its polyurethane counterpart was such a tacky material at ambient temperature that it could not be tested at all.

3.4.3. SAXS

In addition to the AFM images, further verification of the presence of microphase separation in these materials (or lack thereof) has also been obtained by inspection of the ambient temperature SAXS profiles from each film. The profiles for the polyurethane materials are given in Figure 3.6. From Figure 3.6, it is obvious that the microphase-separated polyurethane systems display a somewhat broad but well-defined first order interference peak while the non-separated systems, TDI-U, *m*PDI-U, and HMDI-U (not shown), do not. As thoroughly discussed at an earlier time, the MDI-U film does not show any phase separation whereas the *p*PDI-U, HDI-U, and CHDI-U films do. In addition to the results presented here, the TDI-U and *m*PDI-U samples were also analyzed with SAXS. As expected, they did not show any peaks in the SAXS profile and are not presented here for the sake of simplicity in reading the graph. Though the location of the peak varies for the microphase-separated polyurethane systems, they display an average interdomain spacing or correlation length in the range of 112 Å to 189 Å. These spacings match reasonably well with the general distance between hard segment threads in the corresponding AFMs. Table 3.3 provides a list of interference peaks as measured for both the urethane and urea samples. Figure 3.7 introduces the corresponding data for the polyurea films. Again as expected for a microphase-separated material, each of the seven samples shows a first order interference peak. However, the location of the peak is interesting and not yet well understood. As compared to the polyurethanes shown in Figure 3.6, the polyureas scatter at higher radial angles and therefore have interference peaks at smaller interdomain spacings. The smallest spacing belongs to the TDI-Ur sample with a spacing of 42 Å.

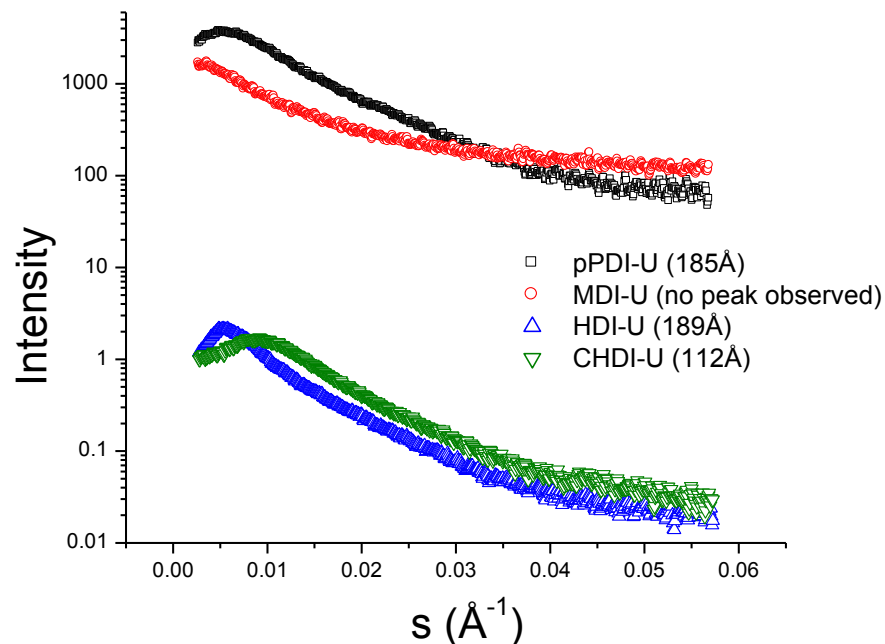


Figure 3.6. SAXS scans showing scattering behavior for *p*PDI-U, MDI-U, HDI-U, and CHDI-U films.

Spacings of polyureas increase from there in the order of *p*PDI-Ur (55 Å), HMDI-Ur (56 Å), *m*PDI-Ur (61 Å), CHDI-Ur (71 Å), MDI-Ur (75 Å), and HDI-Ur (80 Å). The cause of the disparity with the polyurethanes remains unclear. From the DMA and AFM results, the polyureas appear to be better microphase-separated than the polyurethane counterparts. As more HS separates from the SS matrix, the number of hard phase strands per unit area (as seen in the AFM) increases as well. As more and more strands are packed into the same volume of material, the clear result is a reduction in the average distance between scattering species. What is clear is that *the trend is consistent for all urea samples studied*.

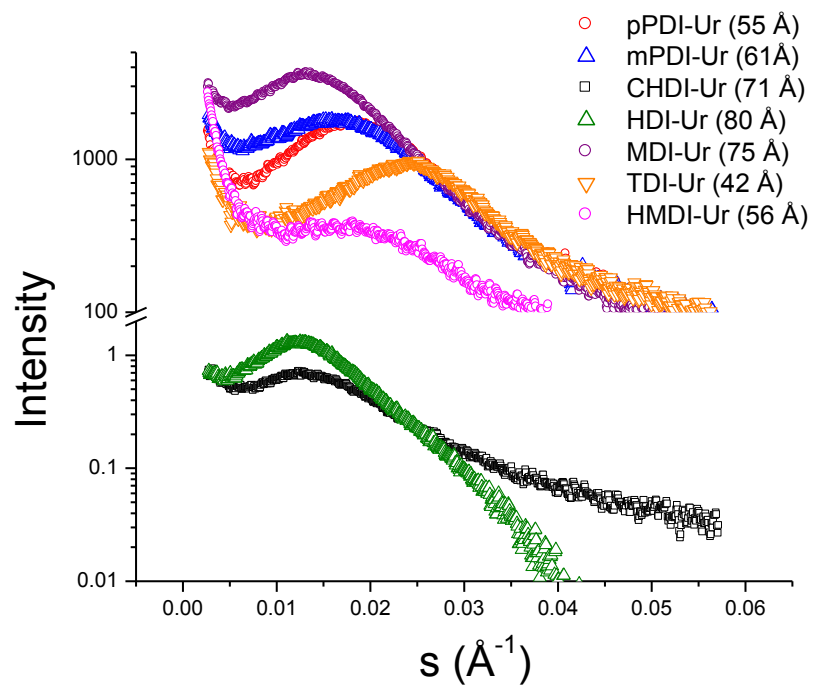


Figure 3.7. SAXS scans showing scattering behavior for polyurea films.

Table 3.3. Location of SAXS first order interference peaks.

Sample	SAXS peak [Å]
<i>p</i> PDI-U	185.0
<i>p</i> PDI-Ur	55.0
TDI-U	none
TDI-Ur	42
<i>m</i> PDI-U	none
<i>m</i> PDI-Ur	61
HMDI-U	none
HMDI-Ur	56
MDI-U	none
MDI-Ur	75
HDI-U	189
HDI-Ur	80
CHDI-U	112
CHDI-Ur	79

3.4.4. WAXS

The AFM and SAXS data indicate that many of these materials do indeed phase separate. The AFM phase images shows that the hard phase has assembled into a thread-like structure which in many cases is well percolated throughout the soft segment matrix. However, the morphological state of the hard phase is still unknown; at this point in the discussion, it could be either amorphous or semicrystalline. To determine the true nature of the SS and the HS packing WAXS was employed. If the SS were crystalline, one would expect to see the familiar two ring diffraction pattern. If the patterns lack that two ring pattern, any diffraction rings that *are* observed must be attributed to hard phase diffraction since the hard phase is the only phase left that could display crystallinity.

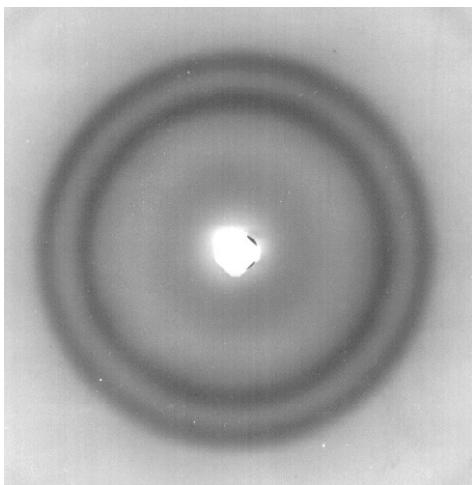


Figure 3.8. WAXS flat plate diffraction pattern from PTMO2k oligomer.

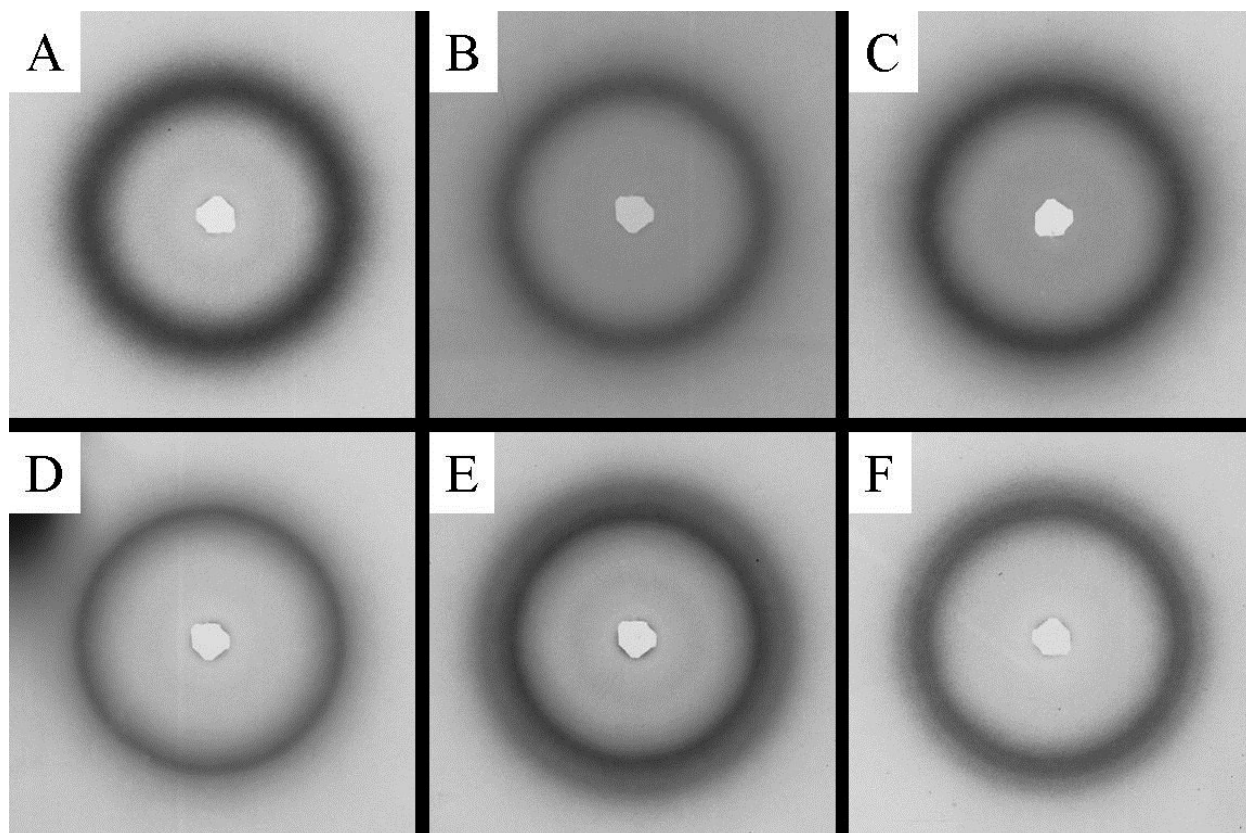


Figure 3.9. WAXS scans of polyurethanes: A) MDI-U; B) *m*PDI-U; C) TDI-U; D) CHDI-U; E) *p*PDI-U; F) HDI-U.

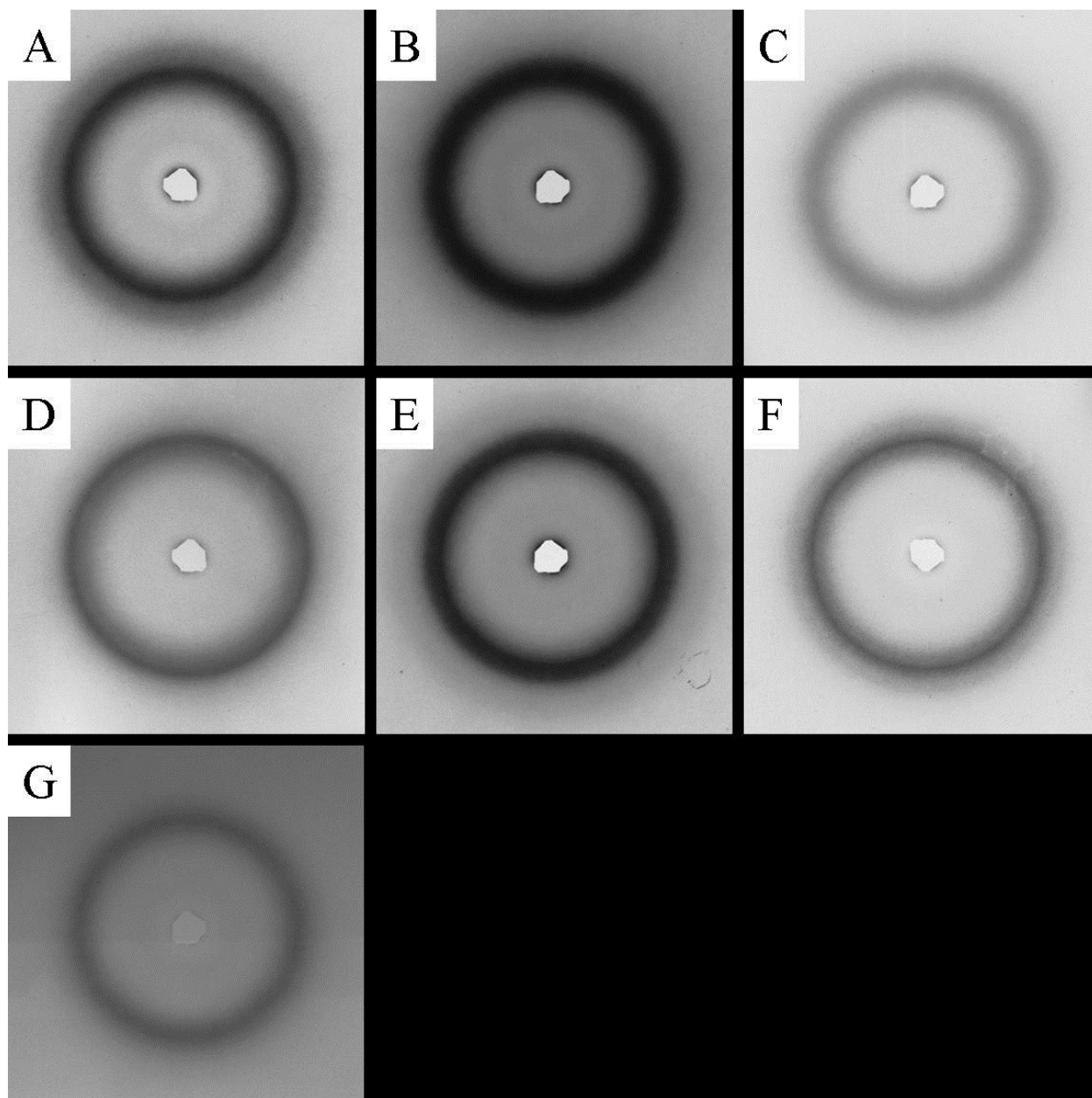


Figure 3.10. WAXS scans of polyureas: A) MDI-Ur; B) *m*PDI-Ur; C) TDI-Ur; D) CHDI-Ur; E) *p*PDI-Ur; F) HDI-Ur; G) HMDI-Ur.

The WAXS profiles for the six polyurethanes investigated in this study are provided in Figure 3.9 and those of the seven polyureas are provided in Figure 3.10. The patterns of the polyurethanes support the conclusions drawn thus far. That is, those samples that displayed poorer properties in the DMA and were thought to be mixed systems (*m*PDI-U, TDI-U, and MDI-U) do not show any apparent crystallinity for their respective WAXS patterns. Each sample has only a broad amorphous halo due to the unordered soft matrix region. However, in

each of the cases where microphase separation was proposed, there is also evidence of HS crystallinity. Specifically, in each case (*p*PDI-U, CHDI-U, and HDI-U) a sharp diffraction ring occurs. This sharp ring must be due to an ordered crystalline hard phase. Again, the diffraction pattern would display the familiar two ring pattern if the diffraction measured were due to SS crystallinity. The crystalline hard phase of these three materials boost the ambient temperature E' values as measured in the DMA to higher plateau moduli than the mixed systems. In addition to the microphase-separated structure acting as physical crosslinks to boost the stiffness of the materials, the hard phase is also semicrystalline, further strengthening the films. Thus, the upper temperature limit of the service window as defined by the DMA traces is determined to be a HS melting transition and not simply a HS T_g .

The WAXS patterns shown in Figure 3.10 were photographed from the seven polyurea materials. Only the TDI-Ur and HMDI-Ur do not show evidence of HS crystallinity as each lacked a sharp diffraction ring and showed only the broad amorphous halo. They do show interference peaks in their SAXS profiles, however, indicating that while the HS may not crystallize *during* the microphase separation process, the separation still occurs. Hence it is clear that the phase separation is not driven by the crystallization process. Just as in the polyurethanes shown in Figure 3.9, the diffraction rings of the other five materials (*p*PDI-Ur, *m*PDI-Ur, MDI-Ur, CHDI-Ur, and HDI-Ur) are not attributable to a PTMO SS crystallization. As each of these other five samples has been shown to display a microphase-separated structure, the diffraction must be due to a crystalline hard phase.

It is now quite clear that the *p*PDI-U, CHDI-U and HDI-U polyurethane samples contain a microphase separated structure with a crystalline HS. In addition, all seven polyureas display microphase separated structure with crystalline HS. That morphology is likely to have a large impact on the ambient temperature mechanical properties of these materials. The well percolated structure witnessed in the AFM may prove to strengthen the material until and unless that structure is broken in some manner. Also of interest from an engineering point of view is the materials' ability to recover after deformation.

3.4.5. TENSILE PROPERTIES

The mechanical properties of each of the materials synthesized for this study were also determined via uniaxial tensile deformation. Figure 3.11 presents representative tensile curves for each of the materials tested. The first graph displays the results of three polyurethanes. As mentioned before, the MDI-U, TDI-U and *m*PDI-U were extremely soft and tacky at ambient conditions and during mechanical testing they showed such lower stiffness that the samples deformed under their own weight. Hence, meaningful mechanical property data could not be obtained for them and those curves are not included here. However, the *p*PDI-U, CHDI-U and HDI-U materials each displayed mechanical behavior that could be exploited for engineering use. First, each material necked upon deformation. This neck is an indication that the well percolated thread-like structure is being damaged/disrupted during deformation. The samples continued to strain harden as deformation continued until failure. Each material had average elongations at break over 900%. Table 3.4 presents the average moduli, tensile strengths, and elongations at break for the samples used in this study as well as some relevant comments about each sample's behavior during and after testing.

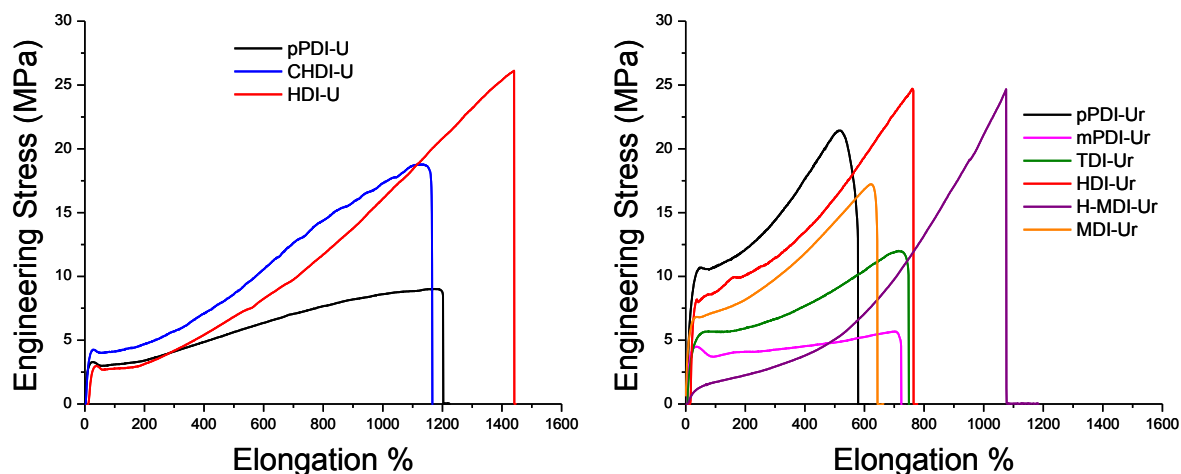


Figure 3.11. Representative tensile stress-strain curves for the polyurethanes (left) and polyureas (right).

Some polyurea samples also showed necking behavior upon deformation. Those samples were the *p*PDI-Ur, *m*PDI-Ur, and HDI-Ur. The TDI-Ur, HMDI-Ur and MDI-Ur *did not* show

necking behavior. These materials were notable in that they displayed almost complete recoverability immediately after the testing finished—see Table 3.4. CHDI–Ur samples were not tested due to limitations on the amount of sample available for testing. When comparing the three polyurethanes that were tested with their polyurea counterparts, in all cases the polyureas have higher moduli, higher ultimate tensile strengths and shorter elongations at break. Once more, the differences between monodentate and bidentate hydrogen bonding are evident.

Table 3.4. Average mechanical testing data for the polyurethanes and polyureas studied.

Sample	Modulus (MPa)	UTS (MPa)	Elongation at break (%)	Comments / Observations
<i>p</i> PDI–U	28.71 ± 8.16	8.36 ± 1.18	940 ± 240	necking, little if any recovery
<i>p</i> PDI–Ur	75.59 ± 4.37	19.44 ± 1.83	537 ± 36	necking, little if any recovery
TDI–U	N/A	N/A	N/A	no recovery
TDI–Ur	51.83 ± 4.05	12.32 ± 2.83	756 ± 155	complete recovery
<i>m</i> PDI–U	N/A	N/A	N/A	no recovery
<i>m</i> PDI–Ur	63.08 ± 8.47	5.39 ± 0.90	703 ± 191	necking, <i>ca.</i> 50% recovery
HMDI–U	N/A	N/A	N/A	
HMDI–Ur	5.58 ± 0.09	26.5 ± 3.25	1086 ± 33	almost complete recovery
MDI–U	N/A	N/A	N/A	no recovery
MDI–Ur	45.53 ± 11.29	16.86 ± 5.13	663 ± 190	complete recovery
HDI–U	24.61 ± 2.29	22.83 ± 3.47	1377 ± 182	necking, still decent recovery
HDI–Ur	120.03 ± 24.71	24.68 ± 6.25	763 ± 67	necking, still decent recovery
CHDI–U	49.8 ± 5.1	20 ± 1.5	1156 ± 98	necking
CHDI–Ur	N/A	N/A	N/A	

3.5. CONCLUSIONS

A series of segmented polyurethanes and polyurea copolymers based on a PTMO soft segment was synthesized using seven different diisocyanates as hard segments. The materials were synthesized without the use of chain extending molecules. Hence, the monodisperse hard segments of these copolymers consisted of a single diisocyanate molecule. The diisocyanates were chosen such that variables such as diisocyanate symmetry and hydrogen bonding strength could be isolated and studied. Solvent cast films of these materials were made for the

investigation of structure-property relationships for the segmented copolymers. Many of these materials generated films with good ambient temperature properties comparable to common chain extended systems in areas such as storage modulus, service window, stiffness, modulus and elongation at break.

In cases where both the polyurethane and polyurea films had significant stiffness to be measured, the bidentate hydrogen bonding of the polyureas had a number of distinct effects on the film properties. In general, the bidentate bonding led to a higher and broader service window as the upper temperature limit of the dynamic storage modulus was increased. DMA, AFM and SAXS measurements confirmed that many materials had a microphase-separated microstructure responsible for the increased mechanical and thermomechanical properties of the films. In many cases, the microphase separation was accompanied by a crystallization of HS in a hard phase, a result often predicted based on the symmetry of the diisocyanate used in the synthesis of the material. The introduction of bidentate hydrogen bonding via urea linkages in the copolymer chain backbone also altered ambient temperature properties. The polyurea films had higher modulus values, higher tensile strengths and did not attain elongation at break values as large as their polyurethane counterparts due to the higher bond strength of the bidentate bond.

4. THE EFFECT OF CHANGING SOFT SEGMENT MOLECULAR WEIGHT ON THE STRUCTURE–PROPERTY RELATIONSHIPS OF SEGMENTED POLYURETHANES LACKING CHAIN EXTENDERS

4.1. INTRODUCTION

The structure–property behavior of linear segmented copolymers continue to be an area of aggressive research due to their wide range of industrial and commercial applications [7, 17, 90, 123]. They display unique characteristics resulting from the choice of both the soft segment (SS) and hard segment (HS) type. Soft segments generally have lower molecular weights (less than 3000 g/mol) than traditional anionic block copolymers (often greater than 10,000 g/mol). In the case of polyurethanes, SSs are often aliphatic polyethers such as poly(tetramethylene oxide) (PTMO) or polyesters such as poly(tetramethylene adipate) (PTMA) with glass transition temperatures (T_g) well below room temperature. The hard segments of commercial or “conventional” segmented polyurethane products are composed of diisocyanates and chain extender moieties used to increase HS length and thereby molecular weight of the HS. Typically, chemical incompatibility between the soft and hard segments also increases as the segment lengths increase. The incompatibility drives the microphase separation process, leading to the promotion of a service temperature window often defined by the SS T_g and the upper temperature softening transition of the HS domains.

Segmented polyurethanes are commonly synthesized with a two-step technique, often referred to as the prepolymer method [3, 18, 29]. In the first step, the selected SS polyol and diisocyanate are reacted to form a capped ‘prepolymer’. In the second step, the prepolymer is reacted with diol chain extender and often excess diisocyanate. A less common synthesis method is a one-step process in which the polyol, diisocyanate, and chain extender are simultaneously mixed together to form the final product. In both cases, a chain extender is used to increase HS content and to modify the physical properties. This chapter deals with the synthesis of polyurethanes using the “one-step process”. As will be discussed in further detail in the section concerning synthesis, hydroxyl terminated 975 g/mol and 2040 g/mol PTMO were each reacted with a series of diisocyanates to form a novel set of polyurethane materials. Henceforth, the PTMO segments will be referred to as PTMO1k (indicating the 975 g/mol) or PTMO2k

(indicating the 2040 g/mol) for the sake of simplicity. These samples are unique in that they were *synthesized without utilizing any chain extender molecules* in the synthesis. Therefore the HS of the polyurethanes consist of individual diisocyanate molecules and their terminal urethane linkages that bond them to the PTMO SS. This chapter details the characterization of these new non-chain extended materials with particular attention towards the effect of the decreased HS content in the PTMO2k based materials. A previous chapter detailed work done on a series of PTMO1k based polyurethanes as well as polyureas where the soft segment was based on amine capped PTMO1k. That work detailed the effects of isocyanate chemistry and hydrogen bonding on the morphology and structure–property behavior of those materials [124]. The development with time of the microphase-separated morphology of a polyurethane based on a PTMO1k SS and *para*-phenylene diisocyanate (*p*PDI) has also been described in a separate report [87]. Those results impact on this work as the PTMO1k is used in this chapter for the comparison of PTMO1k and PTMO2k based materials. Though the increased SS length and lower HS content are likely to render the materials impractical for industrial application, these changes answer fundamental questions about the effect of these parameters on the materials’ ability to microphase separate. The effects of HS symmetry can be explored in these chain extended materials as it was in the earlier “single soft segment” work.

Greater strength, stiffness and toughness arise when, under the appropriate conditions, segmented, thermoplastic polyurethanes (TPUs) microphase separate. Given the polarity of the polyurethane precursors often used and the low molecular weights of the segments, the hard and soft segments may show solubility in one another [125]. The microphase separation process, however, can be promoted in part by using chain extenders which raise HS molecular weight as well as their length, and thereby reduce the SS–HS miscibility. The resulting microphase separation leads to a morphology in which two distinct phases exist, each of which contains a high volume fraction of either SS or HS content. In addition, there may be regions of the material which shows evidence of hard and soft domain mixing [107-110]. Generally, the hard phase has the lower volume fraction and therefore segregates itself into hard domains embedded in a soft matrix. With microphase separation, connections exist between the soft and hard phases that act as physical crosslinks for the soft phase and serve to increase stiffness, strength, and toughness over a range of temperatures where the material may be utilized commercially. As the volume fraction of the hard phase is increased, the hard domains begin to make further contact and begin

to develop further connectivity. Depending on the level of connectivity of the hard domains, as well as other factors which will be addressed in the forthcoming sections, a microphase-separated material can be used industrially across a wide range of temperatures. This range is defined as the material's 'service window', a relatively temperature-insensitive region of the storage modulus (E') versus temperature curve, often characterized by a broad rubbery plateau in a DMA trace. This region is bounded at the low end by the SS T_g (or T_m if the soft segment is semicrystalline) and is bounded at the high end by the HS softening point (T_g) or T_m if it can crystallize.

A previous chapter dealt with the synthesis of novel polyurethane and polyurea materials using a series *para*-phenylene diisocyanate (*p*PDI), and *meta*-phenylene diisocyanate (*m*PDI), *trans*-1,4-cyclohexyl diisocyanate (CHDI), hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI) without the use of chain extenders. Those materials were all based on the same 1k-PTMO soft segment and displayed substantial microphase separation and interesting physical properties when solution cast from dimethylformamide (DMF) despite having a HS consisting of only a single diisocyanate molecule. In this chapter, the synthesis of segmented polyurethanes based on 2k-PTMO soft segments is presented and the effect of increased SS molecular weight on film properties is investigated. As in the previous chapter, monodisperse hard segment polyurethanes are produced using *trans*-1,4-cyclohexyl diisocyanate (CHDI) and 1,6-hexamethylene diisocyanate (HDI), but in the present case, they are with 2k-PTMO glycol SS instead of 1k-PTMO glycol. The increase in SS molecular weight should elevate the SS T_m if the SS forms a semicrystalline structure. This in conjunction with the decrease in HS content should influence both the structure and properties of the resulting material. The higher $\langle M_n \rangle$ is also expected to possibly lead to some SS crystallization at ambient temperature, a phenomena not witnessed in the aforementioned study. In addition, the decreased HS content may prevent the extensive percolation and connectivity of the hard phase throughout the soft phase and therefore prevent yielding in the final films during mechanical testing.

4.2. EXPERIMENTAL SETUP

4.2.1. MATERIALS

1,4-Phenylene diisocyanate (*p*PDI) was purchased from Aldrich. *Trans*-1,4-cyclohexyl diisocyanate (CHDI) was purchased from Du Pont and 1,6-hexamethylene diisocyanate (HDI) was kindly provided by Bayer. HDI and CHDI were used as received; *p*PDI was sublimed at 70 °C. Purities of diisocyanates were better than 99.5%. Poly(tetramethylene oxide)glycol (PTMO1k and PTMO2k), with $\langle M_n \rangle$ values of 975 g/mol and 2040 g/mol respectively, were kindly provided by DuPont. Table 4.1 details the chemical structure of the molecules used in the synthesis for this study. It is important to note that all of the diisocyanates used have symmetrical structures.

Table 4.1. The chemical structures of materials used in the preparation of polyurethanes in this investigation.

Chemical Species	Abbreviation	Structure
poly(tetramethylene oxide)glycol	PTMO	
para-phenylene diisocyanate	<i>p</i> PDI	
trans-1,4-cyclohexyl diisocyanate	CHDI	
hexamethylene diisocyanate	HDI	

4.2.2. POLYMER SYNTHESIS

Polymerizations were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. All copolymers were prepared by reacting equimolar amounts of a selected diisocyanate and PTMO oligomers. As stated earlier, no chain extenders were utilized. Polymerization reactions were conducted in DMF solvent at a concentration of about 20 wt% solids. Equimolar amounts of PTMO and diisocyanate were introduced into the reaction flask and dissolved in the reaction solvent. Reactor was heated to 60 °C under strong agitation. 100 ppm of T-12 was used as catalyst in the synthesis of CHDI and HDI based polyurethanes. Completion of the reactions was determined by monitoring the disappearance of the isocyanate absorption peak at 2270 cm⁻¹ by FTIR spectroscopy.

4.2.3. PREPARATION OF TEST SPECIMENS

Polymer films *ca.* 1 mm thick were obtained by pouring the solutions into Teflon molds. The molds were covered with a glass Petri dish to slow down the solvent evaporation and placed in an oven maintained at 60 °C. After evaporation of the solvent, the molds were placed in a vacuum oven at 60 °C for complete drying, which was monitored gravimetrically. The resulting films were then easily removed from the Teflon molds and stored under vacuum at room temperature until needed for testing. Care was taken to note which side of the film was cast on the Teflon so that further AFM characterization would not be compromised by Teflon contamination. Unused portions of these films were cut into pieces and compression molded between Kapton film in order to investigate their melt processability and to compare their solid-state behavior with that of their solution cast analog.

The polyurethane samples prepared are designated using the following nomenclature: <M_n> of the PTMO–diisocyanate. Hence, 1k-*p*PDI indicates a material in which PTMO1k was reacted with an equimolar amount of *p*PDI. The remaining materials are denoted as 1k-CHDI and 1k-HDI. The PTMO2k glycol was reacted with the same diisocyanates in DMF to produce 2k-*p*PDI, 2k-CHDI and 2k-HDI. Table 4.2 provides the nomenclature and the hard segment

content of the polyurethanes prepared and used in this study. Since the polymers are prepared by reacting equimolar amounts of PTMO and diisocyanates, an increase in the PTMO $\langle M_n \rangle$ from 975 to 2040 g/mol (samples 1k-*p*PDI and 2k-*p*PDI) lowers the HS content of the polyurethane from 14.1 to 7.7 wt%. Similar arguments apply to the CHDI and HDI based polyurethanes (Table 4.2).

Table 4.2. Hard segment weight percentages for materials used in this study.

Sample designation	HS wt%
1k- <i>p</i> PDI	14.1
2k- <i>p</i> PDI	7.7
1k-HDI	14.7
2k-HDI	8.1
1k-CHDI	14.6
2k-CHDI	7.7

4.3. EXPERIMENTAL TECHNIQUES

4.3.1. ATOMIC FORCE MICROSCOPY (AFM)

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. Some samples, however, necessitated the use of a much higher free air amplitude of *ca.* 8.0 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4 to 0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz. Care was taken to image the free surface of the solvent cast films as opposed to the side in contact with the Teflon mold.

4.3.2. DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed on a Seiko DMS 210 tensile module with an attached auto-cooler for precise temperature control. Rectangular samples measuring 10 mm in length and 4.5–6.5 mm in width were cut from the cast films. Under a dry nitrogen atmosphere, the films were deformed using a frequency of 1 Hz. The temperature was increased from -150 to 300 °C at a rate of 2 °C/min. Soft segment glass transition temperatures reported by the DMA methodology were denoted as the location of the peak in the $\tan \delta$ vs. temperature plots.

4.3.3. TENSILE TESTING

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. A bench-top die was used to cut dogbone samples with an overall length of *ca.* 25 mm and the width of the grip section of *ca.* 10 mm. The reduced section measured 2.91 mm $\times$ 10 mm (width $\times$ gage length). These dogbones were then tested to failure at a crosshead speed of 25 mm/min and their load vs. displacement values recorded. Three samples were measured and their results were averaged to determine modulus, yield strength, and strain-at-break for each of the five materials. In addition to testing the materials to failure, hysteresis measurements were also made on select materials. For this test, the dogbone shaped samples were stretched to 800% strain at a crosshead speed of 25 mm/min and then immediately returned to its initial position of 0% strain at the same rate. Samples were then immediately redrawn for a second loading. This loading-unloading cycle was repeated twice more to produce a three-cycle hysteresis test.

4.3.4. WIDE ANGLE X-RAY SCATTERING (WAXS)

Photographic flat WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu-K $_{\alpha}$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was set at 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an

evacuated sample chamber. X-ray exposures lasted four hours. Sample thickness ranged from 12–14 mils.

4.3.5. SMALL ANGLE X-RAY SCATTERING (SAXS)

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu- K_{α} doublet, with an average wavelength of $\lambda = 1.54 \text{ \AA}$. The camera used 200 μm , 100 μm and 300 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector, located approximately 65 cm from the sample. After azimuthal averaging, the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source at the Argonne National Laboratory, as a secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s , where $s = 2 \sin(\theta)/\lambda$, and 2θ is the radial scattering angle.

4.4. RESULTS AND DISCUSSION

The temperature dependent storage modulus (E') and $\tan \delta$ were determined for each of the materials using DMA. The results for the 1k- and 2k-*p*PDI are shown in Figure 4.1A. Figure 4.1B and Figure 4.1C show results of the 1k- and 2k-HDI and the 1k- and 2k-CHDI-based samples respectively. Before discussing the traces and their implications in detail, a broad overview of the results is presented to highlight certain attributes of the plots which will be focused on later.

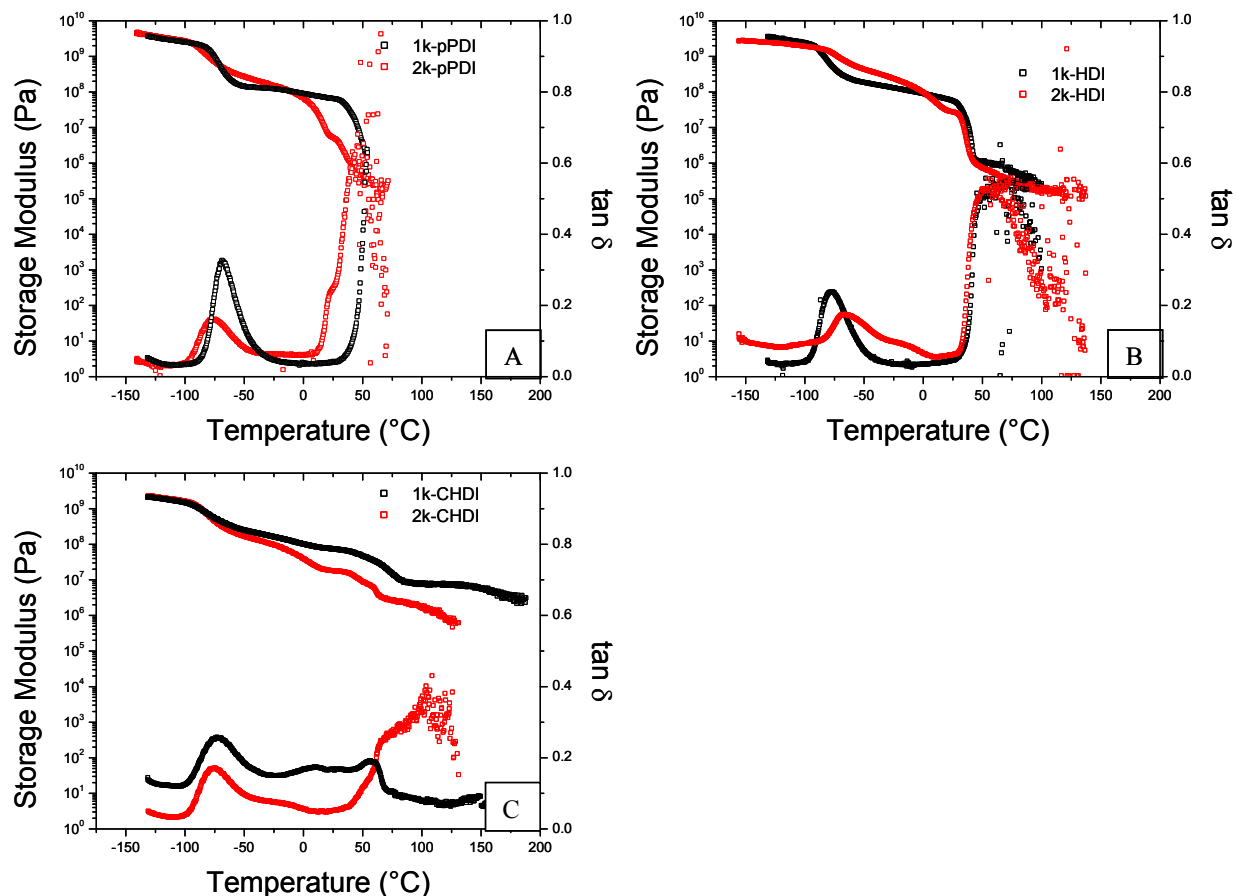


Figure 4.1. Temperature dependent storage modulus and $\tan \delta$ response of materials based on: A) 1k-pPDI and 2k-pPDI; B) 1k-HDI and 2k-HDI; C) 1k-CHDI and 2k-CHDI.

For each of the six materials, below *ca.* -75°C , the samples are very rigid and have E' values greater than 10^9 Pa. Samples were heated through their T_g 's and each trace shows a corresponding peak in its $\tan \delta$ curve. The shape of the $\tan \delta$ traces is important. The 1k-based samples have symmetric peaks whereas the 2k-based samples are asymmetric and are skewed to the right. The implications of this will be addressed later. From the DMA data, a more important observation for structural determination is the magnitude of the E' drop as the samples are heated through their respective T_g 's. In each of the six samples shown in Figure 4.1, the initial drop in E' after T_g is roughly one order of magnitude. After passing through T_g , the E' of each of the 2k-based samples steadily decreases as the samples are heated. The 1k-based materials also experience a decrease in E' , though these materials lose stiffness at a slower rate than the 2k-based samples, a fact witnessed in the lower slope in the E' traces after T_g . In these samples,

particularly the 1k-*p*PDI and 1k-HDI, E' decreases so slowly, often passing through T_g , that the storage modulus traces are almost flat for some time after passing through the T_g region. Looking more closely at the traces of the 2k-based materials, they each display a second drop in E' , between -15 °C and 0 °C for each sample, in a temperature range where the 1k-based materials do not. Continued heating results in the softening of the 2k-*p*PDI sample at *ca.* 25 °C whereas the 1k-*p*PDI softens at *ca.* 35 °C. After this transition, the tests were terminated due to excessive sample softening. Both the 2k-HDI and 1k-HDI soften at *ca.* 30 °C while both the 2k- and 1k-CHDI begin softening at *ca.* 40 °C. The results just described, with temperature transitions and E' values noted, are arranged in Table 4.3 to facilitate direct comparisons.

Table 4.3. Temperature dependent storage modulus behavior of single segment copolymers.

Sample	SS T_g (°C) from $\tan \delta$ peak in DMA	Service Window		Storage Modulus at plateau extremes	
		Lower Plateau Temperature (°C)	Upper Softening Temperature (°C)	E' at Lower Limit (Pa)	E' at Upper Limit (Pa)
1k- <i>p</i> PDI	-68.8	-53	33	1.5×10^8	5.0×10^7
2k- <i>p</i> PDI	-73.8	-58	1	3.2×10^8	6.3×10^7
1k-HDI	-75.5	-70	28	2.8×10^8	5.50×10^7
2k-HDI	-66.0	-47	30	3.9×10^8	2.3×10^7
1k-CHDI	-72.3	-62	56	3.2×10^8	3.80×10^7
2k-CHDI	-73.7	-61	60	2.2×10^8	5.7×10^6

We now return to the beginning of the DMA discussion to examine some important facets of these traces in greater detail and to determine the implications of each transition previously documented. After the first thermal transition upon heating (SS T_g), both the 1k-*p*PDI and 2k-*p*PDI samples experienced decreases in E' to values above 2×10^8 Pa, a reduction of only one order of magnitude. This result for the 1k material was determined in earlier work [87]. The high E' measured after the samples undergo this thermal transition indicates the presence of an interconnected microphase-separated microstructure, although some of this effect is likely due to a crystalline SS in the PTMO2k based material. If the sample does indeed assume this morphology, this suggests that the T_g measured is that of the microphase-separated SS. This is a striking result given the fact that these materials are not chain extended and have HS contents of only 7 and 15 wt% for the 2k-*p*PDI and 1k-*p*PDI respectively. Similar

arguments can be made for each of the HDI- and CHDI-based samples, as they each show stiffness reductions of only an order of magnitude. Further verification of the microphase-separated morphology for each of the six materials will be presented later in the form of AFM and SAXS data. The soft phase is necessarily constructed of PTMO SS, although the crystalline nature of the SS has not yet been discussed. As stated previously, the hard microphase must be constructed of an assembly of HSs. These segments are comprised of single diisocyanate molecules (*p*PDI, HDI or CHDI) and the two urethane linkages that bond them to the PTMO SS. It is surprising that a 7 wt% HS material would experience so small a drop in E' after passing through the SS T_g . Microphase separation alone would be unlikely to account for the high E' value in the 2k-based systems if the hard microphase were not interconnected throughout the material. It is the interconnectedness of the hard microphase and the resulting physical crosslinks it provides to the microphase-separated soft phase that leads to the high E' value for these materials after the SS T_g . As heating progressed the 2k-*p*PDI and 2k-HDI samples maintained a slightly higher E' value than their 1k-based counterparts until the each of the 2k-based samples encountered their second thermal transition. This can be seen in the traces of Figure 4.1. Temperature dependent storage modulus and $\tan \delta$ response of materials based on: A) 1k-*p*PDI and 2k-*p*PDI; B) 1k-HDI and 2k-HDI; C) 1k-CHDI and 2k-CHDI. In each case the 2k-based material, with the HS content of *ca.* 8%, experienced a decrease in E' whereas their 1k-based counterparts did not. The presence of this second transition in the 2k-based samples provides the first clue as to the partially crystalline nature of the PTMO microphase as it is a melting transition of PTMO SS. Its presence in the 2k-based samples, and absence in the 1k-based materials, is due to the increased length of the SS. The PTMO SS is able to crystallize at a molecular weight distinctly above 1000 g/mol. To further confirm the hypothesis of a microphase-separated structure and to further probe the crystalline nature of the two phases, DSC was run on each material. The DSC traces of the 1k- and 2k-materials are presented in Figure 4.2A–C and Figure 4.3A–C respectively.

Each plot consists of the initial heating trace, the subsequent cooling curve, and a second heating (reheating) trace. As shown in Figure 4.3, each 2k-based material exhibited a clear endothermic peak beginning at roughly 0 °C which is attributed to the melting of PTMO SS, a peak not seen in the 1k-based materials of Figure 4.2. This coincides with the second thermal transition seen previously in the DMA traces, indicating that the second decrease in E' is due to

the SS T_m . The DSC traces of the 1k-based materials lacked a clearly defined peak in this region. Recall that the DMA traces of the 1k-based samples did not show any thermal transitions in this temperature range either. The first peaks in the 1k-based materials DSC traces occurs at *ca.* 50 °C, the same temperature that the drop in E' was measured in the DMA. Thus, the shorter SSs of the 1k-based samples did not display crystallization. There is undoubtedly an endothermic peak in each of the 1k-based materials' DSC traces; however, the onset of this peak occurs at *ca.* 50 °C indicating that it is not associated with the soft phase. Since the materials are microphase separated, it is conjectured that this peak at 50 °C must be due to the melting of a semicrystalline hard phase. This conclusion will be given further support as more DSC results are introduced and a more detailed discussion of the crystalline nature of the hard phase will be presented when AFM and WAXS results are addressed.

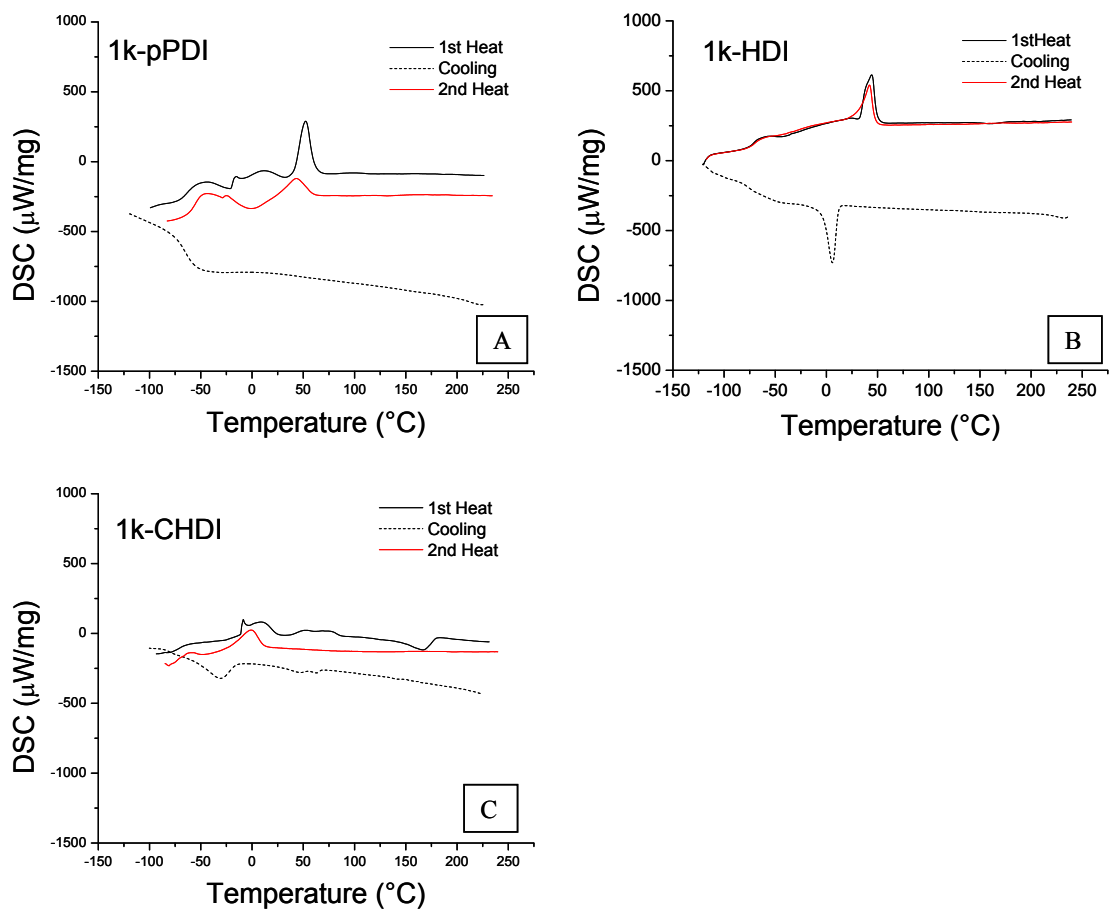


Figure 4.2. DSC heating and cooling traces of the PTMO1k materials beginning at subambient temperatures: A) 1k-*p*PDI; B) 1k-HDI; C) 1k-CHDI.

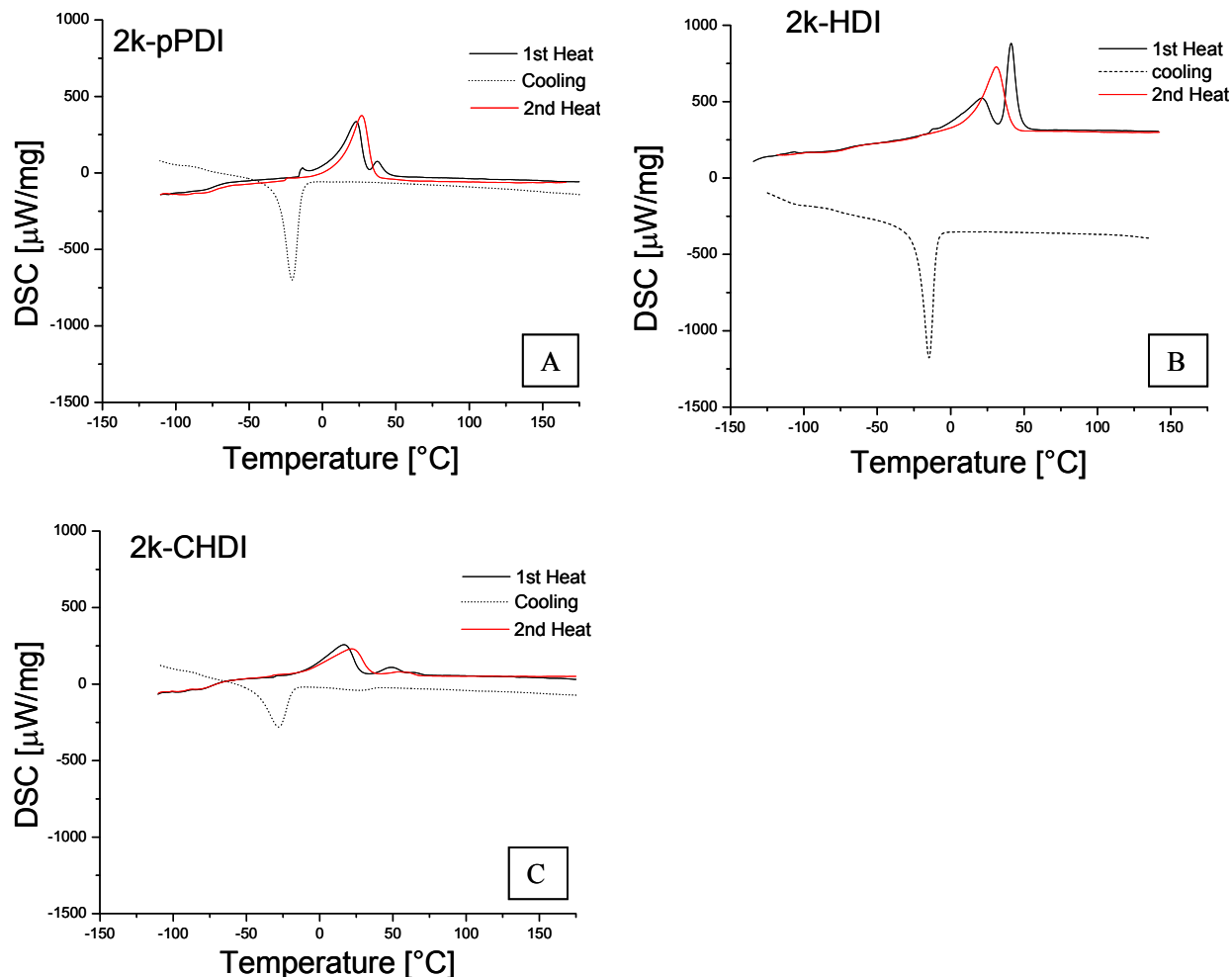


Figure 4.3. DSC heating and cooling traces of the PTMO2k materials beginning at subambient temperatures: A) 2k-*p*PDI; B) 2k-HDI; C) 2k-CHDI.

The source of the PTMO SS crystallization in the 2k-based materials are now discussed. Each of the samples measured in the DSC and DMA experiments were first cooled to -125 °C prior to data collection. During this cooling step, the PTMO SS of the 2k-based systems crystallized due to its longer SS as compared to the 1k-based samples. The polyurethanes based on PTMO1k did not crystallize upon cooling due to their shorter SS. The PTMO2k soft segment crystallization during DMA and DSC cooling is a subject which will be explored during the discussion of results from other characterization techniques. Techniques that did not necessitate the quenching of the samples (WAXS, SAXS, tensile testing) do not show evidence of a crystalline SS as those samples were not cooled before testing. Support for this conjecture is shown in Figure 4.4 and Figure 4.5.

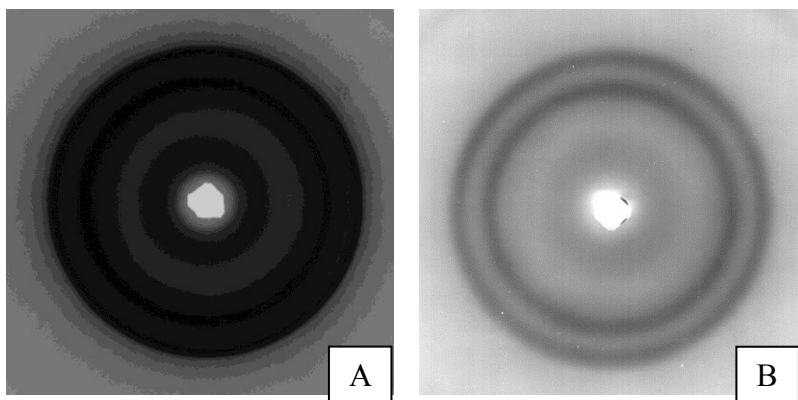


Figure 4.4. Ambient temperature WAXS diffraction patterns of PTMO1k and PTMO2k oligomers.

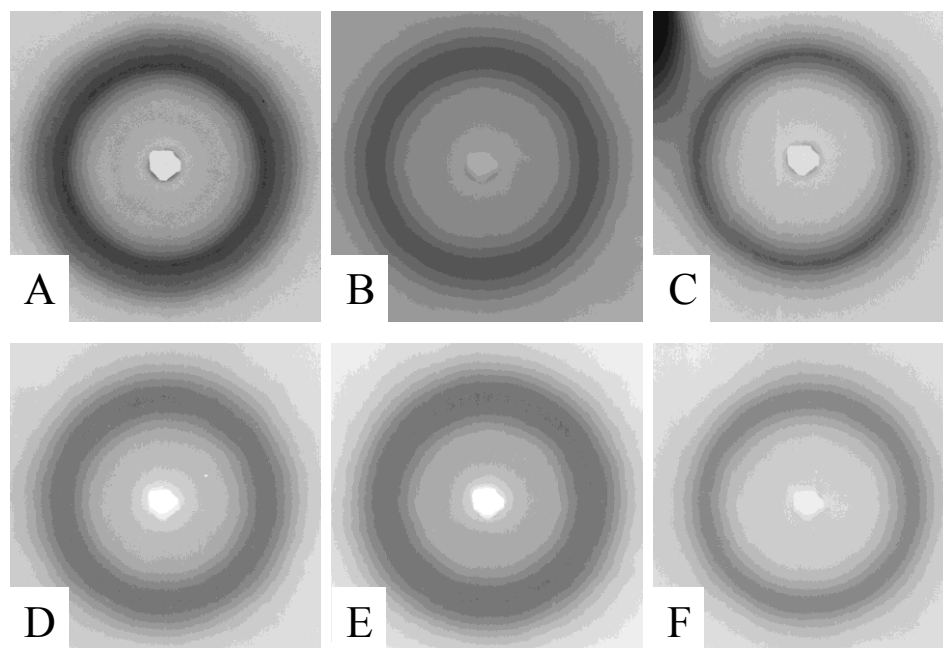


Figure 4.5. Ambient temperature WAXS diffraction patterns: A) 1k-*p*PDI; B) 1k-HDI; C) 1k-CHDI; D) 2k-*p*PDI; E) 2k-HDI; F) 2k-CHDI.

Figure 4.4A and Figure 4.4B contain the WAXS patterns of *pure* PTMO1k and PTMO2k oligomer samples respectively, at ambient temperature. The diffraction pattern of each shows two concentric rings indicating that, as pure oligomers, each PTMO sample is semicrystalline. Figure 4.5 shows the ambient temperature WAXS patterns of the segmented polyurethanes used in this study. Addressing the 2k-based materials first, note that the patterns from these materials (Figure 4.5D–F) do not show the two prominent rings that are evident in the diffraction pattern of the neat PTMO2k oligomer. The diffraction patterns show only an amorphous halo; hence,

none of the 2k-based materials appears crystalline at ambient temperature. The lack of crystalline diffraction may also be due to the very low HS content (7%) of these samples. At this level of HS content, even a fully crystalline hard phase would mean the segmented copolymer could only achieve 7% crystallinity. Recall that the 2k-based polyurethane samples discussed earlier as having semicrystalline SS were quenched prior to testing, and that the quenching step itself induced the crystallization measured during testing.

Studying Figure 4.5A–C, it is clear that the polyurethanes based on a 1000 g/mol SS are semicrystalline at ambient temperature. However, when compared to the PTMO1k oligomer pattern in Figure 4.4, the polyurethane patterns lack the two concentric PTMO rings that would indicate the presence of crystalline PTMO1k. Hence, the lone ring in each pattern must be due to a semicrystalline HS. This conclusion adds support to the earlier interpretation of the DSC results in which the endothermic peak at 50 °C was attributed to a HS melting transition.

For additional proof that the diffraction ring in the 1k-based materials is due to a crystalline HS and not the SS, DSC experiments were performed on each of the six materials without the initial quench of the earlier scans. In these experiments, the samples were heated from ambient temperature to 150 °C at 10 °C/min. The results of these experiments are presented in Figure 4.6 which contains the heating traces of the 2k-based samples and a listing of the calculated specific heats of the transition. There is a clear endothermic peak in each 2k-based sample above 35 °C. Based on the earlier DMA, DSC, and WAXS pattern discussions, this peak represents the melting transition of the hard microphase. However, as verification of that hypothesis, a comparison of the specific heats of these transitions was made. The area of each endothermic peak was calculated to be 8.4, 9.5, and 3.9 J/g for the 2k-*p*PDI, 2k-HDI, and 2k-CHDI samples respectively. The areas of the 1k-*p*PDI, 2k-HDI, and 2k-CHDI were calculated to be 13.0, 22.3, and 10.2 J/g respectively. As the HS contents roughly double when the change is made from PTMO2k to PTMO1k based materials, so too do the specific heats of the melting transitions. If the melting transition were in fact due to a melting of SS, the opposite trend would be expected.

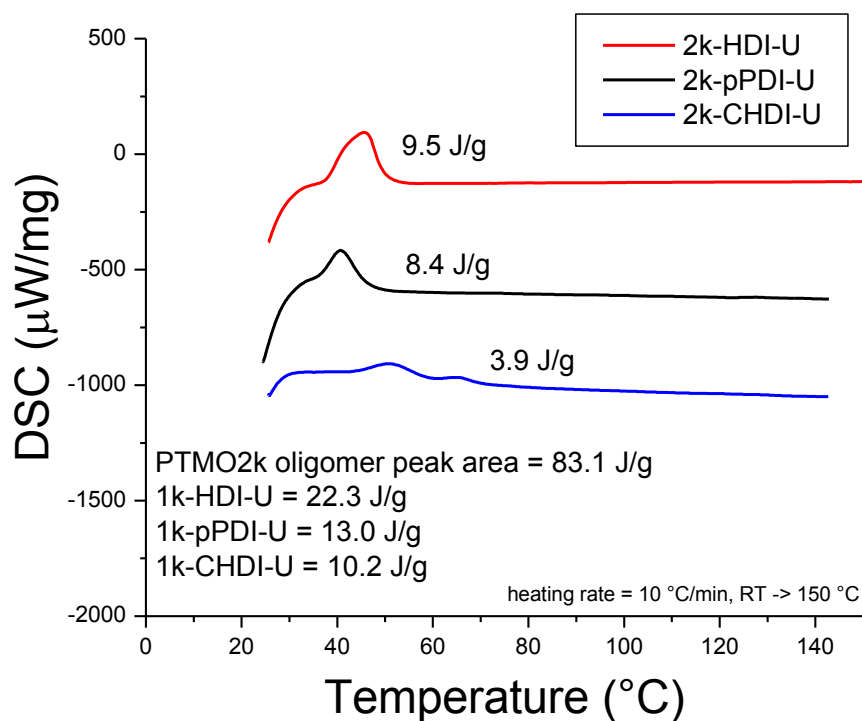


Figure 4.6. Initial DSC heating traces of the 2k-*p*PDI, 2k-HDI, and 2k-CHDI materials beginning at ambient temperature.

The recent DSC results introduced above raise a question concerning the WAXS results. DSC showed each sample to have a HS T_m . Knowing that the HS is crystalline, why then does no diffraction ring appear in the WAXS patterns of the 2k-based materials taken at ambient temperature? This is likely due to the very low crystallinity present. Recall that the HS content is only *ca.* 7% in these materials and that all of the HS is not likely crystalline. Hence, the crystallinity of the sample as a whole is less than even 7% and at such low levels, the photographic flat-plate WAXS technique certainly cannot determine crystallinity as accurately as a directly measured diffracted intensity scan.

The DMA results show that upon further heating of the materials beyond the 0 $^{\circ}\text{C}$ transitions, the samples encountered the softening point of the hard microphase and consequently E' decreased again. As has been determined using the DSC and WAXS results, the softening is due to a HS melting transition (T_m). Reflecting on the region of the E' curves between the SS T_g and the upper temperature HS T_m , some traces are relatively flat and temperature insensitive,

though too narrow to make the materials attractive for engineering use. The higher volume fraction of hard phase in the 1k-based material makes it more likely that distinct hard domains encounter one another and lead to a more interconnected structure. This observation holds true for all of the materials in the study shown in Figure 4.1A–C. In each case the 1k-based material has an equal or higher upper temperature softening point than its 2k-based counterpart which indicates that the 1k-based materials are likely more percolated.

Based on the preceding arguments for the presence of a microphase-separated structure [124], we expect to see *visual* evidence of that structure with AFM. However, AFM may not show distinct microphase separation due to the lower HS content in the 2k-based materials. Figure 4.7A–C shows the phase images obtained for the three 1k-based materials used in this study. In these AFM micrographs, light portions of the images correspond to harder regions of the film whereas darker portions of the images correspond to softer regions. In each of these samples, there is a clear microphase-separated structure. This confirms the hypotheses concerning the materials' morphologies developed during the examination of the DMA results.

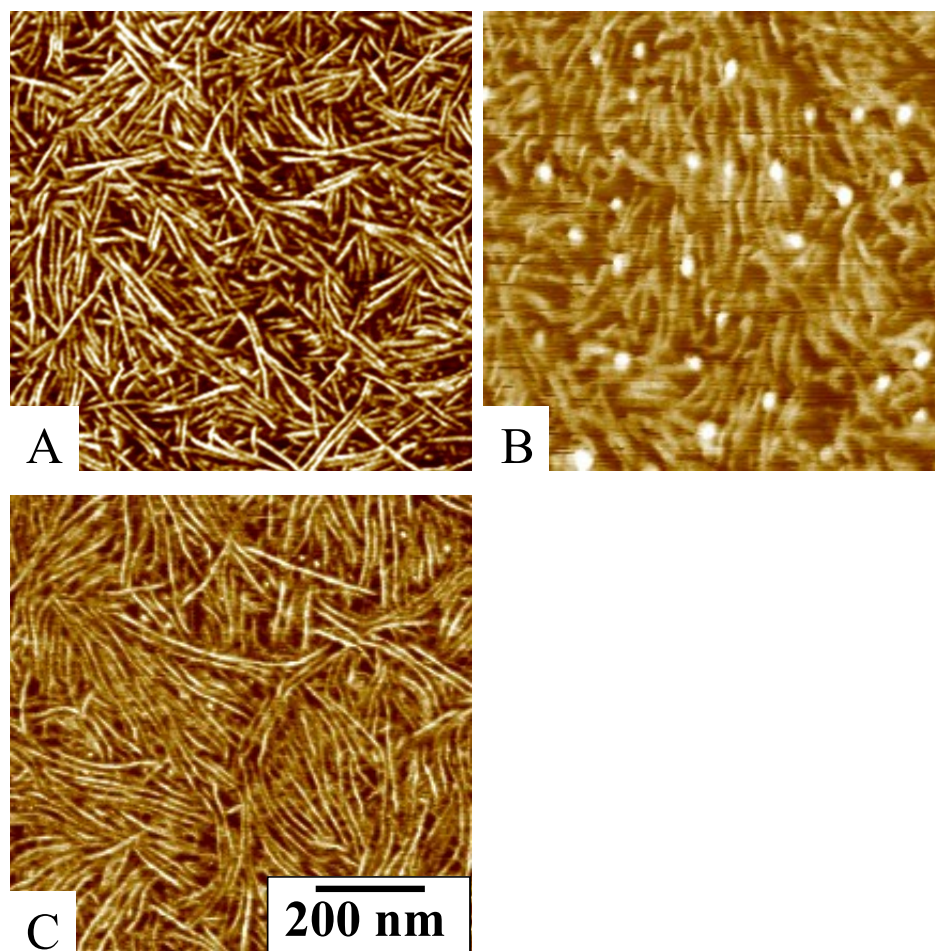


Figure 4.7. AFM phase images of PTMO1k based materials: A) 1k-*p*PDI; B) 1k-HDI; C) 1k-CHDI.

The AFM phase images show that the hard phase is assembled into long threads in the 1k-*p*PDI, 1k-HDI, and 1k-CHDI materials. The threads of the 1k-HDI sample are not as sharp as those of the 1k-*p*PDI and 1k-CHDI materials because the images were obtained at ambient temperature, very near the upper service temperature for the 1k-HDI material. Therefore the poor contrast between the soft and hard phases in this image may be a result of a softening of the hard phase and/or the result of greater phase mixing at a temperature closer to the materials' T_m , either of which would also lead to a decrease in stiffness. Nonetheless, the threads of 1k-*p*PDI, 1k-HDI, and 1k-CHDI appear to be well percolated throughout the material as different portions of the samples show similar structure to the images presented. Individual threads do not appear to be interconnected but are interwoven, accounting for the high modulus of the materials at elevated temperatures mentioned during the discussion of the DMA results. The average

spacings between these threads were determined by SAXS scans that will be introduced after a brief discussion of the 2k-based materials' AFM images.

Due to the lower HS contents (7%) compared to that of the 1k-based materials (14%), the DMA results for 2k-*p*PDI and 2k-HDI, suggest that those two materials were not likely to show high-contrast phase images with the AFM. The technique was performed on each of the three 2k-based materials and phase images were obtained. Recall from Figure 4.1A and Figure 4.1B that like the 1k-HDI sample, the upper temperature softening in 2k-*p*PDI and 2k-HDI occurs at approximately ambient temperature. This is the temperature at which the AFM images were obtained. Hence, softening of the hard phase in addition to possible mixing of previously separated microphases has likely occurred, causing a reduction in the stiffness contrast between the hard and soft microphases. Indeed, the 2k-*p*PDI and 2k-HDI did not show any visual signs of microphase separation with the AFM. While not addressed here, the 2k-*p*PDI and 2k-HDI urea analogs to these two materials, did produce microphase separated structures that were verified with AFM [126]. The image of the 2k-CHDI film shown in Figure 4.8 is the only high-contrast image obtained on any of the 2k-based systems. With only 7% HS content, the 2k-CHDI image did show some contrast between the hard and soft phases, though not to the degree of its corresponding 1k system. Not surprisingly, it also lacked the high degree of percolation of the 1k-CHDI material. Contrast the 1k-CHDI and 2k-CHDI images of Figure 4.7C and Figure 4.8. The difference between them is informative in light of the DMA results. The DMA traces in Figure 4.1C implied that the 1k-CHDI material has both a higher HS content and a higher level of hard phase percolation for reasons mentioned previously. Looking ahead, a well-percolated thread-like structure that displays high E' plateau values is likely to prove to be a stiff and tough material during mechanical testing. These two AFM images support this as the threads in the 2k-CHDI image are fewer in number do not display the same level of connection as the 1k-CHDI sample.

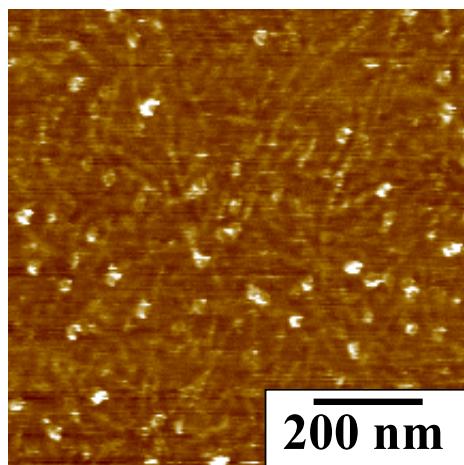


Figure 4.8. AFM phase image of the 2k-CHDI sample.

As mentioned previously, the SAXS method allowed for the calculation of the average spacing between HS regions. Figure 4.9 shows these ambient temperature SAXS scans on each of the six films. To prevent confusion, it should be noted that the two graphs have different scales on their abscissa. Each of the 1k-based samples (Figure 4.9A) displays a first order interference peak, further confirming the microphase-separated structure, ranging from 112–189 Å. Figure 4.9B shows the results for the 2k-based systems and again, the 2k-*p*PDI stands out. This sample does not show a distinct peak at ambient temperature. However, a peak may occur at angles below the detection limits of the camera. The 2k-HDI and 2k-CHDI samples exhibit first order interference peaks at 201 Å and 113 Å respectively. Table 4.4 presents the measured peaks for each of the six samples. While it might be expected that 2k-based polyurethanes would display larger spacings than the 1k-based materials because of the longer SS used, in the cases where interference peaks did occur the differences in peak locations were negligible.

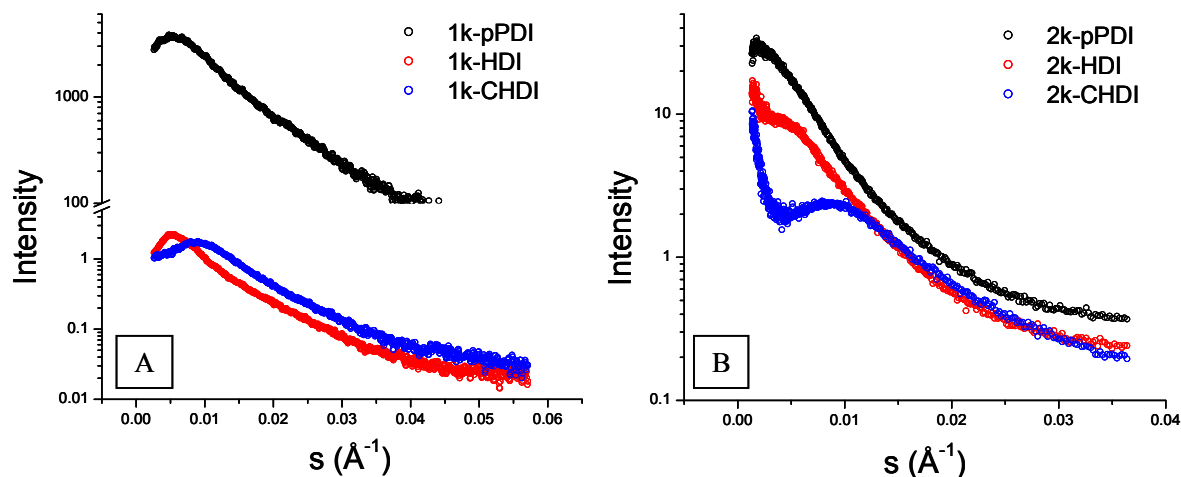


Figure 4.9. SAXS first order interference peaks: A) PTMO1k-based polyurethanes; B) PTMO2k-based polyurethanes. Note the different scales on the abscissas.

Table 4.4. SAXS spacings derived from first order interference peaks for the PTMO1k and PTMO2k based polyurethanes.

Sample designation	SAXS peak (Å)
1k- <i>p</i> PDI	185
2k- <i>p</i> PDI	none
1k-HDI	189
2k-HDI	201
1k-CHDI	112
2k-CHDI	113

The microphase separation documented thus far undoubtedly should have a large impact on the mechanical properties of these materials. As stated earlier, without microphase separation, these materials would have very poor mechanical properties at ambient temperature, specifically with regard to stiffness. Evidence of poor mechanical properties such as low E' values would likely have been measured with DMA. In addition, the crystalline hard phase of the 1k-based materials should also have added stiffness to the films. Figure 4.10 shows representative stress-strain curves for the polyurethanes and Table 4.5 provides a list of pertinent data. The 1k-*p*PDI and 1k-HDI samples (Figure 4.10A) necked upon drawing, an indication that the well-percolated HS microphase-separated structure (the thread-like structure observed with AFM) was being disrupted. The samples then continued to elongate and each material attained an average breaking strains in excess of 900%.

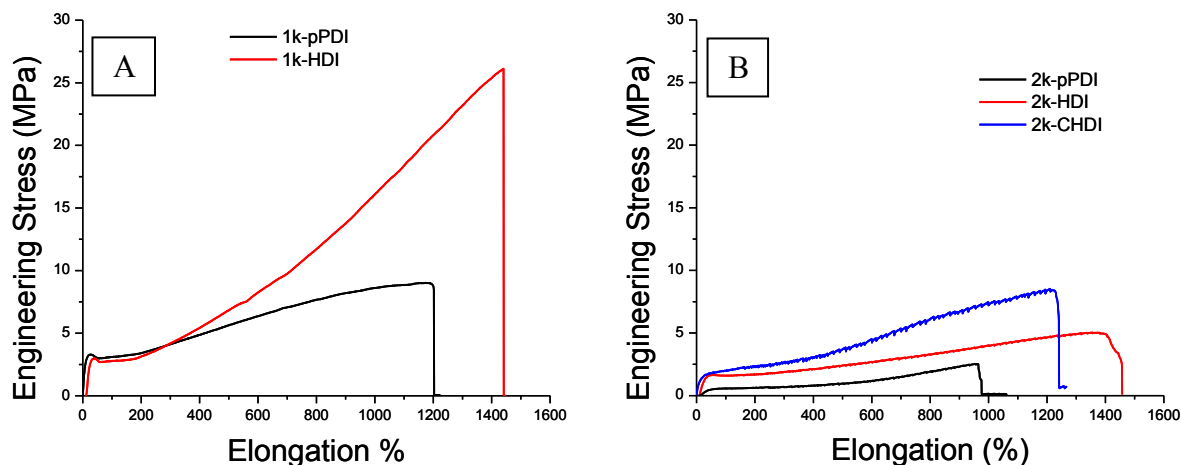


Figure 4.10. Representative stress-strain results: A) PTMO1k-based materials; B) PTMO2k-based materials. 1k-CHDI is not included due to sample limitations.

The 2k-based materials are shown in Figure 4.10B. None of these lower HS content materials necked as the 1k-based materials did, though the 2k-HDI samples did show a slight yield point. This difference in behavior between 1k- and 2k-based segmented polyurethanes is in strong agreement with an earlier study conducted from this laboratory on their polyurea analogs [126]. If necking of the 1k-materials was a result of the breaking up of the percolated HS structure, then the lack of necking in the 2k-materials agrees in part with the AFM results. Recall that the 2k-*p*PDI, 2k-HDI, and 2k-CHDI did not show the high level of interconnectedness among the thread-like microphase-separated structure that the 1k-based materials did. The lack of interconnectedness of hard microdomains results in the absence of a distinct yield point in the tensile curves. The lack of SS crystallinity at ambient temperatures in the 2k-based materials, in conjunction with their lower HS contents, resulted in much lower tensile strengths for these samples. The differences in the elongation at break of the 1k-*p*PDI and 2k-*p*PDI samples were negligible.

Table 4.5. Stress-strain data for the 1k- and 2k-SS based single segment polyurethanes.

Sample designation	UTS (MPa)	Elongation at break (%)	Comments
1k- <i>p</i> PDI	8.4 ± 1.2	940 ± 240	necking
2k- <i>p</i> PDI	2.5 ± 0.1	980 ± 80	no necking
1k-HDI	22.8 ± 3.5	1380 ± 180	necking
2k-HDI	5.0	140	yield, grip failure
1k-CHDI	N/A	N/A	N/A
2k-CHDI	8.8 ± 0.6	1260 ± 100	Grip slip

4.5. CONCLUSIONS

Novel segmented polyurethane copolymers were synthesized based on 975 and 2040 g/mol PTMO soft segments without the use of chain extenders. Lacking the chain extenders usually found in segmented polyurethane copolymers, the three diisocyanates (*p*PDI, HDI, and CHDI) and the two urethane linkages constituted the entire hard segment of their respective materials. Nevertheless, each combination of SS $\langle M_n \rangle$ and diisocyanate was shown to form at least a partially microphase-separated structure with a relatively flat service window between the lower and the upper temperature limits of the storage modulus plateau.

The materials based on PTMO1k were composed of an amorphous soft microphase with a SS T_g and crystalline hard microphase and corresponding T_m . In each film, clear visual evidence of a thread-like microphase-separated structure was imaged with AFM. The hard microphase was shown to be semicrystalline with by DSC and WAXS. In all cases, the PTMO2k-based materials resulted in lower HS content polyurethanes than the PTMO1k-based materials. The 2k-based materials still displayed some signs of a partially microphase-separated structure. The hard microdomains of the solvent cast films showed no signs of HS crystallinity with WAXS though DSC results indicated that low levels of crystallinity did in fact exist. The contradictory results are likely due to the inability of the photographic flat-plate WAXS technique to directly detect low levels of crystallinity that a diffracted intensity scan could. The lower hard segment content (and volume) of the 2k-based samples reduced the storage moduli; reduced the size, and level of interconnectedness of the percolated hard phase; softened the materials at ambient temperatures; and limited the hard phase from crystallizing—an event that

could have increased the mechanical properties of the materials. Conversely, the 1k-based materials, with their higher HS contents and low levels of crystalline hard phase helped to increase mechanical properties over a wide temperature range. The higher HS content also increased the width of the thread-like structure and its interconnectedness leading to stronger films with higher possible upper use temperatures.

5. THE EFFECT OF VARYING SOFT AND HARD SEGMENT LENGTH ON THE STRUCTURE–PROPERTY RELATIONSHIPS OF SEGMENTED CHAIN EXTENDED POLYURETHANES BASED ON PTMO SOFT SEGMENT

5.1. INTRODUCTION

Microphase separation generally occurs in segmented polyurethanes due to the thermodynamic incompatibility resulting in the insolubility of the hard segments within the soft segments [3]. Soft segments typically are composed of a relatively long, flexible polyester or polyether diol with a molecular weight of 1000–3000 g/mol. They are termed soft segments in part because they impart softness and flexibility to the material as they are noncrystalline at their use temperatures and of course their T_g 's are below the lower use temperature of the polymer, resulting in a rubbery material. The hard segments are typically formed by the reaction of diisocyanates with diol chain extender (CE) molecules, the most common being 1,4-butanediol. The resulting hard segments serve to increase the stiffness, alter toughness, and affect other mechanical properties of the material. A key characteristic of the HS from an applications standpoint is their polar nature due to the urethane groups they contain. These groups are able to form intra-, or particularly, intermolecular hydrogen bonds with ether or ester soft segments and also with other urethane groups. When bonding with other urethane groups, they can segregate themselves into domains rich in HS. Hence, a microphase separated morphology develops with interdomain spacings on the scale of *ca.* 100 Å. The chemical linkage between the relatively short soft and hard segments of these segmented copolymers prevents phase separation on larger length scales that can often occur in traditional block copolymers which possess block molecular weights that typically far exceed those for segmented polyurethanes. It should be noted that microphase separation due to incompatibility of hard and soft segments is not the only cause that could lead to separation. Crystallization of the hard or soft blocks (at low temperature) can also be a driving force for microphase separation.

The topics of morphology and structural rearrangement of segmented copolymers have long been areas of active research interest. Much of the current work in this field was first grounded in work done by Schollenberger et al. [22, 23] on poly(ester–urethane elastomers)

which introduced the concept of virtual crosslinks in the 1950s. Low levels of HS content often produce either 1) mixed systems (since in typical systems, microphase separation is a function of HS–SS incompatibility due in part to HS segment length) and/or 2) microphase separated structures which contain HS domains that are dispersed throughout a SS matrix with little interaction. The poor domain structure that results in such cases leads to soft materials with poor modulus and poor recoverability. As the HS content is increased by lengthening the HS (generally by addition of chain extender and additional diisocyanate), a better microphase separated morphology can develop. With higher HS content, the long range connectivity of the HS also increases and finally at HS contents in the range of 30 wt%, an interconnected hard phase often results. The percolated structure increases both the stiffness and to a degree the toughness of the polyurethane that makes them interesting from an engineering perspective, although such interconnected structures begin to limit high recoverability following elongation. In addition, if the hard phase is truly interconnected, this will also generally introduce a yield point during tensile testing that results from the breakup of that structure.

The preceding chapters in this dissertation has addressed the structure-property behavior of segmented polyurethane and polyurea materials synthesized without the use of CE molecules typically found in the field of commercial TPUs [87, 124, 126, 127]. Those earlier studies investigated the effect of changes in diisocyanate chemistry and its symmetry on the structure–property behavior of both polyurethanes and polyureas where the hard segment was composed of a single diisocyanate molecule (no CEs were used). In contrast, this chapter will detail the synthesis and characterization of polyurethanes incorporating the linear and symmetric diisocyanate, *p*PDI, that *did* incorporate the more traditional chain extender during synthesis, specifically the conventional CE butane diol (BD). The objective was to determine if the addition of this common chain extender would significantly alter the very pronounced microphase separated structure seen earlier in the single segment (non-chain extended) materials, and to determine what effect traditional CE molecules had on the thermal and mechanical properties of the system.

For the current study, polyurethane samples were also produced so as to investigate the effect of an increased SS and HS content on a material’s morphology and structure–property characteristics as well as the now familiar issues of the effects of chain extenders and diisocyanate symmetry. Hence, samples containing identical MW SS (PTMO) and diisocyanate

(*p*PDI) were reacted with CE molecules (BD) of differing $\langle M_n \rangle$ to produce samples with either 14 and 20 wt% HS content. The single segment materials discussed in our earlier work rarely contained HS contents above 14 wt% [87, 124]. This allowed for the determination of how such changes affect the structure–property relationships of these materials.

Much of the work discussed here was initiated due to two studies in particular. The initial motivation was found in the work of Barikani and Hepburn published in 1987. Their early work was concerned with the effect of various diisocyanate chemical structures on the softening temperature of a series of BD chain extended polyurethanes. This softening point was determined by a marked decrease in storage modulus, E' , as measured by dynamic mechanical analysis [73, 128, 129]. The materials used in those studies were synthesized using the “prepolymer method” in which a polyester SS of polycaprolactone diol (CAPA 225) (MW=2000 g/mol) was first reacted with an excess of the selected diisocyanate. The series of diisocyanates used by these earlier researchers incorporated: *p*PDI, MDI (4,4'), CHDI (*trans*-1,4), HMDI, and TDI (an 80/20 mix of 2,4 and 2,6 isomer). The prepolymer was then reacted with the BD chain extender to form the final polyurethane samples. Of particular interest to this report was the material they synthesized using CAPA 225, *p*PDI, and BD as the SS diol, diisocyanate and CE respectively. Their synthesis resulted in a chain extended polyurethane sample with a 2000 g/mol SS and only *ca.* 20 wt% HS. The subsequent analysis of the elastomeric material showed a relatively flat, temperature insensitive E' plateau with a magnitude in excess of 10^7 Pa at ambient temperature. The temperature at which *the value of E' for each material distinctly changed was the key point for Barikani and Hepburn, not the actual value of E' .* The materials were noted to have displayed good thermal stability to temperatures around 155 °C [73].

The intriguing mechanical properties of the CAPA 225/*p*PDI/BD material having a HS content of *ca.* 20% and a SS/diisocyanate/CE ratio of 1/2.6/1 spurred interest in using a different SS diol, in this case the commonly utilized polyether SS PTMO, in an attempt to achieve similar or better results. Looking at Figure 5.1 (adapted from the original [73]) there is a distinct difference in modulus throughout the temperature insensitive plateau among the materials produced using the linear symmetric (CHDI and *p*PDI) relative to the less symmetric or asymmetric (MDI, HMDI, and TDI) diisocyanates. *This discrepancy in storage moduli and the effect of diisocyanate symmetry was not discussed by the original researchers.* This omission

spurred the second study that motivated this current work. An investigation of segmented polyurethane and polyurea samples *without the use of chain extender molecules was then carried out in our laboratory to try to isolate the effects of diisocyanate chemistry and its symmetry on the structure–property relationships in these materials* [124, 126]. That work demonstrated that the diisocyanate symmetry played a major role in the microphase separation behavior of these materials. That is, when comparing segmented polyurethanes as well as segmented polyureas based on symmetric diisocyanates with those constructed from less symmetric, or kinked diisocyanates, those containing highly symmetric diisocyanates showed distinctly better microphase separation, displayed higher moduli, and could display particularly broader temperature insensitive E' plateaus. In addition, the contrast of monodentate versus bidentate hydrogen bonding (found in polyurethanes and polyureas respectively) showed that the bidentate bonding scheme produced a distinctly more cohesive hard phase which had the effect of increasing the materials' moduli and broadening their service temperature windows.

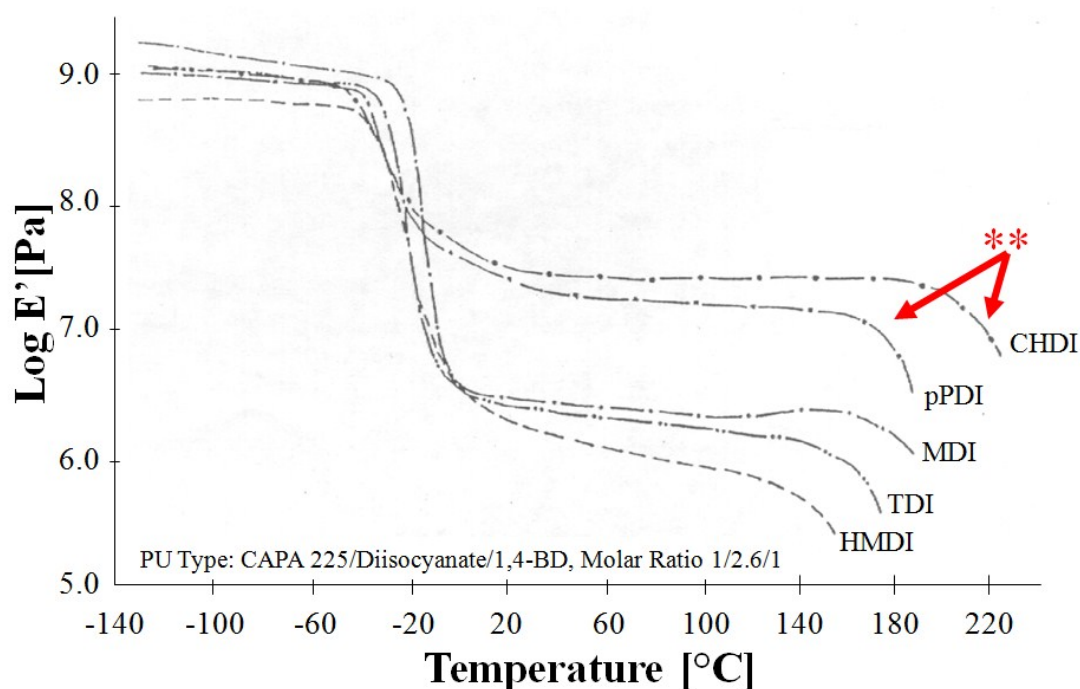


Figure 5.1. DMA results of CAPA 225/Diisocyanate/1,4-BD, Molar Ratio 1/2.6/1 produced by Barikani and Hepburn. Note the starred traces are from materials constructed with symmetric diisocyanates (pPDI and CHDI) whereas the other three traces are from materials constructed with asymmetric diisocyanates (MDI, TDI, HMDI) [73].

5.2. EXPERIMENTAL SETUP

5.2.1. MATERIALS SYNTHESIS

1,4-Phenylene diisocyanate (*p*PDI) and 1,4-butanediol (BD) were purchased from Aldrich. *p*PDI was sublimed at 70°C before use. Poly(tetramethylene oxide)glycol oligomers (PTMO) with number average molecular weights $\langle M_n \rangle$ of 975, 2040, 2900 and 3500 g/mol were kindly provided by DuPont. Reagent grade dimethylformamide (DMF) was purchased from Aldrich and used as received.

5.2.2. POLYMER SYNTHESIS

Polymerization reactions were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. Except for the polyurethane, which was obtained by reacting equimolar amounts of *p*PDI and PTMO1k, all other polyurethanes were synthesized by following a two-step polymerization procedure. In the first step, where prepolymers were prepared, calculated amounts of diisocyanate and PTMO oligomer were introduced into the reactor and slowly heated to 50 °C in the bulk (neat) for 2 hours. Completion of the prepolymer formation was determined by FTIR spectroscopy. Prepolymer was dissolved in DMF to obtain a solution of about 25% solids by weight and heated to 60 °C. A stoichiometric amount of chain extender (BD) was dissolved in DMF (*ca.* 10% solids by weight), introduced into the addition funnel and slowly added into the reactor to promote the chain extension step. Chain extension reactions were also monitored by FTIR spectroscopy following the complete disappearance of the strong isocyanate peak at 2270 cm⁻¹. Usually about 80–85% of the BD chain extender solution was used to complete the reaction. This is expected, due to well-known side reactions taking place during prepolymer formation [130].

5.2.3. PREPARATION OF TEST SPECIMENS

Polymer films with thicknesses of 0.5–1 mm were obtained by pouring the 20% solids solutions into Teflon molds. The molds were kept at room temperature overnight and then placed in an oven maintained at 60 °C. After evaporation of the solvent, the molds were placed in a vacuum oven at 60 °C for complete drying which was monitored gravimetrically. The resulting films were then easily removed from the Teflon molds and stored under vacuum at room temperature until needed for testing. Portions of some of these films were also compression molded (at 200 °C for 5 minutes) in order to access their reprocessability and to compare their solid-state behavior with that of their solution cast analog.

The polyurethane samples prepared are designated using the following nomenclature: PTMO<M_n>–chain extender–HS content. Hence, PTMO2k–BD–14 indicates a material in which PTMO of 2000 g/mol <M_n> was reacted with *p*PDI and BD resulting in a 14 wt% HS material. PTMO3k–BD–14 is the designation of the second 14 wt% HS BD chain extended sample. The chain extended materials with 20 wt% HS, listed in order of increasing SS <M_n>, are denoted as: PTMO1k–BD–20, PTMO2k–BD–20, PTMO2.9k–BD–20, and PTMO3.5k–BD–20. Lastly, one non-chain extended sample, the PTMO1k–*p*PDI–U, discussed in earlier work [124], is also incorporated into this study for comparison with the chain extended materials in this study. That single segment material also contained 14 wt% HS and is therefore useful as a comparative material to those possessing a BD chain extender. *It will be designated PTMO1k–single–14 to remind the reader that it is a single segment system and not chain extended as are the other materials addressed in this study.*

5.3. EXPERIMENTAL TECHNIQUES

5.3.1. ATOMIC FORCE MICROSCOPY (AFM)

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe

tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4 to 0.7, constituting “hard to medium” tapping strengths. Scans were done using a frequency of 1 Hz. All scans were performed on the free air surface of the cast films as opposed to the surface that had been in contact with the Teflon mold during the casting operation.

5.3.2. *DYNAMIC MECHANICAL ANALYSIS (DMA)*

DMA was performed on a Seiko DMS 210 tensile module with an attached auto-cooler for precise temperature control. Rectangular samples measuring 10 mm in length and 4.5–6.5 mm in width were cut from the cast films. Under a dry nitrogen atmosphere, the films were deformed using a frequency of 1 Hz. The temperature was increased from -150 to 300 °C at a rate of 2 °C/min. Soft segment glass transition temperatures reported by the DMA methodology were denoted as the location of the peak in the *tan δ* vs. temperature plots.

5.3.3. *TENSILE TESTING*

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. A bench-top die was used to cut dogbone samples with an overall length of *ca.* 25 mm and the width of the grip section of *ca.* 10 mm. The reduced section measured 2.91 mm × 10 mm (width × gage length). These dogbones were then tested to failure at a crosshead speed of 25 mm/min and their load vs. displacement values recorded. Three samples were measured and their results were averaged to determine modulus, yield strength, and strain-at-break for each type of material.

5.3.4. *WIDE ANGLE X-RAY SCATTERING (WAXS)*

Photographic “flat-plate” WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu-K α radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was set at 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an evacuated sample chamber. X-ray exposures lasted four hours. Sample thickness ranged from 12–14 mils.

5.3.5. *SMALL ANGLE X-RAY SCATTERING (SAXS)*

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu-K α doublet, with an average wavelength of $\lambda = 1.54 \text{ \AA}$. The camera used 200 μm , 100 μm and 300 μm pinholes for collimation of the X-ray beam. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector, located approximately 65 cm from the sample. After azimuthal averaging (though no signs of any azimuthal dependence was observed), the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a 1.07 mm thick type 2 glassy carbon sample, previously calibrated at the Advanced Photon Source at the Argonne National Laboratory, as a secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s , where $s = 2 \sin(\theta)/\lambda$, and 2θ is the radial scattering angle.

5.4. RESULTS AND DISCUSSION

The chain extended polyurethane film samples were first analyzed using DMA. Figure 5.2A–C shows the storage modulus (E') and $\tan \delta$ traces for the three *ca.* 14 wt% samples. Figure 5.2D–G contains the results for all samples containing *ca.* 20 wt% HS materials. Included for the sake of comparison in Figure 5.2A is the PTMO1k–single–14 as it also contains 14 wt% HS but has only a 1k SS. Looking at the data in Figure 5.2, it is clear that at very low temperatures, below *ca.* -80 °C, all seven samples have E' values above 10^9 Pa. As temperature is further increased each sample begins softening at *ca.* -100 °C. This softening transition generates a peak in the $\tan \delta$ curve for each material (due to the T_g of the PTMO soft segment), though not at exactly the same temperature for all samples as shown in Table 5.1.

Table 5.1. Location of T_g as measured by DMA for chain extended polyurethanes based on PTMO SS of varying length.

Material	Location of $\tan \delta$ peak as measured by DMA (T_g)
PTMO1k–single–14	-70 °C
PTMO2k–BD–14	-70 °C
PTMO3k–BD–14	-80 °C
PTMO1k–BD–20	-63 °C
PTMO2k–BD–20	-70 °C
PTMO2.9k–BD–20	-70 °C
PTMO3.5k–BD–20	-80 °C

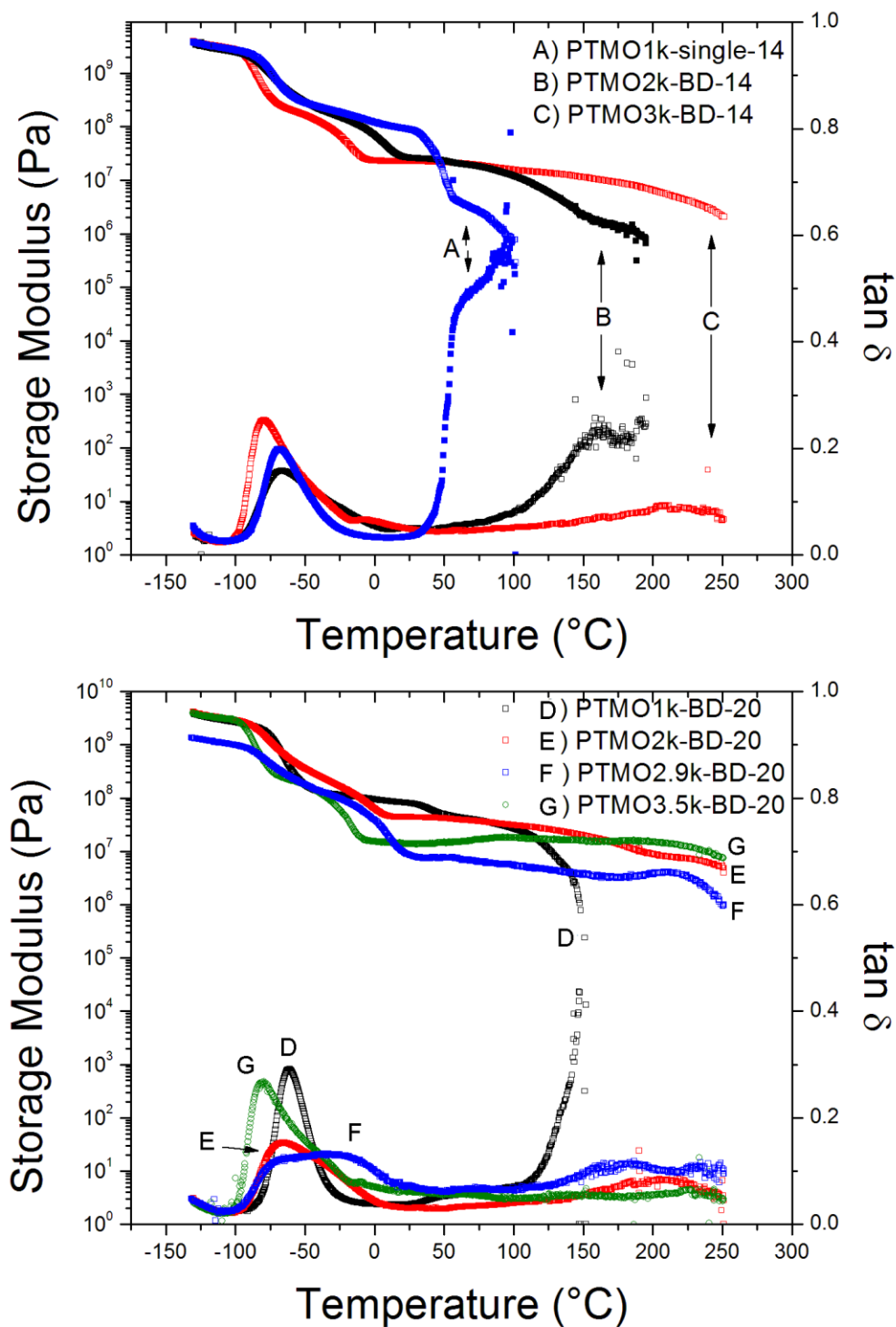


Figure 5.2. Temperature dependent storage modulus and $\tan \delta$ response of polyurethane materials composed of varying PTMO SS molecular weight with: *ca.* 14 wt% HS: A) PTMO1k-single segment material; B) PTMO2k-BD-14 and C) PTMO3k-BD-14, *ca.* 20 wt% HS: E) PTMO1k-BD-20, F) PTMO2k-BD-20, G) PTMO2.9k-BD-20, and H) PTMO3k-BD-20.

As noted within Table 5.1, the lower temperature of the transition in the PTMO3k–BD–14 and PTMO3.5k–BD–20 samples is the first indication that the longer hard and soft segments used in these materials may have increased SS–HS incompatibility, which leads to less interaction between hard and soft domains and fewer restraints placed on hard segments, thereby increasing the level of microphase separation that occurs. Additionally, the longer soft and hard segments reduce the role of chain ends at the SS–HS junction points on the mobility of the middle of the chain.

After passing through this first thermal transition, the value of E' for the PTMO1k–single–14 sample decreases to 8.6×10^8 Pa. As heating continues, the value of E' slowly decreases until the onset of a second softening at *ca.* 30 °C. At this temperature, a larger drop occurs in the value of E' , which corresponds to a rise in the $\tan \delta$ value. Just before reaching this point, the value of E' is almost 8×10^7 Pa. The magnitude of E' between these two softening temperatures strongly indicates that the PTMO1k–single–14 material contains a well microphase-separated structure in which the hard phase has a high level of reinforcement, as will be verified later by AFM. Recall that the 20% HS BDO extended material produced by Barikani and Hepburn showed E' values at ambient temperature of *ca.* 6×10^7 Pa. The PTMO1k–single–14 material displays a stiffness value *in excess of* 10^8 Pa, an E' value higher than the Hepburn material that contained 20% HS. The morphological structure of this PTMO1k–single–14 material was described previously in published work from this lab [124] as well as in chapters 2 and 3 of this dissertation. Evidence of that structure will be presented in the subsequent discussion of AFM results. As the structure shows distinct microphase separation, the two thermal transitions described thus far are clearly believed to be the SS T_g at the lower temperature and a HS T_m at the higher temperature respectively. In brief, these assignments were made after analyzing DSC and WAXS data.

The DMA results and structure-property relationships of the BD chain extended materials are more complicated than those of the single segment material. Between what appears to be the SS T_g and HS T_m in these materials, there occurs another thermal transition; one resulting in a further decrease in E' . The origin of this drop is the melting of the higher molecular weight (above 1000 g/mol) SS crystalline PTMO. As was detailed in chapter 4 which focused on the PTMO2k-based single segment materials, increasing the SS $\langle M_n \rangle$ to 2040 g/mol provided the opportunity for the PTMO SS to display some crystallization at lower temperatures. This appears

to occur as well in the case of both PTMO2k-BD-14 and PTMO2k-BD-20. As would be expected, it also appears to hold true for further increases in SS $\langle M_n \rangle$ beyond 2000 g/mol, as would be expected. Such is the case for the PTMO3k-BD-14, PTMO2.9k-BD-20 and PTMO3.5k-BD-20 materials. Just as the PTMO2k-*p*PDI single segment cited in previous work [126] underwent a SS T_m at *ca.* 0 °C, the current PTMO2k-BD-14 and PTMO2k-BD-20 chain extended samples also experience a SS T_m at about this same temperature. This is an expected result as the CE used in the current materials should not eliminate partial crystallization behavior of the longer PTMO soft segments. With the exception of the 1k-based materials, the shapes of the $\tan \delta$ traces for materials possessing some low temperature crystalline PTMO are different from those seen in earlier work [124, 126]. In observing all the $\tan \delta$ curves of a series of polyurethanes with non-crystalline PTMO1k, each showed a symmetric peak at the SS T_g [124]. In the present case of the 2k and higher SS $\langle M_n \rangle$ samples, the $\tan \delta$ peaks are asymmetric and are skewed with a tail at higher temperatures. This is believed to occur due to near overlap of the SS melting transition temperature and the SS glass transition temperature (as both have broad temperature ranges) an observation supported by looking at the E' curve. This was also witnessed in the 2k-based single segment materials that crystallized [126]. (Recall the DMA results in Figure 4.1 in the previous chapter).

As the chain extended polyurethanes were heated beyond 25 °C, the effects of longer soft and hard segments also become more apparent. As noted earlier, the longer soft and hard segment containing systems are expected to lead to greater incompatibility of the SS with HS, due in part to the introduction of additional polar urethane groups and the increased molecular weight of both segments—the latter which should somewhat increase the χ parameter which is a measure of HS-SS incompatibility. The enhanced SS-HS incompatibility should promote a more complete microphase separation or less microphase mixing, one consequence of which is the reduction of HS content in the SS matrix. Materials with longer SSs and HSs that display a microphase separated structure maintain a more constant E' value at temperatures below the HS T_m . Hence, beyond the SS T_m , the three 14 wt% HS materials of Figure 5.2A-C show a general pattern of higher E' with higher SS $\langle M_n \rangle$. The 20 wt% HS materials in Figure 5.2D-G however, do not show this behavior as a consistent pattern. Specifically, while the increase in SS and HS $\langle M_n \rangle$ from PTMO1k-BD-20 to PTMO2k-BD-20 and from PTMO2.9k-BD-20 to PTMO3.5k-BD-20 each show the expected trends, the increase from PTMO2k-BD-20 to PTMO2.9k-BD-

20 materials do not. Explanation of the discontinuities in the trend is one example of the difficulties in isolating the effects of the longer SS, longer HS and the resulting changes in segment incompatibility in these materials. It should also be noted that across the entire temperature range of the DMA test, the PTMO2.9k-BD-20 sample exhibited a lower E' value than the other samples, even below -80 °C. The origin of this behavior is not fully understood at this time.

As stated above, AFM was used as a means of obtaining direct visual evidence of the proposed microphase separated structure. Figure 5.3 shows phase images obtained of the air surfaces of the 14 wt% and 20 wt% HS solution cast materials.

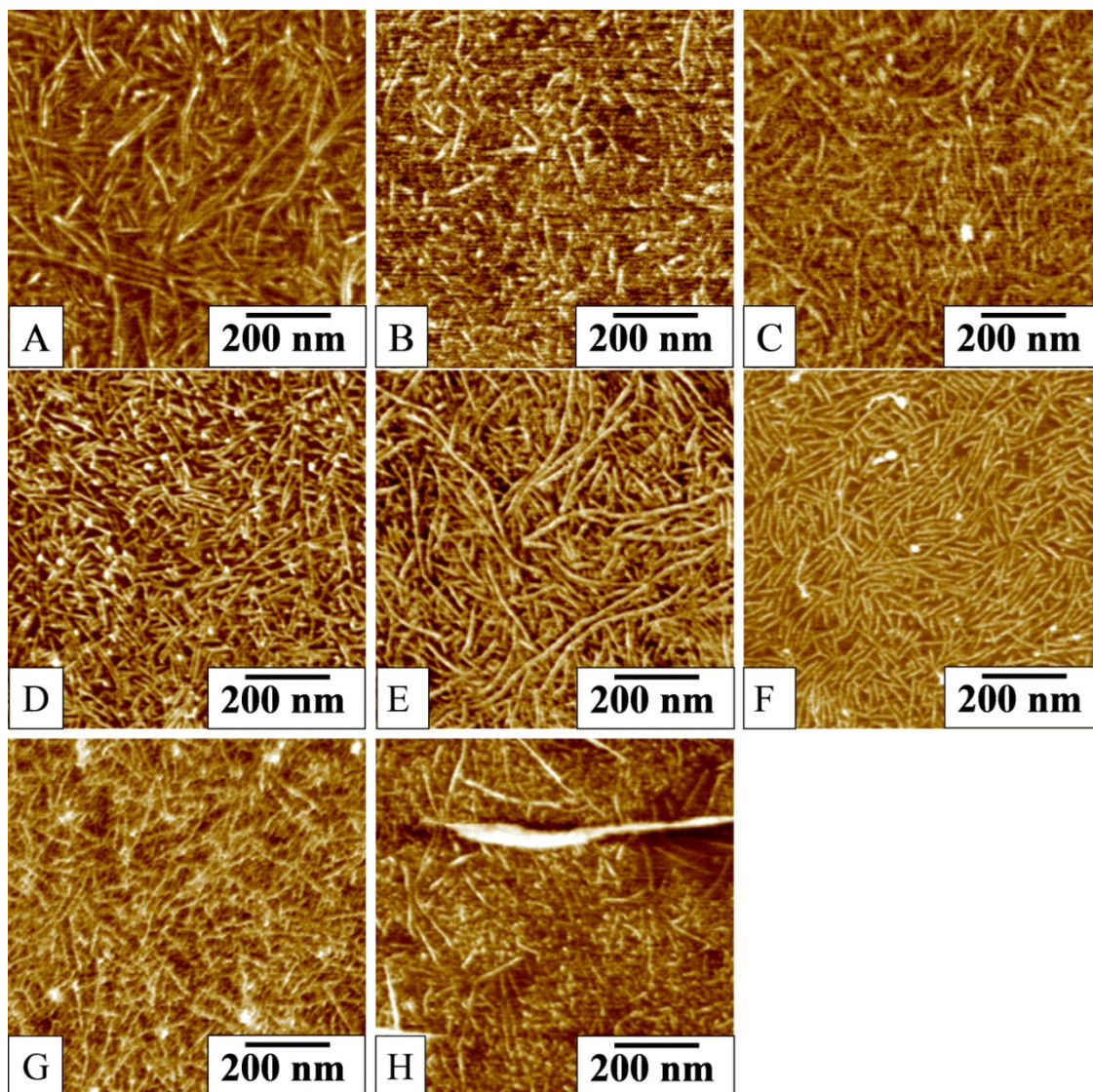


Figure 5.3. AFM phase images of polyurethane materials containing 14 wt% HS: A) PTMO1k–single–14 segment material; B) PTMO2k–BD–14; C) PTMO3k–BD–14, and 20 wt% HS: D) PTMO1k–BD–20; E) PTMO2k–BD–20; F) PTMO2k–BD–20 film remolded in a press at 200 °C for 5 minutes; G) PTMO2.9k–BD–20; H) PTMO3.5k–BD–20.

These images show a distinct phase separation between the lighter-colored phase (and therefore harder) thread-like HS rich regions and the surrounding softer matrix for each of the six BD-extended polyurethane materials used in this study. The reader should be reminded that the AFM is measuring the hardness of not just the surface of the materials, but also the hardness of the material somewhat below the surface; this results in the appearance that there is a higher content of HS in the material in the AFM scan than is truly present. Not only is the thread-like nature of the hard phase evident in each material, it is also clear that the thread-like structure

spans the entire material surface and individual threads are interwoven throughout the entire film. One might question whether these samples can be melted and molded at elevated temperature. Special note should be made of Figure 5.3F which shows the phase image of a molded material formed by pressing portions of the solvent cast PTMO2k-BD-20 material at 200 °C. The material used for high-temperature compression molding was obtained by cutting up unused pieces of the original film. It should be noted, however, that at 200 °C, this sample may not have completely melted. Specifically, recalling Figure 5.2F, at this temperature the material is not above its final melting temperature. However, enough softening did occur at 200 °C so that the cut up film was able to be compression molded into a uniform film. It is clear from the image that the microphase-separated structure is maintained after the molding experiment. It is now certain that the thread-like structure can be obtained via solvent casting or retained during compression molding of these same materials.

As mentioned earlier, the incorporation of the BD chain extender increases the average length of the HS and therefore increases the HS content of the respective materials. When AFM images are obtained from samples with identical HS contents but increasing SS and HS lengths, some trends might be expected in the progression of AFM images. For example, materials with similar HS content but increased SS and HS $\langle M_n \rangle$ should in principle show an increased thickness in thread width. For example, as the PTMO1k-single-14, PTMO2k-BD-14 and PTMO3k-BD-14 images are obtained, the thread thicknesses might be expected to increase proportionately. However, Figure 5.3 does not easily support this comparison. In fact, the thread thickness appears to decrease when comparing the PTMO1k-single-14 to the PTMO2k-BD-14 sample. It does however appear to increase when the PTMO3k-BD-14 sample is imaged. This is another example of the difficulties encountered when trying to deconvolute the effects of multiple variables including increased SS $\langle M_n \rangle$, HS $\langle M_n \rangle$ and increased SS-HS incompatibility. In the 20 wt% HS content materials (Figure 5.3D-H) the observed thread thicknesses do not follow a logical progression either, though this may be due to AFM effects. Apparent thread thickness can also be affected by the tapping strength used when imaging these materials with higher spring constants producing images with increased contrast between soft and hard areas of the film. This also has the effect of increasing the apparent thickness of the threadlike structure. In addition, the portion of the soft segment close to the SS-HS junction point is also restricted in its mobility due to being covalently bonded to the HS. While this portion of the chain is strictly

speaking still part of the soft phase, it may appear “harder” than the bulk soft phase due to these restrictions and therefore measure as stiffer in the AFM image and therefore broaden the width of the hard segment threads.

The general length scale of the microphase separation and inter-thread distance, now seen directly with AFM, can be estimated by the use of SAXS. The results of SAXS scans on each of the 14 wt% materials are shown in Figure 5.4A and those of the 20 wt% materials are shown in Figure 5.4B.

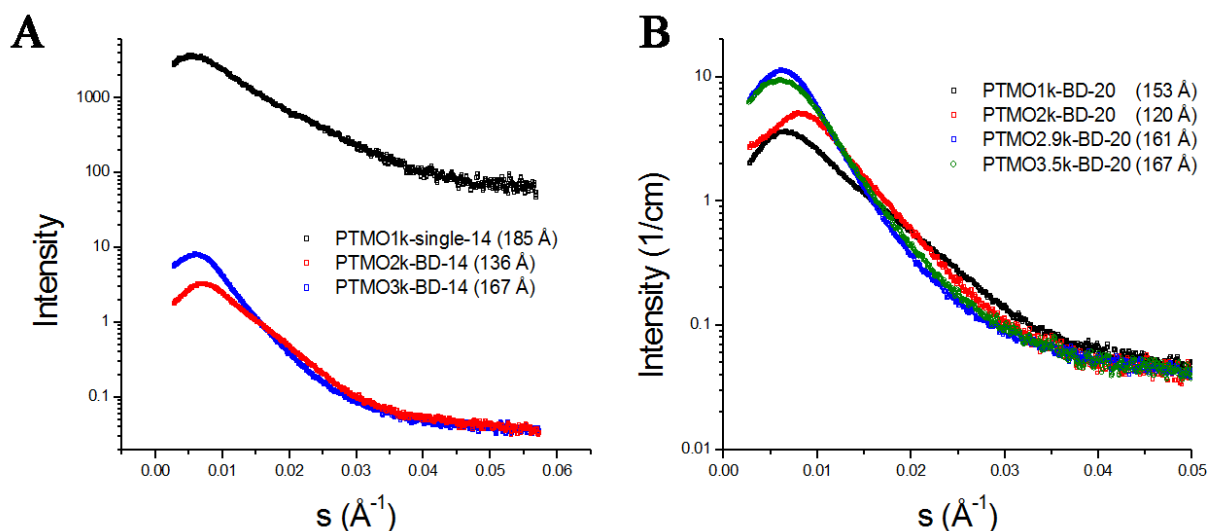


Figure 5.4. SAXS first order interference peaks of PTMO SS, BD chain extended polyurethane materials: A) Samples containing 14 wt% HS; B) Samples containing 20 wt% HS.

The SAXS results provide clear support for the conclusion that a microphase separated morphology exists. Each of the six chain extended samples displays a peak in scattered intensity indicating the presence of microphase separation, in this case, an average inter-thread distance; however, it is clearly not possible to directly couple the location of the spacing associated with each peak with the respective MW and HS content changes among these samples.

The hard microphase shown in the AFM (Figure 5.3) and some quantification of the length scale of the microphase separation has been made via SAXS (Figure 5.4). To better understand if there is order in the hard microphases, WAXS data was obtained at ambient temperature. Figure 5.5 shows the WAXS patterns of the 14 wt% and 20 wt% materials. The shapes of the DMA traces of these materials (Figure 5.2) showed that PTMO1k–single–14 and

PTMO1k–BD–20 materials lacked a PTMO1k SS melting transition as the SS did not crystallize. They both showed a higher temperature softening transition which, based on WAXS results, can be attributed to the melting or disordering of the hard microphase. Upon direct observation of photographic patterns, a single distinct ring (though not of high intensity) within the inner region of the amorphous halo appears is noted for each of these samples. The relatively faint nature of this ring is not surprising given that the materials contain only 14 or 20% hard segment. Even if the hard phase was fully crystalline, which is unlikely, only 14 or 20% of the total material would be available to scatter x-rays, causing a less distinct diffraction ring than would occur with a highly crystalline sample. The observance of only a single ring also suggests but does not confirm that the order in the sample is one-dimensional. This result is in agreement with a first principles molecular simulation based on density functional theory detailed previously [122]. The results of that simulation apply equally well here, as a one dimensional stacking of hard segments is expected due to monodentate hydrogen bonding between urethane groups. The remaining higher SS $\langle M_n \rangle$ samples were shown via DMA to contain PTMO crystals that melt by the time they reach ambient temperature. Therefore, any ambient temperature diffraction from these materials must be attributed to the crystalline structure of the hard phase. Indeed, each of the materials containing longer soft and hard segments showed a weak but recognizable diffraction ring indicating that the hard phases of the microphase-separated structure is semicrystalline.

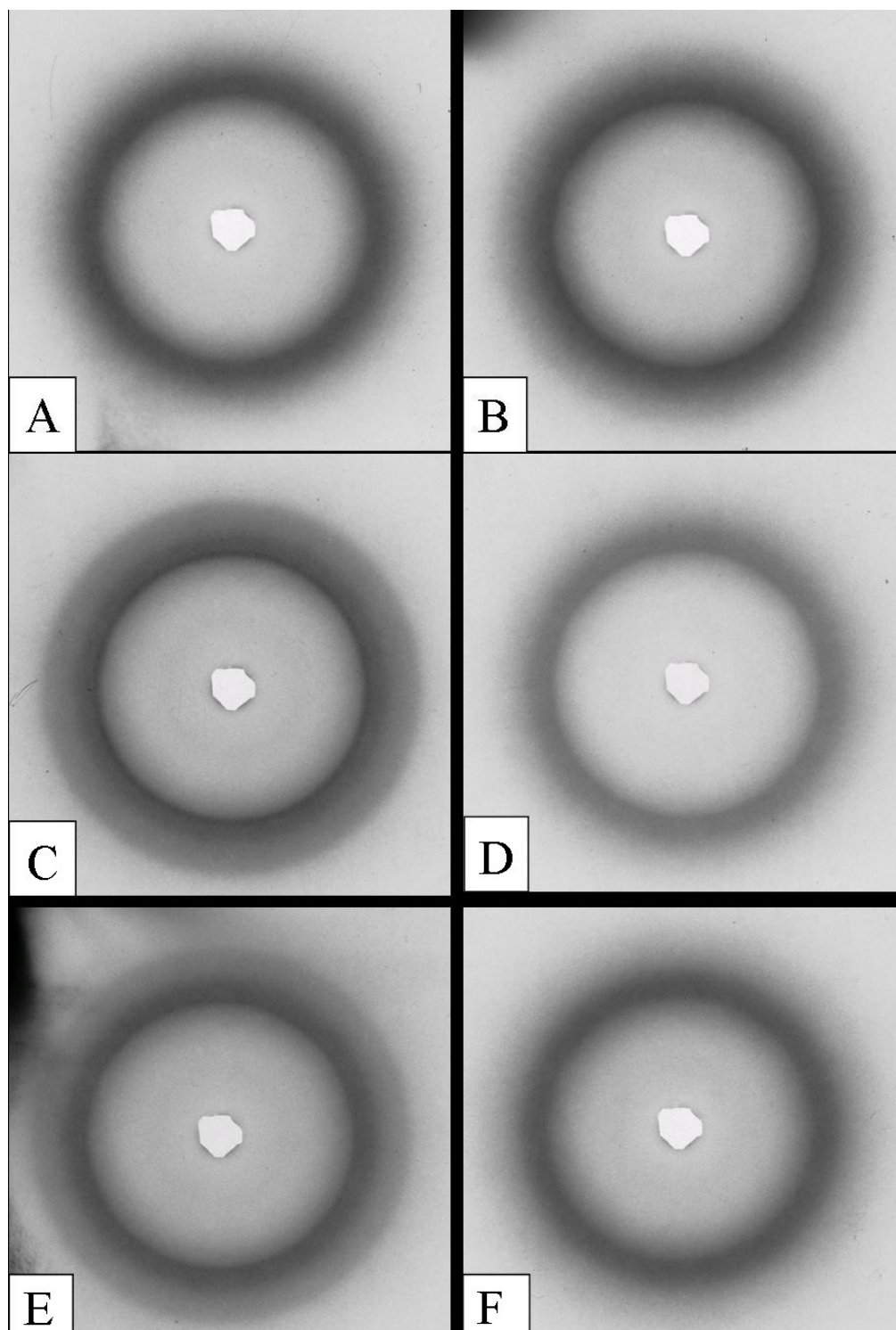


Figure 5.5. WAXS diffraction patterns for PTMO SS, BD chain extended polyurethane samples with 14 wt% HS content: A) PTMO2k-BD-14; B) PTMO3k-BD-14, and 20 wt% HS content: C) PTMO1k-BD-20; D) PTMO2k-BD-20; E) PTMO2.9k-BD-20; F) PTMO3.5k-BD-20.

Lastly, selected mechanical properties of the chain extended materials were determined using uniaxial tensile measurements. Table 5.2 provides the pertinent modulus, tensile strength and elongation at break data. Representative stress-strain curves of each of the 14 wt% materials and 20 wt% materials are presented in Figure 5.6A and Figure 5.6B respectively. A full discussion of the tensile properties of the PTMO1k–single–14 material can be found in chapters 2 and 3 and in the literature [124, 126]. Comparing the PTMO2k–BD–14 and PTMO3k–BD–14 samples, there is a large difference in properties. The change to longer hard and soft segments leads to a severe reduction in both tensile strength (from 16 to 9 MPa) and elongation at break (from 1450 to 890%). In contrast to these observations, Singh has reported melt-processed PTMG2k–*p*PDI–BD samples with tensile strengths of *ca.* 35 MPa and elongation at breaks of *ca.* 600% [131]. The most significant change seen in our tensile data due to the longer soft and hard segment lengths is witnessed in the material’s ability to recover after deformation. This indicates that strain induced crystallization of the SS may well be occurring in some of these samples (PTMO3k–BD–14 and PTMO3.5k–BD–20) although one might expect more of a distinct upturn in the tensile curves at *ca.* 400% elongation.

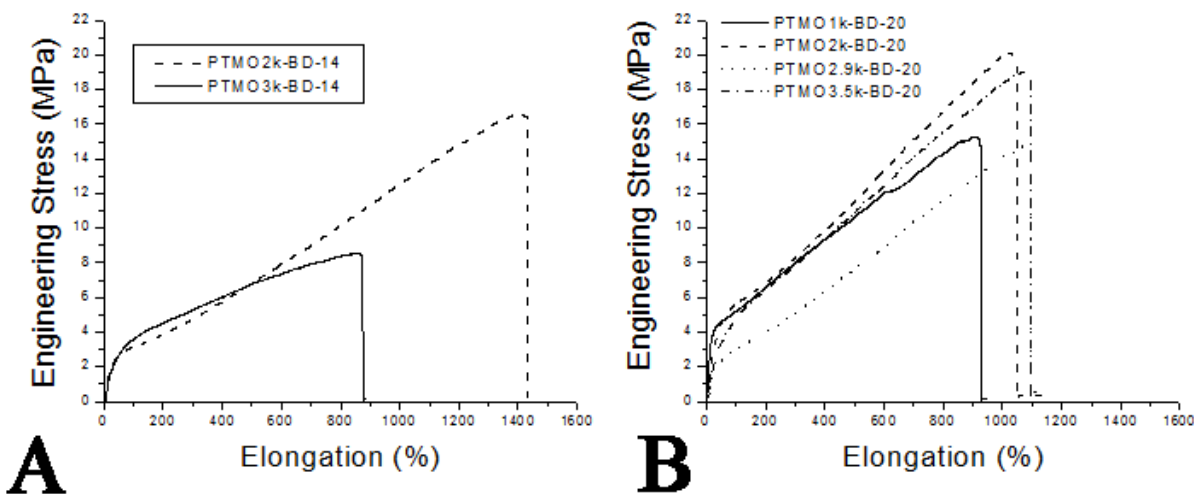


Figure 5.6. Representative stress-strain tensile deformation curves for PTMO SS, BD chain extended polyurethane samples with: A) 14 wt% HS; B) 20 wt% HS.

Table 5.2. Ambient temperature mechanical property data from 14% and 20% HS chain extended samples.

Sample	Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Comments / Observations
PTMO1k–single–14	28.7 ± 8.2	8.4 ± 1.2	940 ± 240	necking, little if any recovery
PTMO2k–BD–14	9.7 ± 1.5	16.4 ± 0.5	1450 ± 90	little if any recovery
PTMO3k–BD–14	10.3 ± 0.1	8.6 ± 0.3	893 ± 42	very good recovery
PTMO1k–BD–20	31.0 ± 7.0	15.1 ± 1.0	935 ± 71	little if any recovery
PTMO2k–BD–20	21.3 ± 1.7	19.7 ± 0.9	1036 ± 49	little if any recovery
PTMO2.9k–BD–20	14.8	14.7	1096	only one sample tested
PTMO3.5k–BD–20	9.3 ± 0.5	17.5 ± 3.7	979 ± 198	very good recovery

The PTMO2k–BD–14 sample showed almost no recovery after breaking at an elongation in excess of 1400%, while the PTMO3k–BD–14 samples recovered to a permanent set of less than 50% elongation, an excellent figure considering the average elongation at break for these materials was over 890%. The recoverability results of the 20 wt% materials are in line with those of the 14 wt% materials. Here too, the most significant difference between the samples was the recoverability of the 3.5k sample with respect to the others of similar HS content as it demonstrated high levels of recoverability (also less than 50% permanent set after 24 hours) due to strain induced crystallization, unlike its lower SS and HS $\langle M_n \rangle$ counterparts. The effect of increasing HS content is substantial. Increasing hard segment content from 14 wt% to 20 wt% results in an increase in both the ambient temperature modulus and tensile strength of the materials as shown in Table 5.2.

5.5. CONCLUSIONS

Segmented polyurethane materials were synthesized using a soft segment based on hydroxyl terminated PTMO with molecular weights of *ca.* 1000, 2000, 2900, 3000, and 3500 g/mol. Each material was synthesized with highly symmetric *p*PDI as the diisocyanate and each used 1,4-butanediol as a chain extender. Materials were synthesized so as to contain either 14 or 20 wt% HS content. This allowed for the study of the effect of both HS content and the

effect of varying the SS and HS $\langle M_n \rangle$'s. Each of the materials showed microphase separation, a fact confirmed with DMA, AFM and SAXS. These results further confirm the results of Barikani and Hepburn in showing that BD chain extended polyurethanes, utilizing linear, symmetric *p*PDI as the diisocyanate, display a microphase separated structure and have storage modulus values in excess of 10^7 Pa over a broad range of temperature. The hard phase of the films clearly segregated themselves into long thread-like domains based on AFM data. These domains showed an interwoven texture in AFM scans, an attribute that leads to the high stiffness of the samples as measured in the DMA. Films based on a 1000 g/mol PTMO SS showed very good microphase separation and exhibited both a SS T_g and a HS T_m as seen in DMA results. While the SAXS and AFM data did not show high correlation with regard to thread thickness and spacings, a crystalline or ordered structure of the hard microphase was confirmed with WAXS. Higher PTMO molecular weights resulted in the crystallization of the microphase separated PTMO. The crystalline SS melted before ambient temperature, however, and therefore did not add to the strength or stiffness of the room temperature properties. In addition, a very slight upturn was noted in the ambient temperature stress–strain curves. One possible cause of this is SS crystallinity reemerging as a result of strain induced crystallization, though the upturn in the curves are not prominent enough to state this definitively. In general, the increased HS content resulted in stiffer and stronger films. When the SS $\langle M_n \rangle$ was increased to 3000 g/mol or higher the materials showed good recoverability. The BD chain extender introduced in this study does not hinder the formation of the threadlike structure that was first observed for non-chain extended systems. Again, at relatively low HS contents (14 and 20 wt%) the polyurethanes in this study formed a microphase separated structure, showing that the symmetry of the *p*PDI diisocyanate used was influential in forming well-ordered hard domains.

6. STRUCTURE-PROPERTY BEHAVIOR OF SEGMENTED POLYURETHANEUREA COPOLYMERS BASED ON AN ETHYLENE-BUTYLENE SOFT SEGMENT

6.1. ABSTRACT

Novel segmented polyurethaneurea copolymers were synthesized using a poly(ethylene-butylene) glycol based soft segment and either hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI) or hexamethylene diisocyanate (HDI) in addition to either ethylene diamine (EDA) or 2-methyl-1,5-diaminopentane (DY) as the chain extender. Dynamic mechanical analysis (DMA), small angle X-ray scattering (SAXS) and in some cases atomic force microscopy (AFM) established the presence of a microphase-separated structure in which hard microdomains are dispersed throughout a soft segment matrix. Wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) imply that the materials are amorphous. Samples that are made with HMDI/DY and have hard segment contents in the range of 16–23 wt% surprisingly exhibit near-linear mechanical deformation behavior in excess of 600% elongation. They also show very high levels of recoverability even though their hysteresis is also considerable. The materials have all proven to be melt processable in addition to solution processable.

6.2. INTRODUCTION

Segmented block copolymers are widely used in several industries including automotive coatings, molded components, sporting goods manufacturing, and in the insulation business [132, 133]. The breadth in the applications for these materials can be attributed in part to their wide range of mechanical and thermal properties. That these properties can be controlled and even tailored to a specific end use makes segmented copolymers a very attractive class of materials.

As a group, segmented thermoplastic polyurethanes, polyureas and polyurethaneureas (TPUs) are a subclass of linear segmented copolymers possessing a backbone comprised of

alternating soft segments (SS) and hard segments (HS). These segments typically have rather low molecular weights compared to triblock copolymers, such as the styrene-butadiene-styrene (SBS) systems, which generally possess block molecular weights of 10,000–100,000 g/mol and are prepared by anionic polymerization [25, 134]. The soft segments in TPUs are often, but not exclusively, polyethers or polyesters and are chosen based on desired functionality, reactivity and molecular weight. The hard segment, also low in molecular weight, is typically formed from the reaction of a diol or diamine chain extender with excess diisocyanate. The isocyanates are either aromatic or aliphatic and the choice is based on a number of factors including cost and reactivity. The specific chemistry and symmetry of the isocyanate has been shown to affect ultimate properties of the materials, and careful consideration must be given to this choice [131, 135]. Diamines are common chain extender molecules used in the synthesis of urea linkages, although other moieties such as water can also be used as is common in the production of "polyurethane" flexible foams [136].

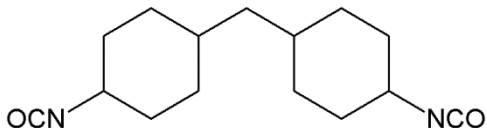
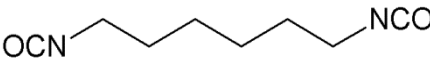
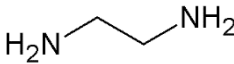
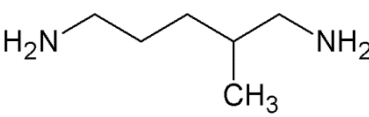
Linear polyurethaneureas are synthesized using a step growth reaction technique first developed by Otto Bayer in the late 1930's [136]. In the more commonly used prepolymer method, linear hydroxyl terminated oligomeric polyether or polyesters are reacted with an excess of a selected diisocyanate to cap the oligomer thereby forming a urethane linkage and leaving an isocyanate functional group at each terminus, forming what is termed a "prepolymer". This prepolymer mixture (containing additional diisocyanate) is then reacted with a diamine chain extender to form the hard segments and increase the molecular weight of the macromolecule. In general, an increase in HS content leads to increased modulus (stiffness) and enhanced tensile strength [137, 138].

The wide range of properties of segmented copolymers is credited to microphase separation, the process whereby hard segments segregate, forming hard microdomains in a matrix of soft segments. These microdomains are generally well dispersed throughout the soft segment matrix and act as physical crosslinks adding modulus, stiffness and strength. In block copolymer materials with non-specific interactions, an examination of the Flory-Huggins χ parameter helps define under what conditions microphase separation will occur [6]. Such an approach, however, cannot easily be utilized in the present case due to specific molecular interactions promoted by hydrogen bonding between the urethane and urea groups in the HS of these materials.

The soft segment phase of these materials usually has a glass transition temperature (T_g) well below room temperature and it is this phase in thermoplastic polyurethanes, polyureas and polyurethaneureas that lowers the elastic modulus and enhances elongational properties. If microphase separation occurs and the hard phase is also well-percolated (interconnected) throughout the material, the percolation will have the effect of further increasing modulus for a given composition, but it will also promote the potential for yielding and enhanced mechanical hysteresis. In urea HS containing systems, the HS microdomains can provide further strength to the material through the development of a bidentate hydrogen bonded network, through intra- or intermolecular interactions. Calculations have shown the bond energy of bidentate hydrogen bonds to be 21.8 kJ/mol [50]. In contrast, polyurethane systems can only display a monodentate hydrogen bonded network between urethane groups on the same or adjacent chains and possess a lower bond energy of 18.4 kJ/mol. The hard segments of polyurethanes or polyureas can also display crystallization if the appropriate process history is utilized and HS symmetry exists. In contrast to the conventional polyether or polyester polyols, the soft segment used in the present study is an ethylene-butylene based polyol, Kraton™ Liquid L-2203.

This ethylene-butylene oligomer was synthesized by the hydrogenation of an α,ω -hydroxy terminated polybutadiene, which was prepared by anionic polymerization. The resulting amorphous SS has no significant polarity compared to polyester or polyether based systems. It also differs in that the SS molecular weight is 3340 g/mol as opposed to typical values of 1000–2000 g/mol used in the majority of linear segmented polyurethanes and polyurethaneureas. Both of these features imply that microphase separation will be strongly favored for typical hard segments based on polyurethane or polyurea chemistry. In preparing the linear segmented copolymers studied here, two different diisocyanates were employed: hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI) and hexamethylene diisocyanate (HDI). The chain extenders chosen were ethylenediamine (EDA) and 2-methyl-1,5-diaminopentane which is sold under the name Dytek® (DY). The chemical structures for both the diisocyanates and chain extenders are given in Table 6.1. These constituents allowed the examination of the role of symmetry in the behavior of linear segmented polyurethaneureas, as EDA is a symmetric molecule but DY is asymmetric.

Table 6.1. General structural information for the materials used in this study.

Chemical Species	Abbreviation	Structure
Hydrogenated 4,4'-diphenylmethane diisocyanate	HMDI	
Hexamethylene diisocyanate	HDI	
Ethylenediamine	EDA	
2-methyl-1,5-diaminopentane (Dytek)	DY	

This study has two foci. First, the properties of segmented polyurethaneurea films comprised of a non-polar ethylene–butylene (EB) soft segment and an HMDI–DY hard segment are examined. Particular attention is given to the way solid-state properties are affected by HS content in the range (16 wt%–23 wt%). Second, an investigation is made into the effect the choice of chain extender has on the properties of ethylene–butylene soft segment based polyurethaneureas. Here, HDI is employed as the diisocyanate and the chain extender used is either EDA or DY.

6.3. EXPERIMENTAL SETUP

6.3.1. MATERIALS

Hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI) (Bayer) and 1,6-hexamethylene diisocyanate (HDI) (Aldrich) with purities of greater than 99.5% were used. Hydroxy terminated Kraton™Liquid-L-2203 was kindly supplied by Kraton Inc. The average functionality and the number average molecular weight ($\langle M_n \rangle$) of Kraton™L-2203, as

determined by $^1\text{H-NMR}$, were 1.92 and 3340 g/mol respectively. It also had a very narrow molecular weight distribution of 1.03, as determined by SEC. Reagent grade ethylenediamine (EDA) was purchased from Aldrich. 2-Methyl-1,5-diaminopentane (DY) was kindly provided by DuPont. HPLC grade tetrahydrofuran (THF), toluene, and isopropyl alcohol (IPA) (Aldrich) were all used as received. The catalyst, dibutyltin dilaurate (T-12) is a product of Witco.

6.3.2. POLYMER SYNTHESIS

Polymerizations were conducted in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer, addition funnel and nitrogen inlet. All copolymers were prepared by using the two-step, prepolymer method. To prepare the prepolymer, calculated amounts of diisocyanate and Kraton™ L-2203 were introduced into the reactor, stirred and heated. When the mixture reached 80 °C, 200 ppm of dibutyltin dilaurate (T-12) in toluene was added as catalyst. Prepolymer formation was monitored by FT-IR spectroscopy, following the disappearance of the broad hydroxyl stretching peak around 3450 cm^{-1} and formation of the N-H peak and C=O peaks near 3300 and 1720 cm^{-1} respectively. After the completion of prepolymer formation, the system was cooled to ambient conditions and the prepolymer was dissolved in toluene or THF. Then it was further cooled to 0 °C in an ice-water bath and diluted with isopropyl alcohol. For chain extension, a stoichiometric amount of diamine chain extender (DY or EDA) was weighed into an Erlenmeyer flask, dissolved in IPA, introduced into the addition funnel and added dropwise into the prepolymer solution at 0 °C, under strong agitation. Completion of reactions was determined by monitoring the disappearance of the isocyanate absorption peak around 2270 cm^{-1} with a FTIR spectrophotometer. Reaction mixtures were homogeneous and clear throughout the polymerizations.

Table 6.2 provides the compositional characteristics of the poly(ethylene-butylene)glycol based polyurethaneureas prepared in this study. SS chain length is constant at 3340 g/mol. HS chain length, as shown on the last column of Table 6.2 varies between 280 and 1020 g/mol, depending on the hard segment content. The convention for sample designation used is as follows: Diisocyanate/chain extender/HS wt%. Therefore, HMDI/DY/16 refers to a polyurethaneurea with an ethylene/butylene SS, HMDI and DY chain extender with a HS content

of 16.2 wt%. HDI/DY/9 and HDI/EDA/8 have identical molar compositions. The small difference in HS content is due to the difference in the molecular weight of the diamine.

Table 6.2. Compositions and average hard segment lengths of poly(ethylene-butylene)glycol ($\langle M_n \rangle = 3340$ g/mol) based polyurethaneurea copolymers.

Sample code	Diisocyanate	Chain extender	HS content (wt%)	HS $\langle M_n \rangle$ (g/mol)
HMDI/DY/16	HMDI	DY	16.2	645
HMDI/DY/19	HMDI	DY	19.4	800
HMDI/DY/23	HMDI	DY	23.4	1020
HDI/DY/9	HDI	DY	8.7	320
HDI/EDA/8	HDI	EDA	7.8	280

Higher values of HS content were prevented due to solubility issues caused by the lengthening of the urea HS. Solution based films were cast from a toluene/IPA mixture into Teflon molds, covered with glassware to slow down the solvent evaporation, and placed into a 60 °C oven overnight. The molds were then removed from the drying oven and placed into a vacuum oven at room temperature for at least two days to complete the solvent removal. The samples were kept under vacuum at room temperature when not in use. Interestingly all films were also compression moldable at 200 °C, at *ca.* 300 psi resulting in clear, monolithic, uniform films.

6.4. EXPERIMENTAL TECHNIQUES

6.4.1. ATOMIC FORCE MICROSCOPY (AFM)

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP150 silicon cantilever probe tips. The tips possessed a 5 N/m spring constant and a resonant frequency of *ca.* 100 kHz. The free air amplitude was normally set at 2.8 V. Some samples, however, necessitated the use of a much higher free air amplitude of *ca.* 8.0 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was

chosen so that the set point ratio fell in the range 0.4–0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz.

6.4.2. DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed on a Seiko DMS 210 tensile module with an attached auto-cooler for precise temperature control. Rectangular samples measuring 10 mm in length and 4.5–6.5 mm in width were cut from the cast films. Under a dry nitrogen atmosphere, the films were deformed using a frequency of 1 Hz. The temperature was increased from -150 to 200 °C at a rate of 2 °C/min. Soft segment glass transition temperatures reported by the DMA methodology were denoted as the location of the peak in the $\tan \delta$ vs. temperature plots.

6.4.3. TENSILE TESTING

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. A bench-top die was used to cut dogbone samples with an overall length of *ca.* 25 mm and the width of the grip section of *ca.* 10 mm. The reduced section measured 2.91 mm × 10 mm (width × gage length). These dogbones were then tested to failure at a crosshead speed of 25 mm/min and their load vs. displacement values recorded. Three samples were measured and their results were averaged to determine modulus, yield strength, and strain-at-break for each of the five materials. In addition to testing the materials to failure, hysteresis measurements were also made. For this test, the dogbone shaped samples were stretched to 600% strain at a crosshead speed of 25 mm/min and then immediately returned to its initial position of 0% strain at the same rate. This loading-unloading cycle was repeated twice more to produce a three-cycle hysteresis test. Lastly, an Instron was also used to perform stress relaxation experiments. In this case, the sample was rapidly stretched to a strain of either 25% or 600% and held while the decay in load as a function of time was recorded.

6.4.4. *WIDE ANGLE X-RAY SCATTERING (WAXS)*

Photographic flat WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu-K α radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was set at 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an evacuated sample chamber. X-ray exposures lasted four hours. Sample thickness ranged from 12–14 mils for the three HMDI/DY samples and 19.5–20 mils for the HDI/ED and HDI/DY samples.

6.4.5. *SMALL ANGLE X-RAY SCATTERING (SAXS)*

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu-K α doublet, with an average wavelength of $\lambda = 1.54 \text{ \AA}$. The camera used 200 μm , 100 μm and 300 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector, located approximately 65 cm from the sample. After azimuthal averaging, the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source at the Argonne National Laboratory, as a secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s , where $s = 2\sin(\theta)/\lambda$, and 2θ is the scattering angle.

6.4.6. *DIFFERENTIAL SCANNING CALORIMETRY (DSC)*

DSC was used to determine potential melting behavior of the segmented polyurethaneureas and was also used as a second method for determining SS glass transition

temperatures. DSC experiments were conducted on a Seiko DSC 220C with an attached auto-cooler for precise temperature control. Samples weighing 10–15 mg were heated in a nitrogen atmosphere from -150 to 200 °C at 10 °C/min, quenched to -150 °C at 10 °C/min, and reheated to 200 °C at 10 °C/min.

6.5. RESULTS AND DISCUSSION

6.5.1. HMDI/DY MATERIALS AS A FUNCTION OF HARD SEGMENT CONTENT

The three HMDI/DY based TPUs which varied by only 7.2 wt% in hard segment content were found to have some similar physical properties as well as some important differences. DMA analysis (Figure 6.1) provided initial insight into the structural features of this series. At temperatures below -63 °C, all three samples behaved as glassy solids with storage modulus (E') values in excess of 3×10^9 Pa. As the samples were heated, the SS phase of each went through a glass transition at *ca.* -50 °C.

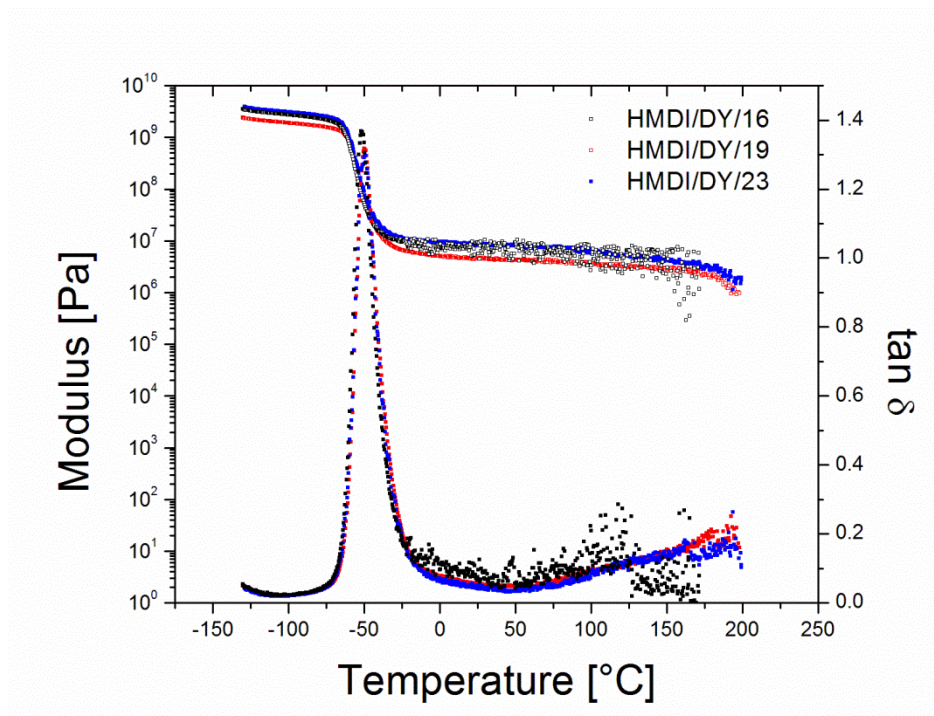


Figure 6.1. Plots of E' and $\tan \delta$ for the HMDI/DY/16, HMDI/DY/19, and HMDI/DY/23 systems.

Accordingly, E' distinctly decreased as the sample passed through T_g and approached an average value of roughly 10^7 Pa. Each sample maintained approximately this level of modulus until it softened beyond the sensitivity of the DMA at temperatures in the range of 150 °C. Thus, the "service window" for these HMDI/DY materials, as defined by the E' plateau between the soft segment T_g and the hard segment softening point, is quite broad (-30 °C to +150 °C) and the storage modulus is relatively temperature insensitive. The relatively high modulus of the material in this region is an indication of a microphase-separated structure with a high level of connectivity of hard domains. The upper temperature limit of the plateau is attributed in part to the bidentate hydrogen bonding between urea linkages on adjacent HS. As noted earlier, the bond energy for bidentate bonding between urea groups has been previously calculated to be 21.8 kJ/mol [50]. As expected, HS bonding serves to enhance segmental cohesion at higher temperatures. DMA analysis (Figure 6.1) clearly supports a well-defined microphase separation in these copolymers.

A microphase-separated morphology was further confirmed by SAXS (Figure 6.2). Increasing the HS content in these materials promotes a corresponding increase in the volume fraction of the HS domains.

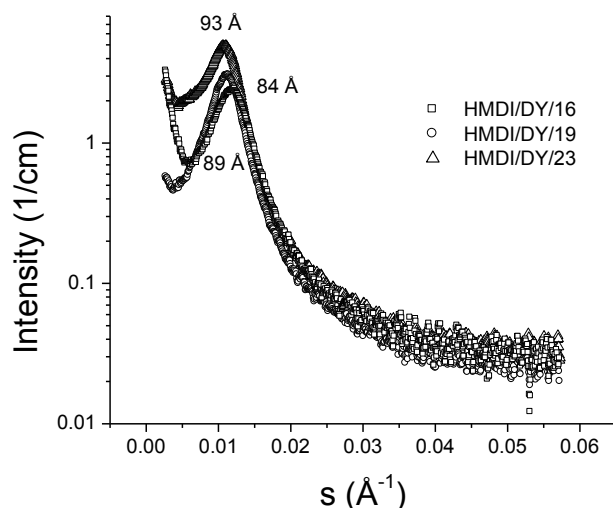


Figure 6.2. SAXS scans showing first order interference peaks of HMDI/DY/16, HMDI/DY/19, and HMDI/DY/23 materials with spacings of 84, 89 and 93 $\text{\AA}$ respectively.

This increase in volume fraction must change the microphase-separated morphology, by an increase in the size, shape or number of the microphase-separated HS domains. Here, increasing HS content results in an increase in domain spacing measured by SAXS, where materials with HS contents of 16, 19, and 23% have spacings of 84, 89 and 93 $\text{\AA}$ respectively. This is most simply explained by an increase in domain size, as is expected in this composition range, whether from a lengthening or thickening of the hard domains. An increase in the number of domains could cause a decrease in the domain spacing, contrary to the observed shifts in the SAXS data. An attempt to attain visual evidence of the microphase-separated structure (suggested to exist by DMA and SAXS) was made with AFM. Unfortunately, none of the three samples provided clear evidence of such a structure.

While HS crystallinity was not expected in view of the asymmetric chain extender, DY, both WAXS and DSC studies gave direct support for this hypothesis. The WAXS patterns (not shown) obtained at ambient temperature of all three materials in the series showed only a broad amorphous halo and no sign of discrete diffraction rings attributable to a crystalline structure.

Furthermore, the DSC traces of each material in the series, while showing T_g 's consistent with the $\tan \delta$ peak in the DMA data, showed no endothermic peaks, nor were any expected, that could be assigned to any melting of the HS phase. Representative DSC traces are shown in Figure 6.3 for HMDI/DY/19.

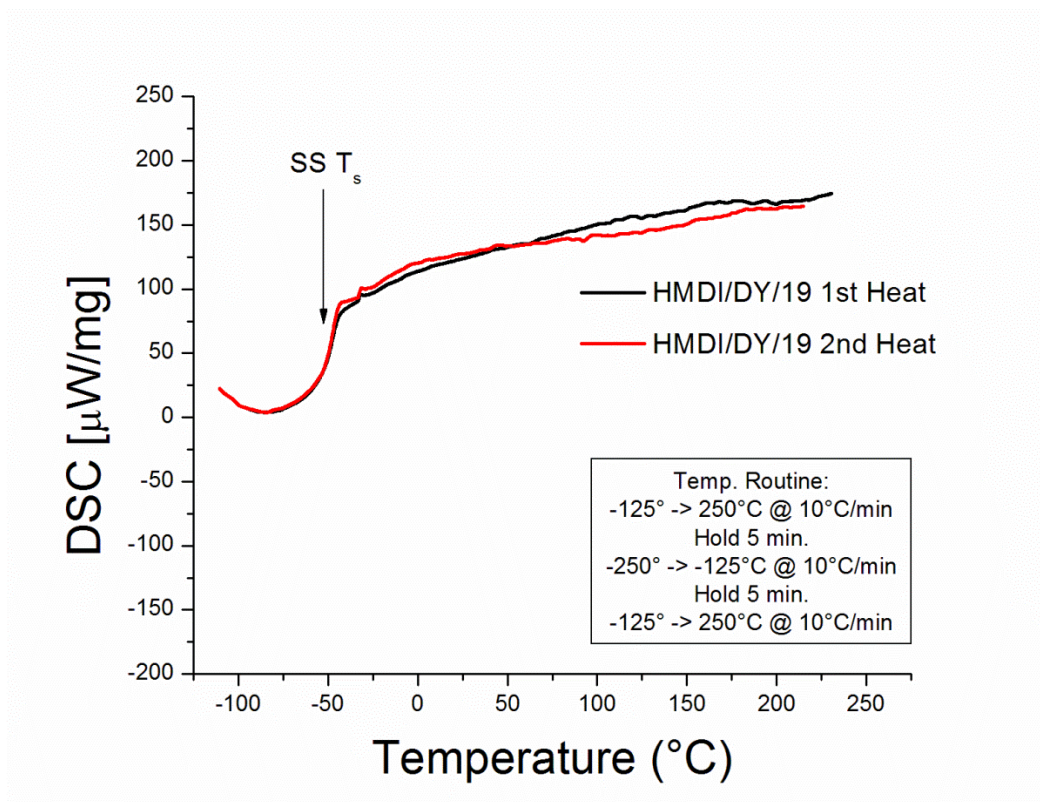


Figure 6.3. DSC traces of first and second heats of HMDI/DY/19. The lack of clear melting peaks indicates that there is no detectable crystallinity.

As seen in other studies on segmented polyurethaneurea systems, increasing HS content generally leads to both higher modulus values and higher tensile strengths and can also often improve toughness in certain ranges of HS content [135, 139-141]. This was also the case in these systems. A representative tensile curve for each material is presented in Figure 6.4. A systematic increase occurred in each of these variables with the growing HS content. The modulus increased as expected with growing HS content as reflected by the rise in slope of the successive stress-strain curves as the HS content rose from 16 to 23 wt%.

An average tensile strength for each material was determined by averaging the results of three tests. For the three HS contents 16, 19, and 23 wt%, the average tensile strengths were 10,

19 and 24 MPa respectively. It should be noted that while higher tensile strengths with increasing HS content were expected, the increase in HS wt% from 16% to 23% led to a *ca.* 150% rise in tensile strength. This significant increase suggests that the level of HS phase connectivity may be quite sensitive in this HS content range. A second cause of this increase in tensile strength we believe arises from the enhanced cohesiveness of the HS domains caused by the larger average HS lengths as the HS wt% increases. The larger HS should lead to an increase in the stress the material can withstand before fracture of the material occurs.

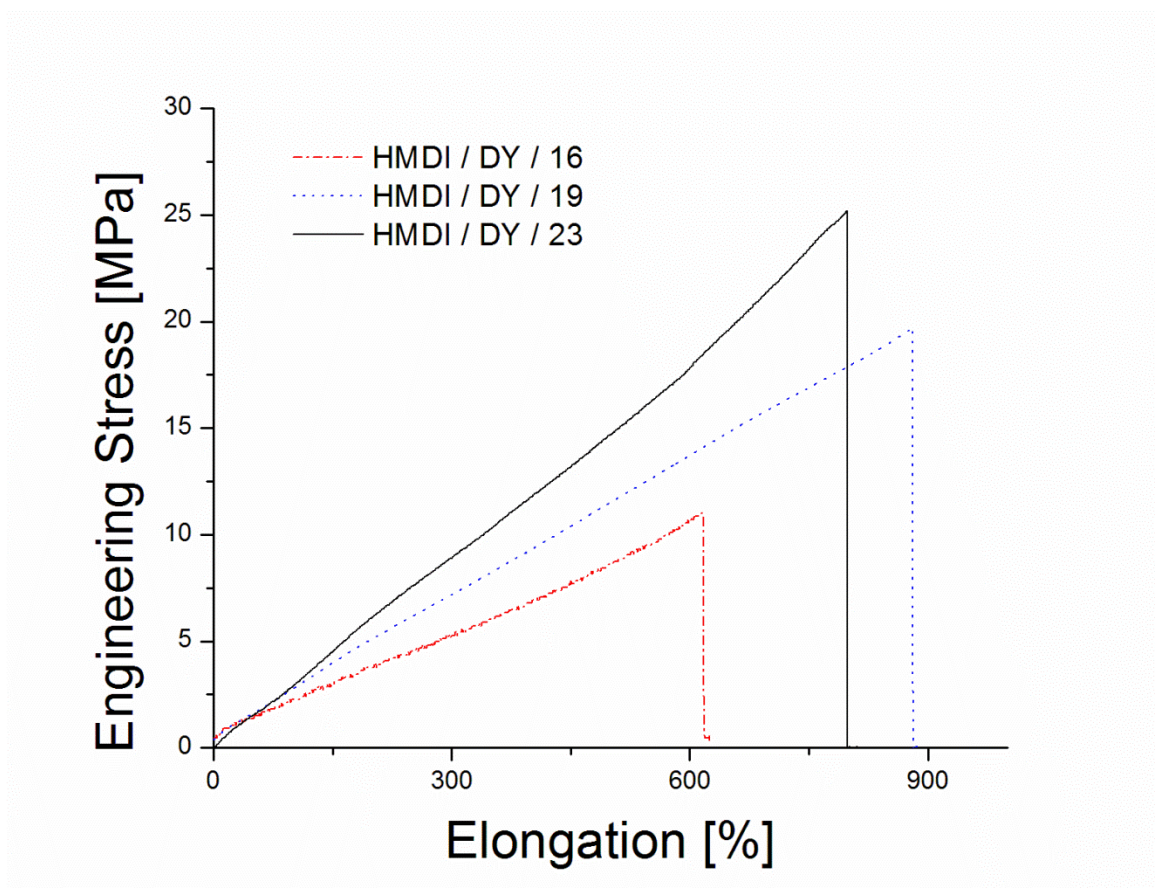


Figure 6.4. Representative tensile curves of samples HMDI/DY/16, HMDI/DY/19, and HMDI/DY/23.

A particularly interesting feature of these tensile curves are their nearly linear, almost Hookean stress-strain response starting at very low deformations and continuing to failure which occurs at levels of extension exceeding 600% (Figure 6.4). An expanded view of three tensile samples of the 19 wt% HS material is shown in Figure 6.5. At present, the authors know of no

other fully polymeric system that displays such near-linear behavior while undergoing tensile deformation to such high elongations.

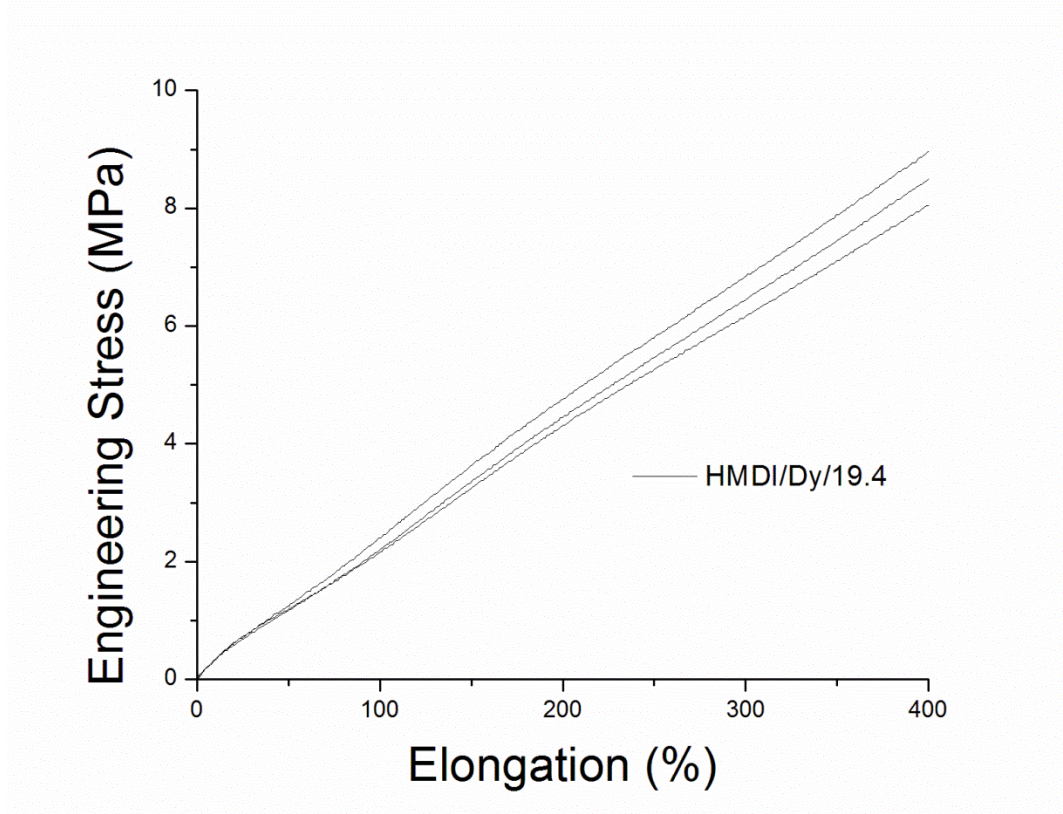


Figure 6.5. Three tensile curves for sample HMDI/DY/19 show the near linear behavior beginning at low deformations.

Increasing the ratio of HS to SS should also increase the toughness values, T , of these materials, which were determined by the area under the stress-strain curves. This area was calculated by integration of the stress with respect to the strain i.e.

$$T = \int_0^{\varepsilon_B} \sigma d\varepsilon \quad (\text{Equation 6.1})$$

where ε_B represents the strain at break. A Hookean behavior is assumed because these materials show nearly linear deformation, and a value of the stress σ can be substituted in Equation 6.1 by use of Hooke's Law,

$$\sigma = E\varepsilon \quad (\text{Equation 6.2})$$

Thus, Equation 6.1 becomes:

$$T = \int_0^{\varepsilon_B} E \varepsilon d\varepsilon \quad (\text{Equation 6.3})$$

The modulus is constant and can be removed from the integrand leaving:

$$T = E \int_0^{\varepsilon_B} \varepsilon d\varepsilon \quad (\text{Equation 6.4})$$

which leads to:

$$T = \frac{E \varepsilon_B^2}{2} \quad (\text{Equation 6.5})$$

Therefore we note that, *if Hookean*, the toughness is directly proportional to the square of the strain in these materials. The toughness of the HMDI/DY/16, HMDI/DY/19 and HMDI/DY/23 samples was calculated to be 33, 99, and 110 MPa respectively. As a comparison, the values calculated by integration of the area under the *actual stress-strain curve* were, 34, 95, and 107 MPa respectively. Therefore, our calculated values vary only 3-4% from the integrated values thereby providing further support of the near-linear Hookean behavior these three systems display. Here again it is interesting to note that the increase in HS wt% from 16% to 23% has increased toughness values by *ca.* 200%.

In light of the observed near-linear stress-strain response, the hysteresis of these materials was also explored. An example of one such test on the 19 wt% HS material is provided in Figure 6.6. Again, the Hookean type behavior was noted to begin immediately at low deformations and the response maintained near-linearity to 600% strain. The sample was then unloaded and recovered much of its initial length though the unloading response was nonlinear. Note that the stress reached a value of zero before the crosshead fully returned to its zero strain position. Therefore there exists some amount of permanent set in the material due to the irrecoverable energy lost in the deformation. This value of set, just below 100% strain, is not, however fully permanent. The sample continues to recover after the first loading-unloading cycle and would continue to do so if it were not immediately stretched a second time. For this reason the onset of stress during the second loading occurred at an earlier strain than where the stress dropped to zero during the first unloading cycle. Upon the second deformation, it was evident that the loading curve did not trace the previous unloading curve. Note also that the second deformation does not display the same near-linear stress-strain response of the first extension, nor was it

expected to, due to the disruption of the HS structure that occurred as a result of the first loading. Clearly considerable structural modification was done to the structure that was responsible for the near-linear response during the initial extension.

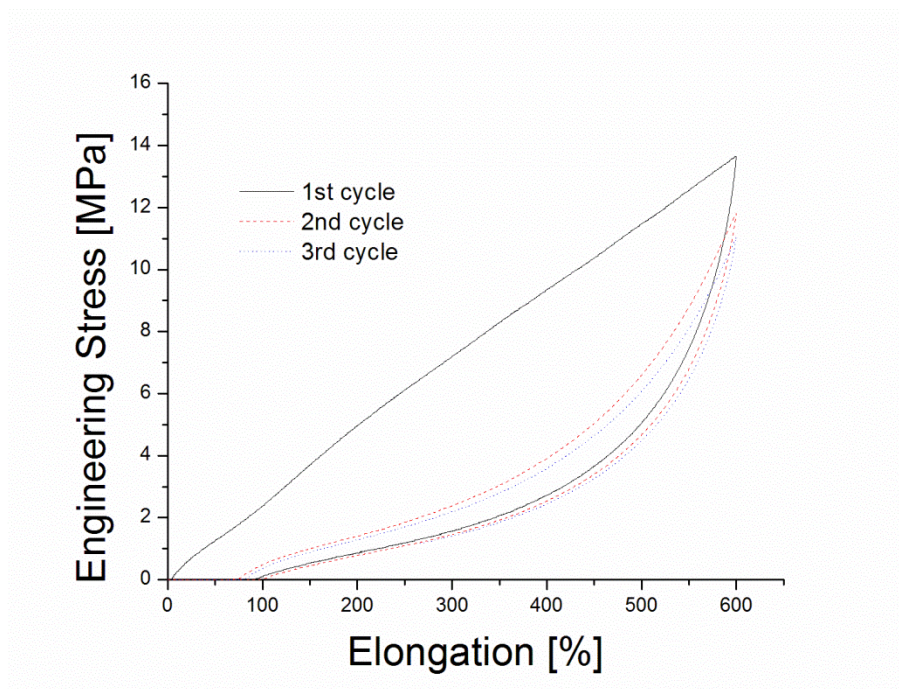


Figure 6.6. Three-cycle hysteresis loops for sample HMDI/DY/19.

All subsequent loading curves show strain hardening behavior and the responses are very similar to one another. This is apparent from the increase in the slope of the loading curves as the materials are again elongated to high strains. After the third and final loading–unloading cycle, the permanent set could be measured more accurately. Immediately after its removal from the testing frame, the residual strain was measured to be 2 mm, or 20%. However, twenty-four hours later the sample *had recovered almost all of its initial length at ambient temperature* and was measured to be 10.5 mm in length (indicating only a 5% permanent set).

The amount of recovery found in these samples raises another question about the morphological features of these materials. Clearly, based on the hysteresis results, this morphology is softened greatly through modification of the HS phase with extension. To address how this disruption of structure influences the time dependence or relaxation behavior of the system, some stress relaxation measurements were undertaken at 600% extension—the results being shown in Figure 6.7. All three materials were stretched at a rate of 100 mm/min so that the

loading was completed in 36 seconds. After extension ended all three materials experienced stresses of *ca.* 20 MPa. The samples were then held at that length for at least three hours, until the rate of change of the stress level was nearly zero.

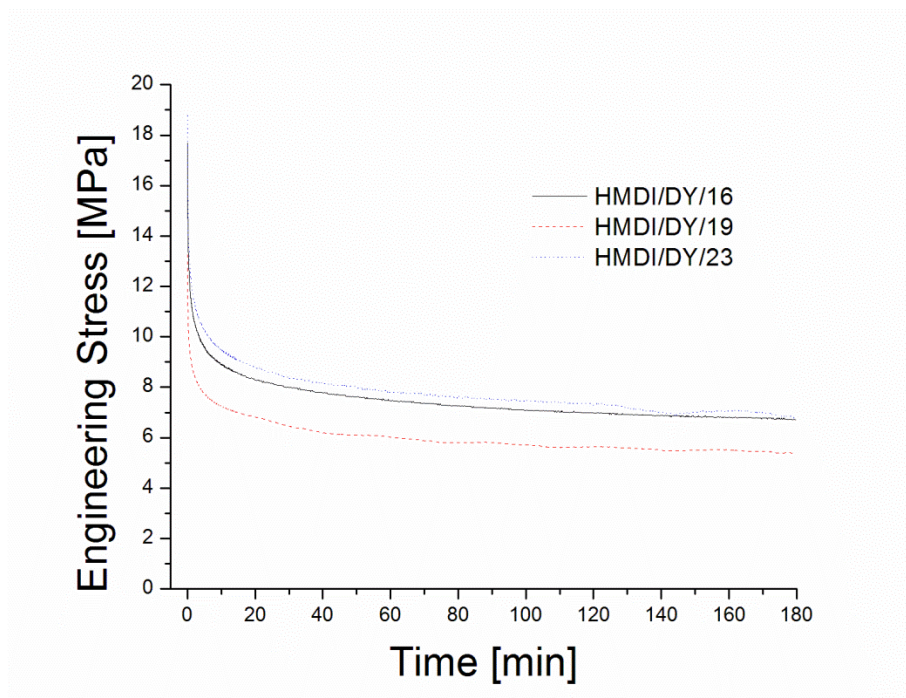


Figure 6.7. Stress relaxation of the three HMDI/DY materials after an initial stretch to 600%.

All samples show that they maintain a stress in excess of 5 MPa after this three hour period. It appears from the curves that two very distinct relaxation mechanisms are occurring, one dominating the short time scale and a second occurring over a much longer time. While an attempt to fit the relaxation curves was made using two Maxwell models in parallel, the fit was deemed too poor to include although certainly the general character of the model captured the general shape of the observed behavior.

Having completed all of the characterization techniques discussed thus far, the ability of each material to be reprocessed was investigated, as this is an important feature of thermoplastic elastomers. Unused pieces of each material were placed in a hydraulic press with platen temperatures of 200 °C. Each material was found to be easily reprocessable as the pressing resulted in a clear and uniform film for each system. The tensile properties of the remolded films were then tested for comparison with the solvent cast films (Figure 6.8). The remolded films display very similar deformation properties to the solvent cast films up to 600% elongation.

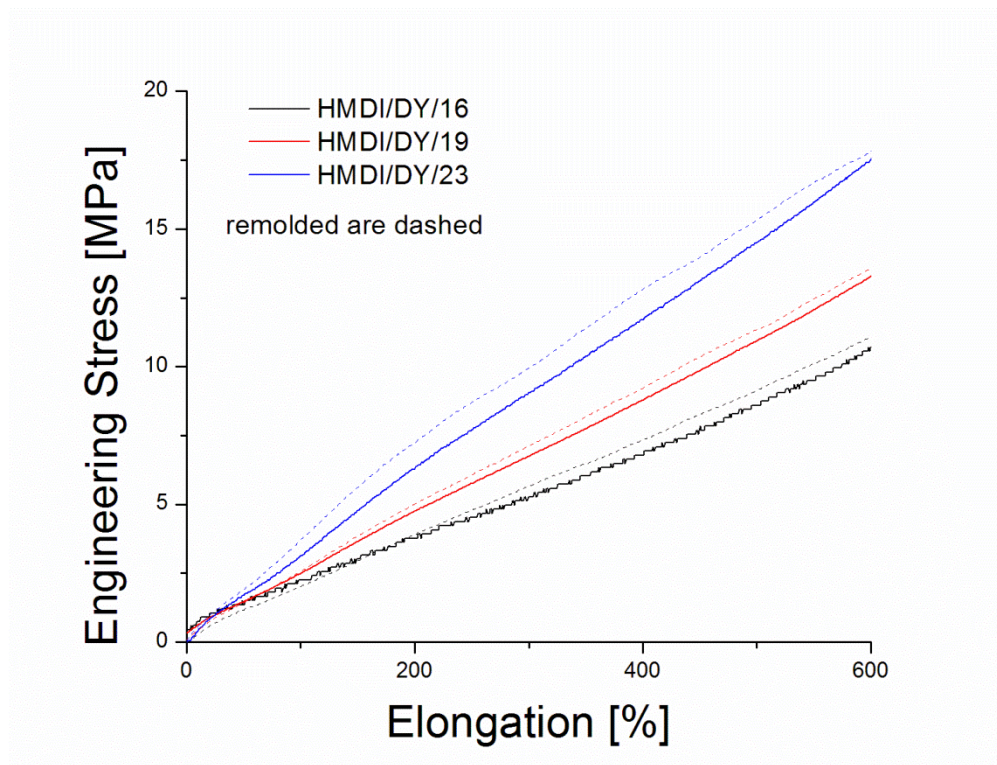


Figure 6.8. Tensile curves of HMDI/DY materials comparing solvent cast and remolded materials.

The modulus values are very close as the deformation curves almost lie atop one another. In addition, the unique near-Hookean linearity of the curves at low levels of deformation is maintained after remolding. Also important is the fact that the remolded materials retain the characteristic of high recoverability.

The similarity in mechanical behavior is an important observation given the different physical and thermal histories of the samples. In some block copolymer systems, such as many of the SBS triblock materials, solvent cast materials have been shown to contain very different structure than their melt processed counterpart [142, 143]. In this case, the HMDI/DY films appear to have a comparable structure, irrespective of whether they were produced with the THF/IPA solvent or have a melt history.

6.5.2. HDI/EDA/8 AND HDI/DY/9 MATERIALS

The two final materials, HDI/EDA/8 and HDI/DY/9, differ from those previously discussed in two respects. First, the latter two were prepared using HDI as the diisocyanate in place of HMDI and second, EDA (symmetric) was chosen as the chain extender for one of the samples as opposed to DY (asymmetric) thereby allowing the effect of chain extender symmetry to be examined. In order to understand the influence of chain extender structure and symmetry on the properties, both samples were prepared with the same molar compositions, which is $[\text{Kraton}]/[\text{HDI}]/[\text{CE}]=2/3/1$. The difference in the HS content comes from the higher MW of DY.

The DMA traces of these two samples (Figure 6.9) show results somewhat similar to the HMDI/DY systems with regard to the SS T_g 's. In this case, the respective SS T_g 's are $-53\text{ }^{\circ}\text{C}$ for HDI/DY/9 and $-54\text{ }^{\circ}\text{C}$ for HDI/EDA/8. As the sample is heated through T_g the material softens considerably and E' decreases from *ca.* 10^9 Pa to *ca.* 10^7 Pa , the same general range of values as noted for the HMDI/DY materials. As with the HMDI/DY samples, the magnitude of the modulus in the plateau region is ascribed to the presence of a microphase-separated structure. An additional conclusion can be drawn based on the similarity of the modulus values of these two sets of materials. Recall that the HDI based materials have a much lower HS content (*ca.* 8% as opposed to 16–23%). This implies that the HDI/DY/9 and HDI/EDA/8 materials must have some level of higher interconnectedness of the hard microphase to account for the similar E' values. This issue will be further addressed later in this report.

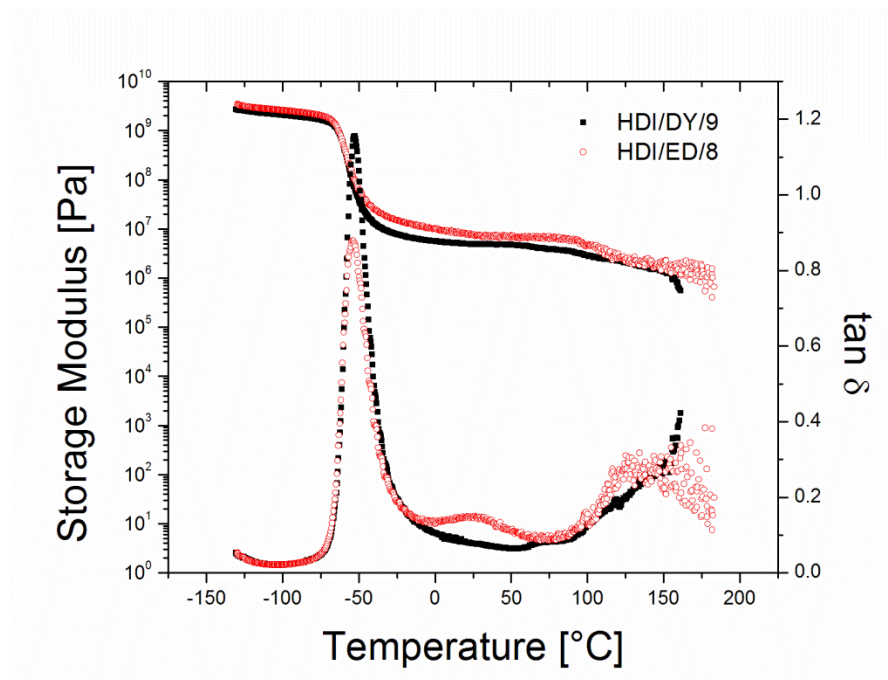


Figure 6.9. DMA traces of E' and $\tan \delta$ for the HDI/EDA/8 and HDI/DY/9 samples.

These materials also display distinct differences from the HMDI/DY materials. Following the SS T_g , there is a relatively flat and broad plateau in modulus between $-30\text{ }^{\circ}\text{C}$ and $+100\text{ }^{\circ}\text{C}$, a smaller thermal window than was observed for the HMDI/DY systems. Therefore, the plateau in these materials spans only $130\text{ }^{\circ}\text{C}$ compared to the $180\text{ }^{\circ}\text{C}$ span of the HMDI/DY materials which possessed both longer HS and a higher HS content. Recall from Table 6.2 that the HMDI based materials had HS $\langle M_n \rangle$ values between 645 and 1020 g/mol whereas the HDI/DY/9 and HDI/EDA/8 have HS $\langle M_n \rangle$ values of 320 and 280 g/mol respectively. The breadth of the rubbery plateau is again due in part to the bidentate hydrogen bonding between urea linkages on adjacent chains. Though each set of polyurethaneureas contains both monodentate and bidentate hydrogen bonds, the combined effect of the lower HS contents and lower HS molecular weights in the HDI based materials is to reduce the number of urea linkages available for bonding. The smaller number of hydrogen bonds is expected to lower the upper temperature limit as the HS domains of the HDI materials begin to soften sooner than their HMDI based counterparts. The use of HDI rather than HMDI may also influence differences in hard segment cohesiveness/packing behavior. Specifically, this reduction in upper temperature modulus could also be due to the melting of the low wt%, symmetric HDI hard segments, although no direct evidence of a crystalline HS was obtained for either material as will be

addressed shortly. Above 100 °C the materials each began softening until *ca.* 150 °C, where both have softened beyond the sensitivity of the DMA. Two key differences are also apparent in the temperature dependent $\tan \delta$ responses of the HDI/DY/9 and HDI/EDA/8 materials. The first difference is the very small peak at *ca.* 25 °C in the HDI/EDA/8 sample. This peak disappears after annealing at 100 °C and may result from residual solvent in the freshly cast material even though this sample had been given the same preparation history as the others. The second difference, unaffected by annealing, is the disparity in magnitude of the $\tan \delta$ peak at the T_g for these materials. The peak in HDI/DY/9 sample has a magnitude of *ca.* 1.2 while the HDI/EDA/8 sample has a peak value of *ca.* 0.9. While not excessively large, this roughly 20% difference in peak height coupled with the similar peak breadths, does imply that the soft segment phase of the HDI/DY/9 sample is less restricted in its motion than the soft segment phase of its HDI/EDA/8 counterpart. It might also be noted that the breadth of the $\tan \delta$ peaks are essentially the same.

The microphase-separated morphologies of both the HDI/EDA/8 and HDI/DY/9 materials were further confirmed by SAXS measurements (Figure 6.10). From those scans, well-defined first order interference peaks were observed at 123 Å and 125 Å respectively. However, the angular locations of these peaks raise a distinct question.

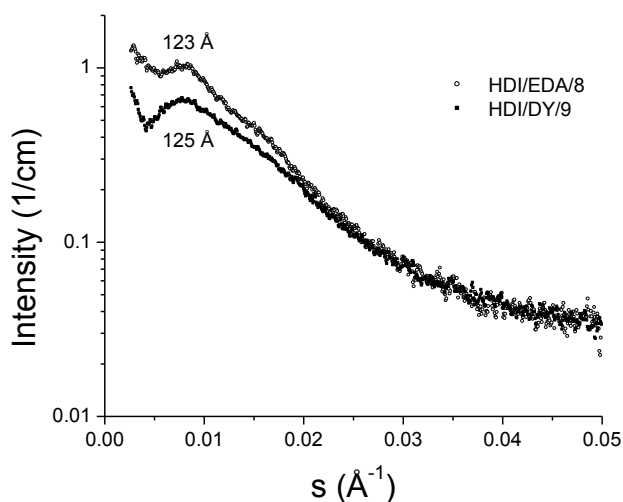


Figure 6.10. SAXS scans showing first order interference peaks for the HDI/ED/8 and HDI/DY/9 materials with spacings of 123 and 125 Å respectively.

Why are the spacings of these lower HS content materials appreciably larger than the HMDI series discussed previously, which had spacings of 84–93 Å? One tentative explanation is

that the difference may be due to, what is on average, a shorter overall HS length in the HDI series. This may result in some of the shortest hard segments dissolving into the SS phase. Indeed, based on the M_n of these segments, they are only 1–3 segments long indicating that dissolution of hard segments may be more likely in these materials. Dissolved HS could effectively lengthen the SS (doubling the effective SS molecular weight to *ca.* 6600 g/mol), resulting in a larger spacing. In addition to shifting the location of the peaks to smaller angles, some dissolved HS would broaden the interference peaks in the SAXS profiles. That this too is observed for the HDI materials (Figure 6.10) lends further support to the explanation proffered.

While it is clear from both the DMA and SAXS data that microphase separation occurs for each material, the exact morphology of the hard phase is not obvious. In further examination of the HDI based materials, neither WAXS nor DSC (Figure 6.11) showed any evidence of crystallinity for either sample. This is qualified with the understanding that the very low levels of HS content may make any crystalline structure that might exist exceedingly difficult to measure.

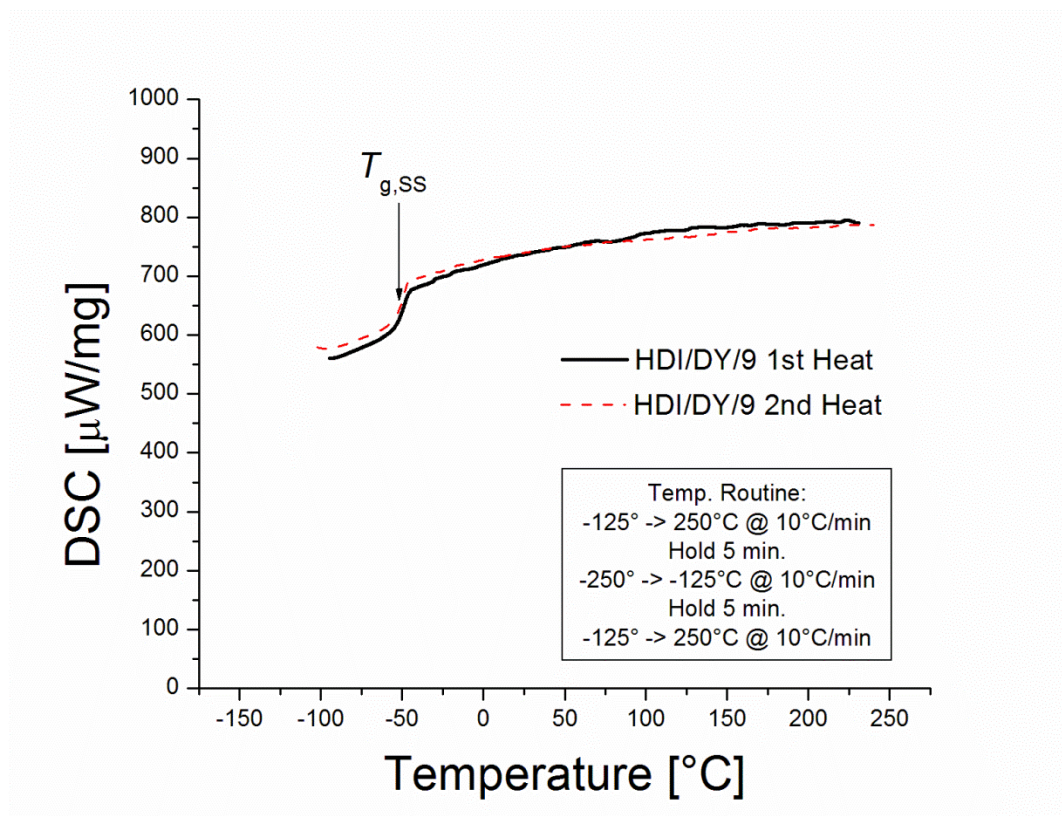


Figure 6.11. DSC trace of HDI/DY/9 sample showing no evidence of crystallinity.

In the interest of obtaining visual evidence of the microphase structure, AFM was employed. AFM phase images were obtained of a well-percolated HS microphase-separated structure for both samples. Figure 6.12a shows the very clear ribbon-like structure of HDI/DY/9 while Figure 6.12b shows the stranded structure of HDI/EDA/8. The three images provide direct visual evidence of two distinct phases: a well-dispersed, interconnected, stranded or ribbon-like hard phase represented by the light portions of the image, embedded in a soft segment matrix represented by the darker portions of the image. As noted earlier, the DMA behavior of the HDI/EDA/8, HDI/DY/9 and the three HMDI/DY materials gives reason to believe that they have somewhat similar microphase-separated structures, despite obtaining clear AFM scans only for the two HDI based samples. In addition to the cast film samples discussed thus far, a second film sample of HDI/EDA/8 was obtained by remolding unused portions of the solution cast material in a hot film press.

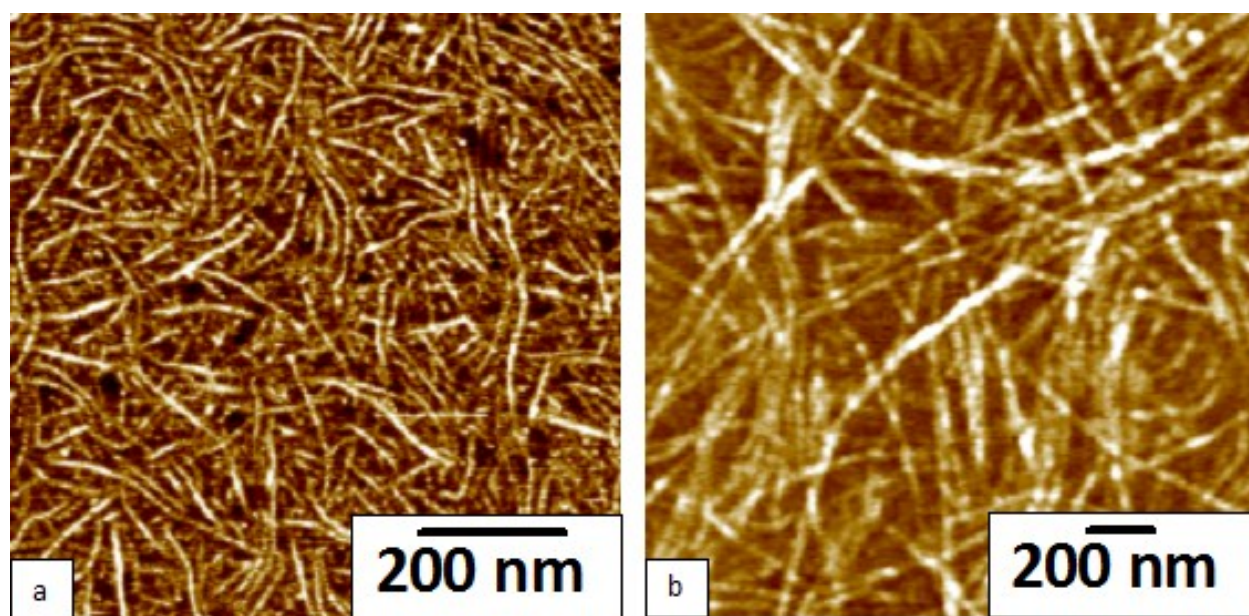


Figure 6.12. (a) AFM phase image of HDI/DY/9 sample showing a well percolated nano-stranded morphology (b) AFM phase image of HDI/EDA/8 showing nano-stranded morphology.

After molding, AFM was performed on the films and the same percolated, microphase-separated structure was found to exist in these films indicating that the material can be reprocessed although the level of HS percolation appears to be somewhat less than within the solvent cast film (Figure 6.13).

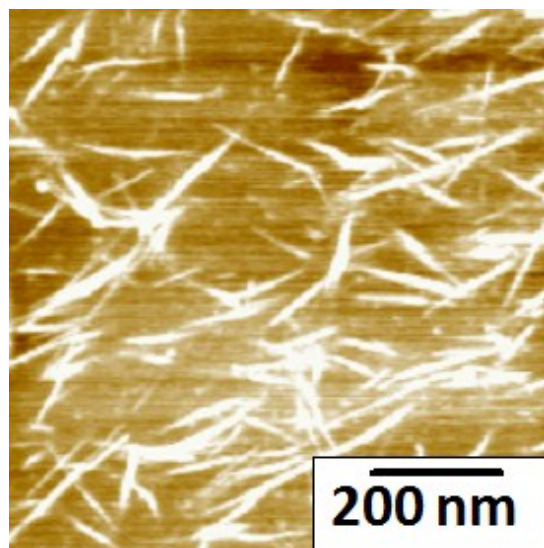


Figure 6.13. AFM phase image of HDI/EDA/8 after remolding in a hot press at 200 °C.

Despite the similarities between the HDI/EDA/8 and HDI/DY/9 samples discussed thus far, there is a surprisingly large difference in the materials with respect to their ambient stress-strain properties. Representative stress-strain curves are shown for each material in Figure 6.14. Both materials display a deviation from linearity at low strains followed by essentially linear behavior until break.

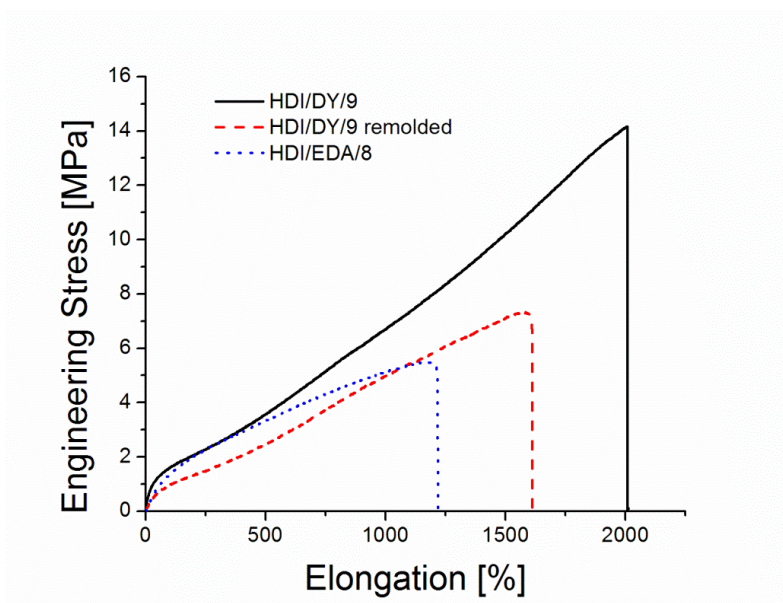


Figure 6.14. Tensile curves of HDI materials comparing solvent cast and remolded materials.

The tensile curves also show the HDI/DY/9 material to have over twice the tensile strength of the HDI/EDA/8 material i.e., 13 MPa versus 5.5 MPa. Furthermore, the HDI/DY/9 sample achieves higher strains at break, 2000% versus 1200%, than the HDI/EDA/8. Lastly, the HDI/DY/9 material displayed a toughness more than three times greater than that of the HDI/EDA/8 sample, 141 MPa to 43 MPa respectively.

The tensile properties of the remolded materials were also measured. Again, the remolded DY based material behaves similarly to the solvent cast material, the tensile curves having roughly the same shape. However, the remolded material does not achieve the same ultimate stress. Consistent with the AFM images, the lower stresses achieved in these tests support the speculation that there is less percolation of the hard segment phase throughout the remolded samples.

6.6. CONCLUSIONS

Novel segmented polyurethaneurea copolymers based on HMDI, an ethylene-butylene soft segment and HS contents between 16 and 23% were prepared. These materials, developed microphase separated morphologies with wide service windows as measured with SAXS and DMA. In addition to the broad temperature insensitive E' plateau, they each displayed a unique, near linear, Hookean-like stress-strain response until fracture at very high levels of strain, in excess of 900% in some cases. The materials were found to be reprocessible as new clear, transparent films were made by melt pressing unused portions of the solvent cast material. The remolded materials were found to display the same near-linear, Hookean behavior upon deformation. The similarities in tensile behavior indicate that similar microstructures are attained for these materials whether they are fabricated as a result of solvent casting or melt pressing.

Ethylene/butylene based segmented polyureas were also synthesized using HDI as the diisocyanate and EDA or DY as the chain extender. These materials had HS contents between 8 and 9%. Both also developed percolated, ribbon-like microphase-separated morphologies with broad service windows, though less broad than the HMDI materials. The more narrow service window is attributable to the lower HS content and shorter HS length in the HDI based materials. This necessarily reduces the number of bidentate bonds in the material and lowers its upper

temperature limit. The shorter HS is also thought to be responsible for the different interdomain spacings as measured with SAXS, whereby the shorter HS leads to dissolution of some hard segments into the SS matrix and "effectively lengthens" the SS, shifting the interference peak to higher length scales. Direct visual evidence of the microphase-separated morphology was obtained by AFM for each of the HDI based materials. Each of these materials was also found to be reprocessable in a melt press as well, producing clear, uniform films.

7. THE INFLUENCE OF SELECTED SOLUTION CASTING VARIABLES ON THE SOLID STATE STRUCTURE OF SYNTHETIC GLUTAMATE FILMS INTRODUCTION

The focus of this work is an investigation of the solid-state structure of solution cast homopolymer polypeptide films based on glutamate substituents. Previous studies by Wilkes [144, 145] in 1972 also investigated the structure of similar polypeptide films. Those studies primarily used small angle light scattering (SALS) and wide angle x-ray scattering (WAXS) to analyze the morphology of the polypeptides in the solid state. It was postulated in those studies that the polypeptide films contained an optically anisotropic rodlike fibrillar microstructure. The basis for those earlier conclusions will be discussed in more detail in the pages ahead.

SALS was the primary technique used in the earlier work, but the proposed rodlike microstructure was not *directly* observed on the sub-micro scale with any available microscopic technique of the time. The advent of atomic force microscopy allows for a more *direct* view of the film's surface microstructure. This work is motivated by the desire to directly determine if such a rodlike superstructure exists and to determine if any correlation can be made with the SALS patterns.

7.1. BACKGROUND ON POLYPEPTIDES

Polypeptides and more complex proteins are built from sequences of amino acids and perform some of the most important functions in the body [99]. They can carry out catalytic functions as enzymes (globular proteins) and structural functions as tendons (structural proteins). They perform certain regulatory functions in the body such as metabolic control and management of hormone levels. Muscle fibers which give rise to movement are also composed of structural protein molecules such as myosin and actin. Proteins also comprise hair, nails, and skin.

Physiological polypeptide chemistry is based on the twenty naturally occurring amino acids, bifunctional organic compounds that contain an amino group and carboxylate group. The differences in properties of the individual amino acids arise due to the chemical nature of the

chemically different "R"-side chains bonded to the α -carbon (Figure 7.1). The α -carbon in these molecules is bonded to four different chemical species and is therefore a chiral center. Depending on the location of the R side group shown in Figure 7.1, the residue is termed an L-isomer or a D-isomer. The difference between these two stereochemically different forms is shown in the three dimensional Figure 7.2.

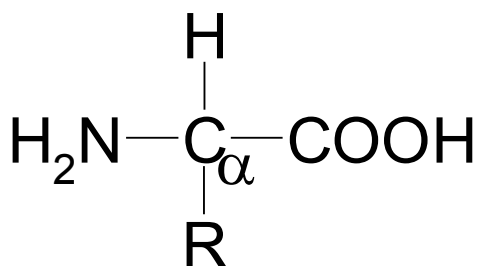


Figure 7.1. Amino acid residue which also shows the chiral alpha carbon center.

The amino acid residues can be chemically bonded to one another via a polycondensation reaction forming low molecular weight linear chain molecules termed peptides. When a peptide molecule grows to *ca.* 50 acid residues in length, it is termed a polypeptide [146]. Thus, peptides, polypeptides and proteins are all made from amino acid starting materials, chemically linked together.

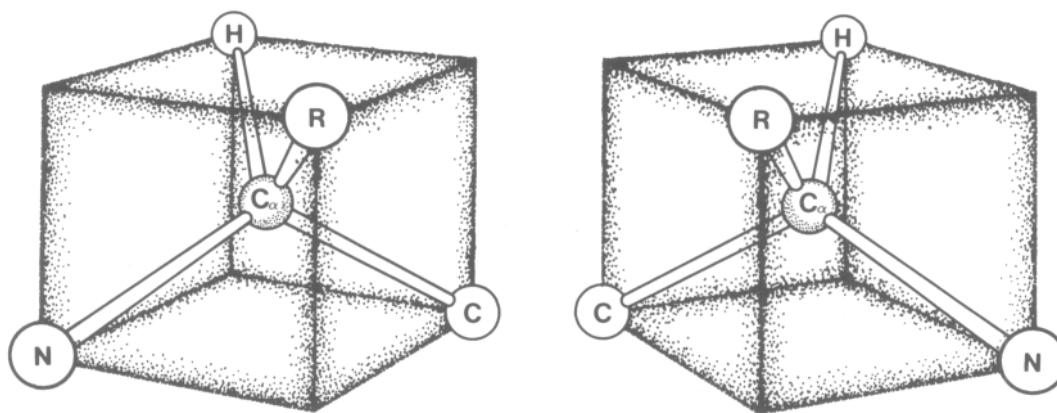


Figure 7.2. Amino acid residues showing L-isomerism and D-isomerism [146].

Focusing on protein and polypeptide structure, the primary structure is determined by the chemical sequence of amino acids that compose the macromolecule. Given the same chirality (L or D), polypeptide chains all contain the same nitrogen and carbon backbone and differ only by

the chemical species of the R-side chain on each amino acid residue. When the R-side chain lies on the left side of the backbone when tracing backbone in the order C–C_α–N, the molecular structure has L-isomerism (proteins found in nature display L-isomerism); when the R-side chain lies on the right side of the backbone, the structure has D-isomerism.

The polypeptide chains can adopt different conformations allowing for the interaction of non-adjacent amino acids via hydrogen bonding in particular. Secondary protein structure is defined by these different conformations, the most common of which are the α -helix and β -sheet structures are shown in a three-dimensional view in Figure 7.3. Again, the issue of chirality is of importance. The chain shown in Figure 7.3 is composed of L-isomer residues and therefore curves into a rightward turning helix. Conversely, a chain constructed of D-isomers would twist into a leftward turning helix.

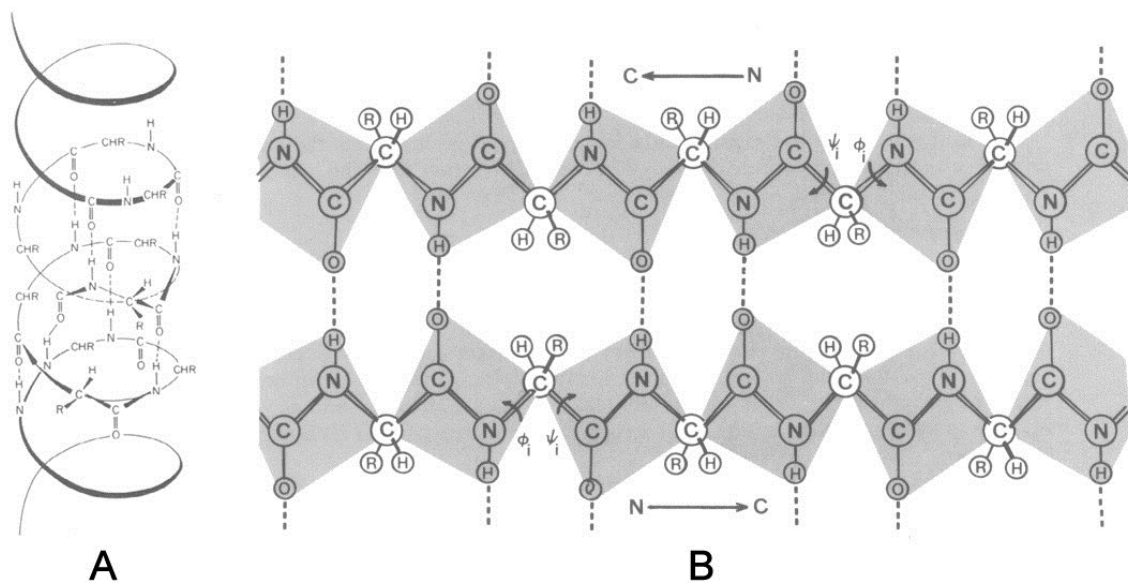


Figure 7.3. Bonding schemes for (A) α -helix displaying intramolecular hydrogen bonding and (B) β sheet conformations displaying intermolecular hydrogen bonding [146]. The schemes are shown at different scales.

The focus of the subsequent discussion will be on the α -helical structure as this is the proposed conformation for the materials used in this study. This conformation allows intramolecular hydrogen bonding to occur between the hydrogen atom of an amino group and an oxygen atom from a non-adjacent carbonyl group in the same chain. To attain this bonding scheme the molecule twists into an α -helix. This successive twisting down the length of the

chain gives rise to an elongated coiled molecule with a high aspect ratio (the ratio of the coil length to its helix diameter) and is stabilized by the intramolecular hydrogen bonds between the N–H groups and O=C groups which occur as the helix turns. The α -helix contains 3.7 repeat units per turn or about 18 amino acid residues in every five turns of the helix [146]. Due to their high aspect ratios, polypeptides in the α -helix conformation are often referred to as "rodlike" molecules. When such rodlike polypeptide molecules come into close proximity with one another they tend to arrange in such a way that their long axes, termed directors, become similarly aligned. This molecular packing can give the polypeptide solutions a degree of short-range order even in the liquid state depending on the concentration of the solution, its temperatures and the choice of solvent [147]. Even as solutions they may exhibit some order in one or two directions, though not the degree of three dimensional long range order of a crystalline material, while still displaying liquid-like properties such as flow under shear. If a material exhibits both liquid-like and one or two-dimensional ordered properties, these materials are often referred to as liquid crystals or mesophase systems. The focus of this study, however, will be the *solid-state* structure of synthetic polypeptide materials cast into film form. Put more succinctly, as the solvent in the polypeptide solution is removed via evaporation, what is the final morphology of the resulting films? And if the morphology is influenced by solvent evaporation, how sensitive is the final solid state structure to the specific casting conditions.

The aforementioned studies using SALS in conjunction with WAXS suggest that much is already known about the properties of polypeptide films, in particular poly- γ -benzyl-L-glutamate (PBLG), and poly- γ -ethyl-L-glutamate (PELG). SALS patterns obtained from polypeptide films indicate the presence of randomly oriented anisotropic rodlike structures. The exact nature and origin of the oriented structure is not yet fully understood. Work has also been done which demonstrates that this macroscopically random orientation can be modified and a longer scale preferential orientation induced in a number of ways. Preferentially oriented films and non-equilibrium structures will be briefly discussed later in the text. In addition, earlier WAXS studies have shown that samples produced from PBLG [148, 149], PELG and poly- γ -methyl-L-glutamate (PMLG) and poly- γ -methyl-D-glutamate (PMDG) [150] solutions are often semicrystalline depending on the sample's processing conditions.

This work focuses primarily on the three synthetic polypeptides mentioned thus far: PBLG, PELG and PMLG, though brief mention will be made of poly-N-hexyl-L-glutamate

(PnHxLG) as well. The solid-state structure of such films will be explored using a variety of techniques including the aforementioned SALS and WAXS but also including Polarized Optical Microscopy (POM), Scanning Electron Microscopy (SEM) and, particularly important, is the method of Atomic Force Microscopy (AFM). In addition to these measurement techniques, computer modeling of the SALS patterns from anisotropic rod scattering will be utilized to develop some insight on the length scales of certain features of these materials when they are in the solid state.

Prior to detailing particular results, it is important to ensure that the reader is comfortable with certain experimental techniques with which he or she might not be familiar. For this reason, a brief description of SALS is given here to assist the reader.

7.2. BRIEF REVIEW OF THE RELEVANT ASPECTS OF SMALL ANGLE LIGHT SCATTERING (SALS)

The SALS technique is one of the many methods for investigating the scattering behavior of solid polymeric samples in order to understand their superstructure. It was first used nearly fifty years ago by Stein and co-workers to study the structure of semicrystalline polymer films [151, 152]. The method uses polarized monochromatic electromagnetic radiation in the visible region to probe the morphological structure of polymers. The technique can be used when the sample is at rest or even while the sample is undergoing elongation or flow [151, 152].

The photographic SALS technique was first applied to polymeric films by Plaza and Stein [151]. Rather than the lasers used in light scattering work today, they first used polarizers and a mercury lamp for the light source. In 1959 they used the scattering of light at angles below 10° to characterize the structure of spherulitic polyethylene films. Measuring the scattering patterns of polyethylene films of different densities, they were able to quantitatively determine the diameter of the spherulitic structures in the films. Since that time, numerous other studies have been conducted on a wide array of polymeric samples that have shown that SALS can be used in many systems and can be a useful qualitative and quantitative tool [153, 154].

Before addressing the physics and mathematics governing the scattering of light in polymer systems, it is useful to outline the basic SALS experimental set-up. This should provide

some understanding of the experiment itself as well as supply sufficient background information so that further mathematical descriptions and derivations provided later will have a clearer physical meaning. An example of the typical experimental set-up is shown in Figure 7.4.

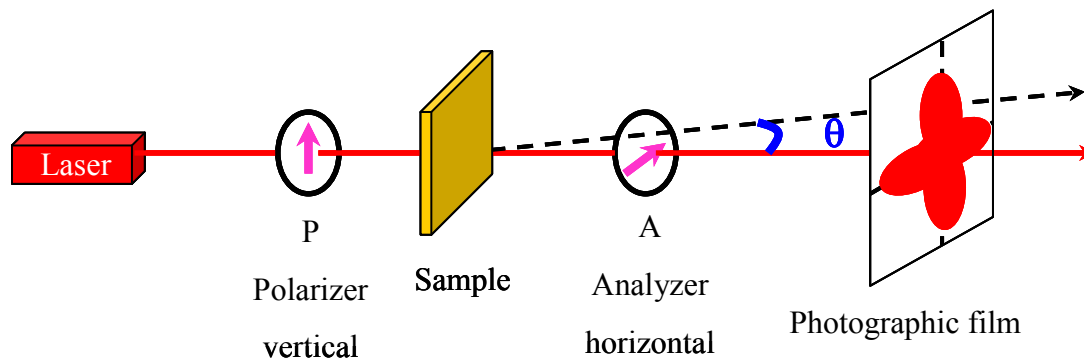


Figure 7.4. Typical SALS device set-up for H_v scattering.

There are several key features to the SALS device shown. The first is a monochromatic plane-polarized light source, typically a helium-neon laser producing an electromagnetic wave with a wavelength of 632.8 nm. In the absence of a plane polarized light source, a linear polarizer can be used to ensure a linearly polarized source of radiation. The electromagnetic wave propagates through the air striking the polymer sample of interest (as well as the glass slide the sample was cast upon and a thin layer of immersion oil used to minimize surface scattering [155]). Typically, the sample surface is also coated with a thin layer of non-interactive silicone oil with a refractive index similar to the refractive index of the sample. This layer of oil serves to reduce the effects of reflection and refraction from what would otherwise be a rough surface. In this way, the whole of the observed pattern can be attributed to the bulk scattering of the sample. The transmitted and scattered rays then pass through a second polarizer, commonly denoted as the analyzer, that has its polarization vector generally set in one of two ways. If the vector is set parallel to the polarization direction of the laser, the scattering is denoted as V_v scattering since both polarization directions are set vertically. If the analyzer is rotated 90° to the laser (as shown in Figure 7.4) it is denoted H_v scattering as the analyzer is horizontal and the polarizer is vertical. Other analyzer/polarizer arrangements such as H_h and V_h are also possible but are infrequently used. After passing through the analyzer, the light continues to propagate until it strikes a detector. The detector used in this work was a sheet of photographic film; however, other detectors such as CCD cameras have been utilized which allow the pattern to be recorded for

subsequent analysis. A standard H_v SALS pattern produced from an optically anisotropic PBLG film is shown in Figure 7.5. In this figure, the scattered intensity forms a four-lobed pattern around a center spot of high intensity and the intensity drops monotonically with scattering angle, θ . This high intensity spot is due to the transmitted beam and cannot be completely removed due to the partial inefficiency of the crossed polarizers. The lobes are formed around this spot oriented at several azimuthal angles, here: 0° , 90° , 180° and 270° to the vertical direction. Henceforth, patterns displaying four lobes at these angles will be termed a $0^\circ/90^\circ$ pattern.

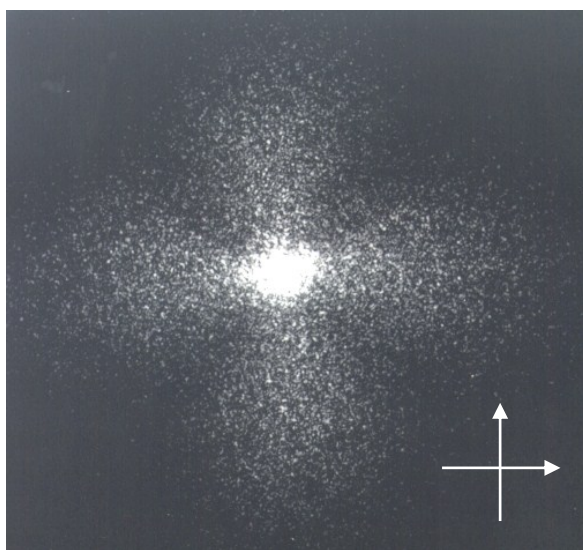


Figure 7.5. Typical H_v SALS pattern generated by a solution cast PBLG film. The arrows denote the directions of the polarizers described in Figure 7.4.

Prior to examining how the patterns produced in the SALS process are analyzed, it should be noted that there are a number of assumptions often made to ease analysis. Violation of any of these assumptions, which will be detailed subsequently, may render the analysis meaningless. As the light passes through the sample, its intensity decreases due to scattering caused by the variations in the dielectric tensor of the medium. These variations can be caused by a number of sources including: density fluctuations, fluctuations in local anisotropy that *do* correlate with the structure or orientation in the sample, fluctuations in local anisotropy that *do not* correlate with the structure or orientation in the sample, and optical rotation. Of concern in this study are the fluctuations in anisotropy that are attributable to the structure, order, and orientation in the film. Here, in the case of H_v scattering, the other sources of variation do not

seem of great concern. SALS evidence that optical rotation in particular is not affecting these patterns will be provided later.

The velocity of a linearly polarized electromagnetic wave in vacuum is denoted v_o . The film sample to be probed is assumed to be a nonabsorbing medium. Given that, the velocity of an electromagnetic wave entering such a medium undergoes a decrease in velocity to v_m . The ratio of the velocity of the wave in a vacuum to its velocity in the medium is defined as the refractive index of the medium, i.e.

$$n = v_o / v_m \quad (\text{Equation 7.1})$$

In these SALS experiments, it is assumed that any changes in refractive index of the system being studied are much less than 1. More specifically,

$$\left| 4\pi\Delta n \frac{l}{\lambda_{med}} \right| \ll 1 \quad (\text{Equation 7.2})$$

Equation 7.2 is known as the Rayleigh–Gans approximation [156]. If this assumption were shown to be invalid for a particular scattering system, the Mie approximation would likely need be used [156]. Since that is not expected in this study, the complexities of the Mie approximation will not be discussed. One final assumption is that the sample is thin enough to allow *ca.* 75% of the light to be transmitted; otherwise secondary scattering becomes an issue.

Generally, the patterns produced by polypeptide films in this work show four very distinct lobes with no obvious maxima in intensity as one scans any given lobe as a function of radial scattering angle, θ . This is in marked contrast to SALS patterns produced by optically anisotropic spherulites. The topic of spherulitic scattering, though not observed in this work, is briefly introduced as a comparison to the rod scattering from the polypeptide materials. As already mentioned, a good deal of work has been done on the SALS behavior of spherulites and the microstructural information that can be obtained from them is well known. As will be shown here, anisotropic rod scattering differs from spherulitic scattering in two respects. First, spherulites generally scatter producing a four-leaf clover pattern with lobes oriented at $\pm 45^\circ$, though this is not always the case, rather than in the $0^\circ/90^\circ$ pattern discussed previously (Figure 7.5). A typical spherulitic scattering pattern is shown in Figure 7.6.

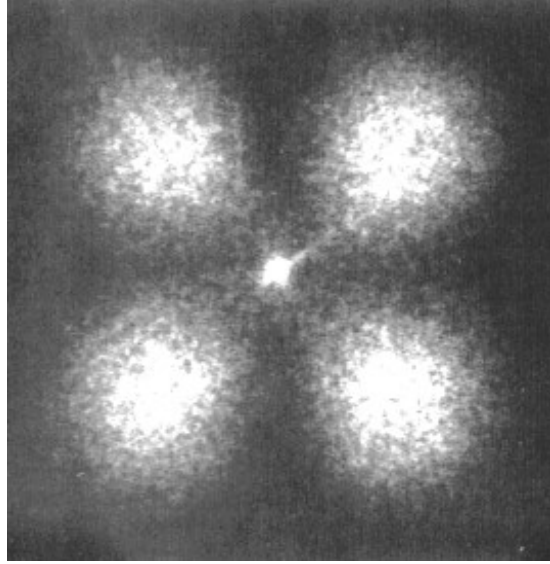


Figure 7.6. Typical well developed H_v SALS scattering pattern from an optically anisotropic spherulite. The sample utilized in this case was poly(ethylene terephthalate) (PET).

Secondly, spherulitic patterns typically display a distinct maximum in intensity as one scans through the radial scattering angle in the direction of a lobe. The location of this peak in intensity, if present, can be directly correlated with the size of the spherulite. For an H_v scattering set-up, the spherulite radius R_0 can be quickly calculated from Equation 7.1 [157]:

$$\frac{4R_0}{\lambda_m} \sin\left(\frac{\theta_{\max}}{2}\right) = 4.09 \quad (\text{Equation 7.3})$$

Here, λ_m is the wavelength of the scattered wave in the medium and $\theta_{\max}$ is the radial scattering angle at which the maximum in intensity is measured.

Obviously then, SALS can be a very useful technique for quickly characterizing the size of a spherulitic sample's superstructure. However, scattering from optically anisotropic rods is very different and the interpretation of scattering patterns is not straightforward. This subject will be addressed in the next section.

7.3. SMALL ANGLE LIGHT SCATTERING MODELS WITH EMPHASIS ON OPTICALLY ANISOTROPIC RODS

Once a SALS experiment is performed and a light scattered pattern is produced, it is hoped that the pattern can be analyzed to obtain morphological information. Figure 7.7 shows a second example of an H_v SALS pattern; in this case the sample is PBLG cast from a chloroform solution. This pattern may be analyzed using one of the approaches detailed in the next sections. Such analysis has traditionally been done in one of two ways, utilizing either a “structural” model or a statistical approach depending on certain factors.

The model approach assumes a specific morphological structure that may allow for the calculation of the expected scattering pattern. When lacking previously known structural information, a statistical approach is often used instead. In that method, an analysis is performed on the scattered pattern to obtain information regarding average isotropic and anisotropic fluctuations in refractive index, correlation length and various correlation functions [157]. This less informative approach is not necessary for systems where an appropriate structural model can be justified. As will be made clear in the present investigation, the polypeptide films studied display an optically anisotropic rod structure that warrants the use of the model approach.

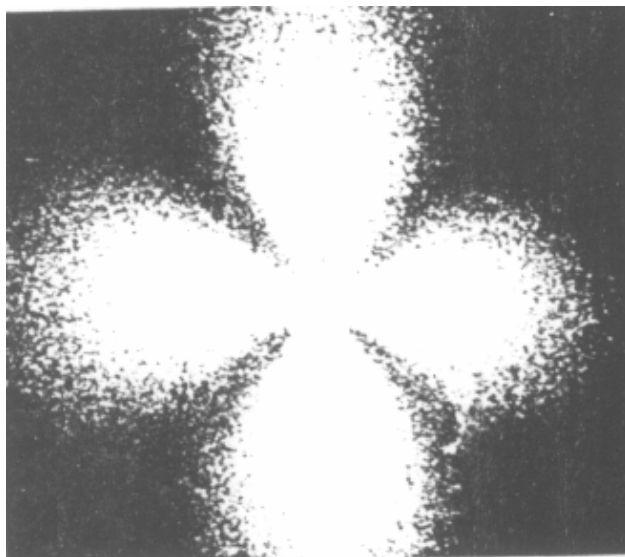


Figure 7.7. An H_v SALS pattern produced from a chloroform cast film of PBLG. The pattern can be analyzed to determine structural information [144].

The basic anisotropic rod model utilized for this work was first derived by Rhodes and Stein in 1969 [158]. It allows for the calculation of both H_v and V_v scattering patterns based upon the angle that the direction of maximum polarization (and the direction of maximum refractive index) makes with the rod axis. It also allows for the calculation of scattering patterns when the direction of maximum polarizability has changed relative to a reference axis in the sample due to any orientation of the rods that might be induced in the sample. Such global orientation of the rodlike molecules can often be produced in a number of ways: mechanically, electrically [159-162], or magnetically [144, 163]. Examples of each of these orientation methods and results from them will be presented later in the text. The model approach also allows for the quantification of the level of rod orientation in the samples via an orientation distribution parameter. What follows is a summary of the derivation of the scattering equation by Rhodes and Stein [158]. To provide some physical meaning to what follows, a schematic presentation of the coordinate system utilized is presented in Figure 7.8.

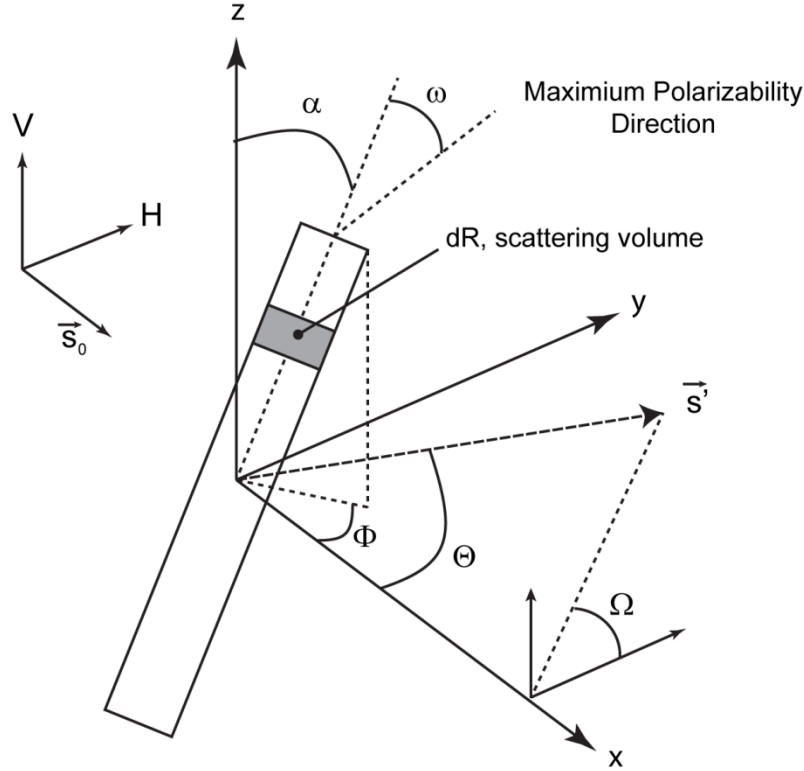


Figure 7.8. Anisotropic rod scattering coordinate axes. V is the direction of the vertical polarizer, H is the direction of the horizontal polarizer, $\vec{s}_0$ is the direction of the incoming wave, $\vec{s}'$ is the scattered wave direction. ω is the angle between the long axis of the scattering rod and the direction of maximum polarizability. α is the angle between the z-axis and the long axis of the scattering rod. The angles Θ , and Ω are the angles between $\vec{s}'$ and the x and y axes respectively.

The model begins with an expression for the amplitude of a scattered electromagnetic wave from a single scattering center. This classic result is:

$$dE = \rho e^{ik(\vec{r} \cdot \vec{s})} d\vec{r} \quad (\text{Equation 7.4})$$

In Equation 7.4, dE represents the amplitude of the scattered wave from a single volume element with length $d\vec{r}$ located at a distance r from the origin. Here we assume that these are rods of infinitesimal thickness such that their width is negligible compared to their length L . The scattering amplitude per unit length of rod ρ is independent of r . The wavenumber k is defined here as $2\pi/\lambda_m$. Note that λ_m is wavelength of the radiation inside the scattering medium. The last undefined term in Equation 7.4 is $\vec{s}$, which can be defined by:

$$\mathbf{s} = \mathbf{s}_0 - \mathbf{s}' \quad (\text{Equation 7.5})$$

where, referring back to Figure 7.8, $\mathbf{s}_0$ is the unit vector along the x-axis and $\mathbf{s}'$ is in the direction of the scattered wave. From the geometry of the coordinate system shown in Figure 7.8, one can derive the classical relationship:

$$(\mathbf{r} \bullet \mathbf{s}) = ar \quad (\text{Equation 7.6})$$

where a is defined as:

$$a = \sin \alpha \cos \phi (1 - \cos \theta) - \sin \alpha \sin \phi \sin \theta \cos \Omega - \cos \alpha \sin \theta \sin \Omega \quad (\text{Equation 7.7})$$

This a term can be further simplified for the case where $\phi = 90^\circ$ to,

$$a = -\sin (\alpha + \Omega) \sin \theta \quad (\text{Equation 7.8})$$

Substituting Equation 7.6 into Equation 7.4, one obtains the expression:

$$dE = e^{ikar} dr \quad (\text{Equation 7.9})$$

Integrating this expression over the total volume from $-L/2$ to $L/2$ (reference Figure 7.8) one obtains the total amplitude of the scattered radiation. The solution to that integration is,

$$E = \rho L [\sin (kaL/2)] / (kaL/2) \quad (\text{Equation 7.10})$$

where ρ is defined as the scattering power of the rod. The following relationship is used to define the nature of ρ :

$$\rho = \rho_0 [\delta \sin \alpha \cos \alpha \sin \phi] \quad (\text{Equation 7.11})$$

ρ_0 is the scattering power of a rod per unit length per unit incident field strength when the rod is oriented at $\alpha = 0^\circ$.

When this result is substituted into Equation 7.9 and integration is performed, one can obtain the amplitude of a scattered wave due to any experimental set-up. For H_v scattering, the integrated solution is:

$$E_{Hv} = \rho_0 L \delta \sin \alpha \cos \alpha \sin \phi [\delta \sin \alpha \cos \alpha \sin \phi] \quad (\text{Equation 7.12})$$

where δ is the optical anisotropy of the rod, i.e. the difference in the polarizability of the rod in the longitudinal and tangential directions. From electromagnetic theory, the intensity of a scattered wave is proportional to the square of its amplitude. To obtain the intensity, one simply

sums the scattered amplitudes from all the scattering rods in the assembly and promotes the square of this result.

Note that until this point, no mention has been made of any orientation of the rod molecules. If we now assume that there is a nonrandom distribution of rods and that the distribution is restricted to a two-dimensional assembly (which would be reasonable for the case of a thin film sample), a useful distribution function, $N(\alpha)$, has been defined by Stein as:

$$N(\alpha) = N_0 (\varepsilon^{-2} \cos^2 \alpha + \varepsilon^2 \sin^2 \alpha)^{-1/2} \quad (\text{Equation 7.13})$$

where N_0 is the number of rods per unit of volume each being of length L and having a scattering power of ρ_0 . In Equation 7.13, ε defines the degree of orientation of the rod assembly. To provide some physical meaning to the parameter, when $\varepsilon = 1$, $N(\alpha)$ is constant and equal to N_0 . In this case, there are equal numbers of rods associated with all values of α , i.e. a random distribution of rods. Here, the rods have no net orientation and are aligned in all directions equally. If $\varepsilon = 2$, there are now twice as many rods at $\alpha = 0^\circ$ (recall Figure 7.8) as compared to the undeformed state. The following plot (Figure 7.9) may help further elucidate the meaning of this orientation parameter, ε . Note again that at $\varepsilon=1$, the population of rods is equal for all values of α . However, as ε varies, the distribution of rods changes. With increasing values of ε , there are more rods aligning near $\alpha = 0^\circ$ values and fewer at angles greater than 45° . Here then, we see the gradual alignment of rods in the scattering assembly as a whole.

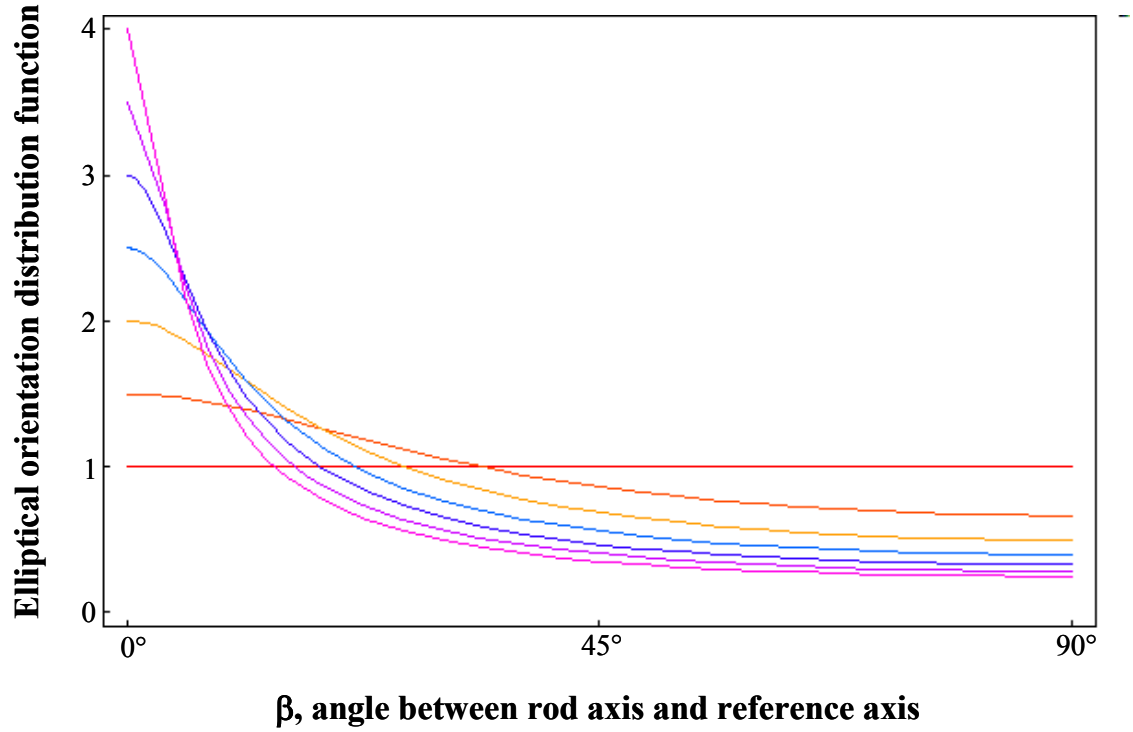


Figure 7.9. Two-dimensional distribution of rods calculated as a function of rod orientation with a reference axis. Values other than $\varepsilon = 1$ indicate that the scattering bodies are preferentially oriented with higher values indicating higher levels of orientation.

Combining Equation 7.13 with Equation 7.12 and integrating, one arrives at the final equation for the scattered intensity for the H_v case:

$$I_{H_v} = \rho_0^2 N_0^2 L^2 \int_{\beta=0}^{\pi} \left(\varepsilon^{-2} \cos^2 \beta + \varepsilon^2 \sin^2 \beta \right)^{-1/2} \delta^2 \sin^2 \beta' \cos^2 \beta' \left[\frac{\sin(kaL/2)}{kaL/2} \right]^2 \partial \beta$$

(Equation 7.14)

This equation will be discussed in further detail in a subsequent section where it is modeled using a computer routine. The effects of individual parameters will be discussed later and their impact on the conclusions noted.

Having now discussed the general direction of the study and some of the basic scattering theory behind the SALS technique, we turn our attention to the specifics of this project.

7.4. EXPERIMENTAL SETUP

7.4.1. MATERIALS

7.4.1.1. Polypeptides

Polypeptide homopolymer samples were purchased from Sigma-Aldrich Inc. Samples included: poly (γ -benzyl L-glutamate), poly (γ -ethyl L-glutamate), poly (γ -methyl L-glutamate), and poly (γ -N-hexyl L-glutamate). The chain properties of the individual polypeptides are provided in Table 7.1. In general, the focus of this work will be on PBLG and PELG materials.

In each material, the peptide backbone is identical to that shown in Figure 7.10. The specific substituents for the “X-group” are also provided.

Table 7.1. Polypeptide molecular weight data as provided by Sigma-Aldrich Inc.

Polypeptide	MW (g/mol) (viscosity)	DP (viscosity)	MW (g/mol) (light)	DP (light)
PMLG	37,200	260	25,000	175*
PBLG	110,000	502	134,500	614
PELG	268,000	1,707	384,600	2,450
PnHxLG	48,700	228	60,500	284

* The degree of polymerization as measured by light is lower than when measured by viscosity for this sample. These numbers were provided by the manufacturer and are included with that odd caveat.

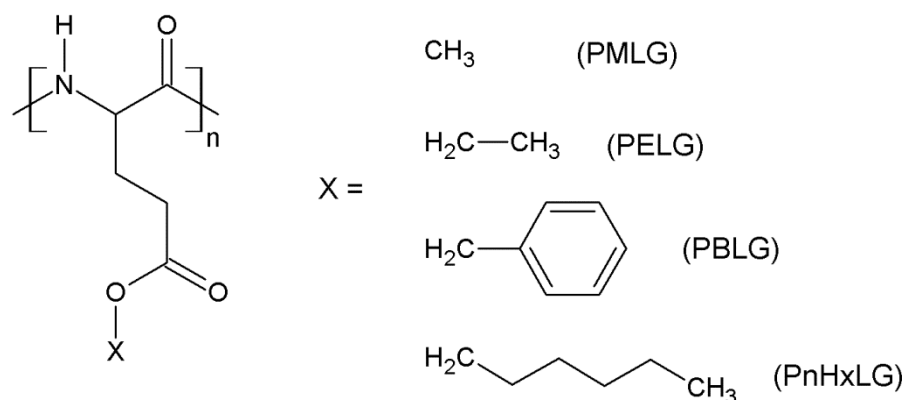


Figure 7.10. Repeat units of polypeptides used in this work.

7.4.1.2. Solvents

Solvents used were purchased through Sigma-Aldrich Inc. They included formic acid (CH_2O_2) from Fluka Chemie AG. Formic Acid has a molecular weight = 46 AMU and a boiling point of 100.8 °C (213.4 °F). The 1,1,2,2-tetrachloroethane (TCE), ($\text{C}_2\text{H}_2\text{Cl}_4$), was from Aldrich Chemical Company and has a molecular weight = 168 AMU and a boiling point of 145 °C (293 °F). The chloroform (CHCl_3) used was from Burdick & Jackson and has a molecular weight of 119 AMU and a boiling point of 62 °C (143 °F).

7.4.2. SAMPLE PREPARATION

Polypeptide solutions were prepared by dissolving a small quantity (*ca.* 50 mg) of solid polypeptide at ambient temperature in one of three solvents; FA, TCE, or chloroform to the final desired solution concentrations. Three specific concentrations were used in this study were 0.5%, 5%, or 15% (g/ml) and are noted in the text.

Polypeptide film samples were produced by casting from solution using the following procedure. A small volume of solution was poured onto one end of a silica glass or quartz slide. A doctor blade set to a predetermined height was then drawn across the surface of the slide. The shearing force applied via the doctor blade caused the solution to spread evenly across the face of the slides in *ca.* 1 sec. Care was taken to try to draw the doctor blade across the glass slides at the same speed for each sample. Slides hereafter denoted as “fast cast” were then left in a fume hood

while the solvent evaporated off. Evaporation times varied from a few seconds to minutes depending on the boiling point of the solvent used. Alternatively, slides denoted as “slow cast” were placed inside a crystallization dish that had been saturated with the same solvent as the polypeptide solution from which the films were cast. Using this method, the evaporation rate of the solvent coming off the slides could be slowed considerably. Slides were placed in the desired casting environments while film formation took place over the course of a few hours to days.

7.5. EXPERIMENTAL TECHNIQUES

7.5.1. SMALL ANGLE LIGHT SCATTERING (SALS)

SALS experiments were carried out in a darkroom allowing for the exposure of a single piece of Polaroid 10.16 cm × 12.7 cm black and white sheet film. One of two laser light sources was used to produce scattering patterns. Some patterns were produced with a Spectra Physics Stabilite™ model 120 He–Ne laser powered by a Spectra Physics 256 Exiter. An instability developed during the use of the laser that later prompted the purchase of another laser source. This was a JDS Uniphase model 1137P He–Ne laser powered by a JDS Uniphase Power Supply model 1202-1. In either case, the wavelength produced by the laser remained $\lambda = 632.8$ nm. A piece of vertical polarizing Polaroid film was placed in the path of the laser to ensure a plane-polarized beam. Having passed through the film sample, the laser beam encountered a horizontal piece of polarizing film, termed the analyzer, and the resulting transmitted and scattered rays were collected by using the photographic film sheet. In this study, the sample to film distance was generally 101.6 cm. A user controlled camera shutter was placed in the beam path and was used to set the exposure time of the film precisely. The resulting photographed film patterns were then analyzed to determine the size and shape of the scattering structures in the film samples. A schematic of the SALS set-up was shown previously in Figure 7.4.

7.5.2. *MATHEMATICA*[®] COMPUTER CALCULATIONS

A computer routine was developed based on the fundamental light scattering equations discussed earlier and which had been derived first by Rhodes and Stein. Using the software package *Mathematica*[®] produced by Wolfram Research, SALS patterns were predicted as a function of numerous scattering variables including: radial scattering angle θ , azimuthal scattering angle μ , length of optically anisotropic rod L , angle between optic axis and rod axis ω , and the orientation parameter ε . A printout of the computer code required to run the modeling routine is provided in the appendix.

7.5.3. *POLARIZED OPTICAL MICROSCOPY (POM)*

Optical microscopy was performed with a Zeiss Axioskop from Carl Zeiss, Inc. The microscope possessed a rotational and centerable mechanical stage with coaxial controls. The stage provided x, y graduation on the coaxial controls and was rotatable through a full 360°. Micrographs were taken with an SLR camera using Kodak Gold ISO 200 film.

7.5.4. *ATOMIC FORCE MICROSCOPY (AFM)*

AFM was performed using a Digital Instruments (now Bruker Corp.) Dimension 3000 atomic force microscope with a NanoScope IIIa controller. The microscope was operated at ambient temperature in the tapping mode using Nanodevices TAP300 silicon cantilevers with a 40 N/m spring constant and an approximate 300 kHz resonant frequency. The free air amplitude was normally set at 2.8 V. The tapping force was varied by controlling the set point for each scan and was varied depending on sample conditions. Typically, a value was chosen so that the set point ratio fell in the range 0.4 to 0.7, constituting hard to medium tapping strengths. Scans were done at a frequency of 1 Hz.

7.5.5. SCANNING ELECTRON MICROSCOPY (SEM)

Electron microscopy was performed using the Leo 1550 Field Emission–Scanning Electron Microscope (FE–SEM). To attain a conducting surface for the purpose of good electron conduction, samples were sputter coated with a 4 nm layer of gold using a Cressington 208 HR sputtercoater in conjunction with a Cressington mtm 20 thickness controller.

7.5.6. WIDE ANGLE X-RAY SCATTERING (WAXS)

Photographic flat WAXS studies were performed using a Philips PW 1720 X-ray diffractometer emitting Cu–K $_{\alpha}$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The operating voltage was set to 40 kV and the tube current set to 20 mA. The sample to film distance was set at 47.3 mm for all samples. Direct exposures were made using Kodak Biomax MS film in an evacuated sample chamber. X-ray exposures lasted four hours. Sample thicknesses ranged from 0.25 mm to 0.43 mm.

7.5.7. CASTING OF PBLG SOLUTIONS IN AN ELECTRIC FIELD

In some instances, films were cast from solution in the presence of a DC electric field. To prepare samples, electrical tape was used to form a channel on the conductive side of an Indium Tin Oxide (ITO) coated glass slide. The backside of the slide was also taped over to prevent the chemical etching solution from attacking the back of the glass which could lead to an opaque slide. The thickness of the ITO layer ranged from 150 to 200 nm. After taping, the slides were placed in a 1:1 hydrochloric acid (HCl):deionized water (DI) solution for one hour. The slides were removed from the solution and rinsed with DI. Slides were then placed in a base cleaning solution of 92.5 mL DI, 10.25 mL hydrogen peroxide (H $_2$ O $_2$), and 17.25 mL ammonium hydroxide (NH $_4$ OH) for 30 minutes. After removal from the base bath, the tape was removed and the slides were again rinsed in DI and dried with a stream of nitrogen gas. The resulting slide has a non-conductive etched channel in the middle of a conductive ITO layer. Copper tape electrodes were attached to the conductive sides of the slide and DC power source was used to apply the

desired field (50 V/mm) across the channel. Polypeptide solutions were then added dropwise to the center of the channel. The solvent was allowed to evaporate while the electric field was applied.

7.6. RESULTS AND DISCUSSION

In this study, polypeptide films were first analyzed using the SALS technique. As previously mentioned, it was assumed that the scattering patterns were not affected by optical rotation in the sample, i.e. the four lobes stay in the same position as the film thickness is increased. As justification for that assumption, two figures are presented below which differ in their thicknesses but not their chemistry Figure 7.11.

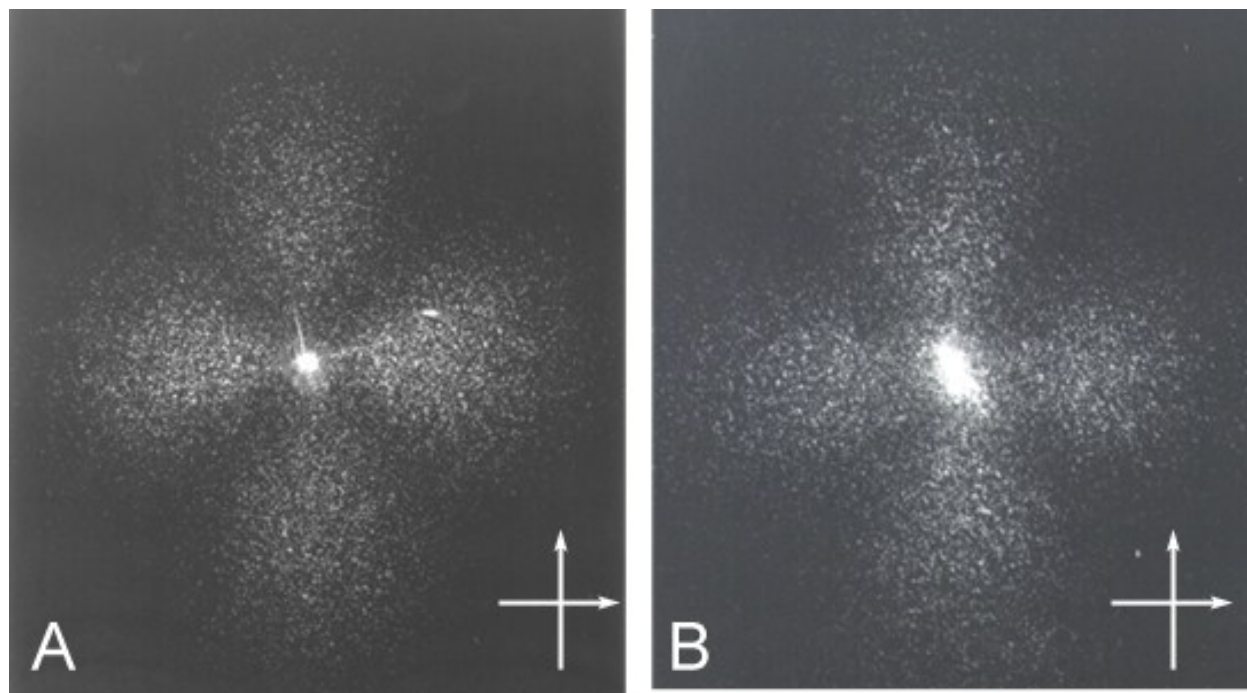


Figure 7.11. PBLG H_v SALS patterns: A) film cast from 1% chloroform solution; B) film cast from 5% chloroform solution.

These PBLG films were cast from solutions of different concentration which resulted in film thicknesses of 0.06 mm–0.11 mm. Having ruled out optical rotation as a factor in the scattering patterns, we can make the assertion that the H_v scattering from the sample is due only

to the fluctuations in local anisotropy that correlate with the structure or orientation in the sample. This is obviously an important result as now any changes in the scattering pattern are attributable to the morphology of the film sample being studied.

Recall from the earlier discussion that SALS patterns taken of spherulitic structures allowed for the calculation of a length scale for the scattering body. However in the present case of anisotropic rod scattering the patterns lack a maxima in intensity as a function of scattering angle, θ . Therefore there is no direct way to easily measure the size of the scattering body as one can often do with spherulitic patterns. To have the ability in some way to quantify or estimate the scattering system of these polypeptide films, a computer routine was developed, the results of which will be discussed in a later section.

The samples used in this study were predominantly PBLG and PELG. Figure 7.12A, B shows two H_v SALS patterns that are representative of the results for each of these two materials. Both patterns were taken on films cast from chloroform solutions. These same patterns, though not presented here, are seen in films cast from TCE as well. Samples of PELG and PMLG cast from 5% formic acid did not display this type of scattering behavior. The H_v patterns produced by PELG films were typically halos of equal intensity at all angles θ , whereas the PMLG samples produced very little scattering at all.

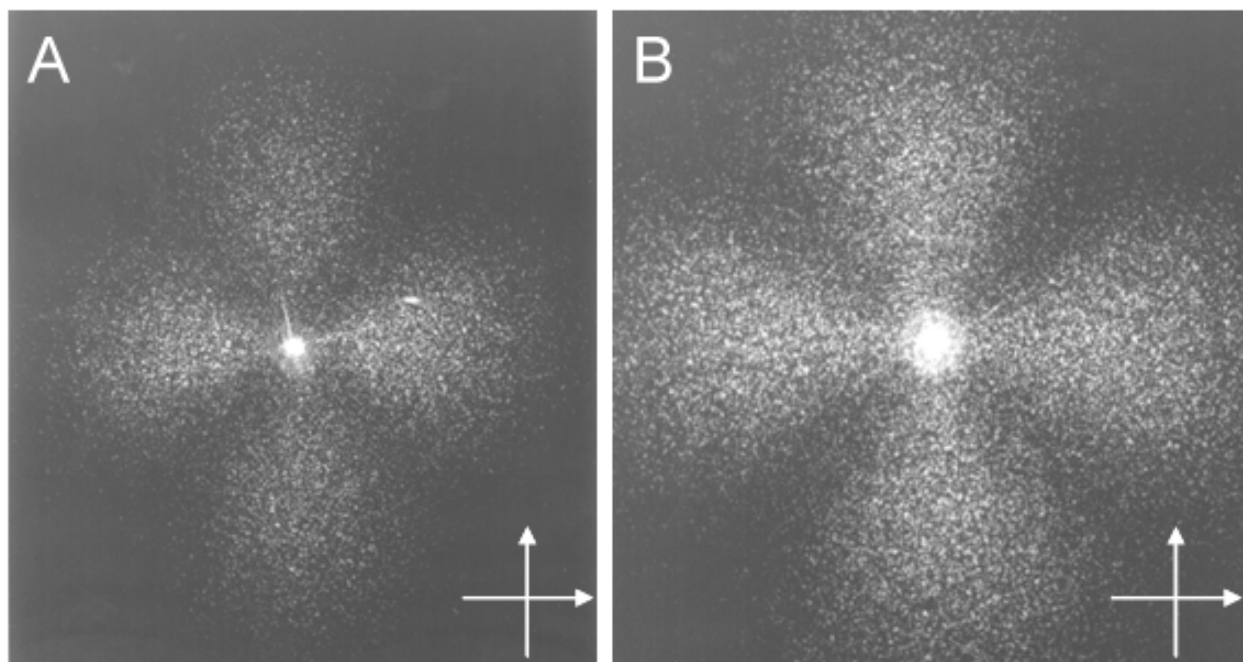


Figure 7.12. A) PBLG H_v SALS pattern film cast from 1% chloroform solution; B) PELG H_v SALS film cast from 5% chloroform solution.

Fast cast PBLG, PELG and some PMLG films, cast from both chloroform and TCE, showed the characteristic pattern with lobes oriented at $\mu = 0^\circ$ and $\mu = 90^\circ$. These patterns all indicate that the films have an optically anisotropic rod packed structure, a structure similar to those seen in previous studies of both synthetic and naturally occurring polypeptide systems [164-166]. Because PBLG would not dissolve in formic acid, no films of this polypeptide were produced from this solvent.

Slow cast films from solution concentrations as low as 0.5% were also analyzed. These solutions were cast and placed into a solvent saturated environment with the hope that given a longer evaporation time than the other samples, the thermodynamically preferred structure would develop in these films. However, without the use of the closed environment system, solvent evaporation would still proceed quickly, locking in a structure which may not be thermodynamically preferred. These lower concentration PBLG and PELG samples cast in chloroform and TCE saturated environments also displayed $0^\circ/90^\circ$ patterns, showing that the rodlike structure is maintained when cast from very low concentration solutions. *It follows from the similar results of slow cast 0.5% and fast cast 5% solution cast films that the rod-like*

microstructure is not concentration dependent, or rate of evaporation dependent over the concentration range investigated.

Beyond the identification of a preferred structure, in this case optically anisotropic rods, it would be useful to determine a characteristic size of the scattering bodies. As stated previously, quantitative information about the size of the scattering body must be addressed with a technique other than light scattering.

As stated earlier, in order to gain a more complete understanding of the small-angle light scattering patterns, a computer routine was written. Using this routine, a user has the ability to vary one parameter in the scattering equation and monitor how that change affects the size and shape of the resulting scattering pattern. A summarized derivation of the equation that predicts the scattered intensity profile from just such a system was discussed earlier. That equation for scattered intensity (Equation 7.14) was programmed using *Mathematica*[®] software. The equation allows for the variation of the orientation parameter, ε , angle of maximum polarizability, ω , and length scale, L . It is important to note some of the assumptions used in the model so that its use can be justified.

The model does not take into account which polypeptide is being modeled. In fact, it does not assume that the scattering material is a polypeptide at all. The main assumption used is that the scattering bodies are anisotropic rods of infinitesimal thickness. Anisotropic rods seem a plausible model for these systems given previous work done with both synthetic and naturally occurring polypeptides [145, 164-166]. The assumption also seems justified here in light of the fact that observed SALS scattering patterns are in fact predicted quite well with this model. In addition to the SALS patterns, optical micrographs will also support this conclusion. A discussion of those results will come later.

The routine was first applied to see how different ranges of scattering angle would affect the SALS patterns observed. Figure 7.4 will remind the reader of how this angle is measured in relation to the incident light beam. Four calculated SALS patterns are shown in Figure 7.13; each calculated as having no net orientation (orientation parameter $\varepsilon = 1$), angle of maximum polarizability $\omega = 45^\circ$, and a rod length scale of $L = 1 \mu\text{m}$. It is clear that the observed pattern looks quite different depending on the radial angular window used. This is true despite the fact that the pattern is in fact the same. The labeled angles associated with each pattern indicate the angle as measured from the center of the pattern out to the pattern edge moving either vertically

or horizontally. The corners of the calculated patterns are at angles noted and therefore the sides of the patterns are actually at smaller angles than the labels indicate.

It is clear then, that it is of supreme importance to keep in mind the sample-to-film distance, previously noted as *ca.* 101.6 cm, as one works with the SALS photographs obtained by the investigator because the size and shape of the scattered pattern is related to the observed angular scattering “window”. It would be easy to misinterpret the structure without knowledge of the range of radial scattering angles encompassed within a given H_v pattern.

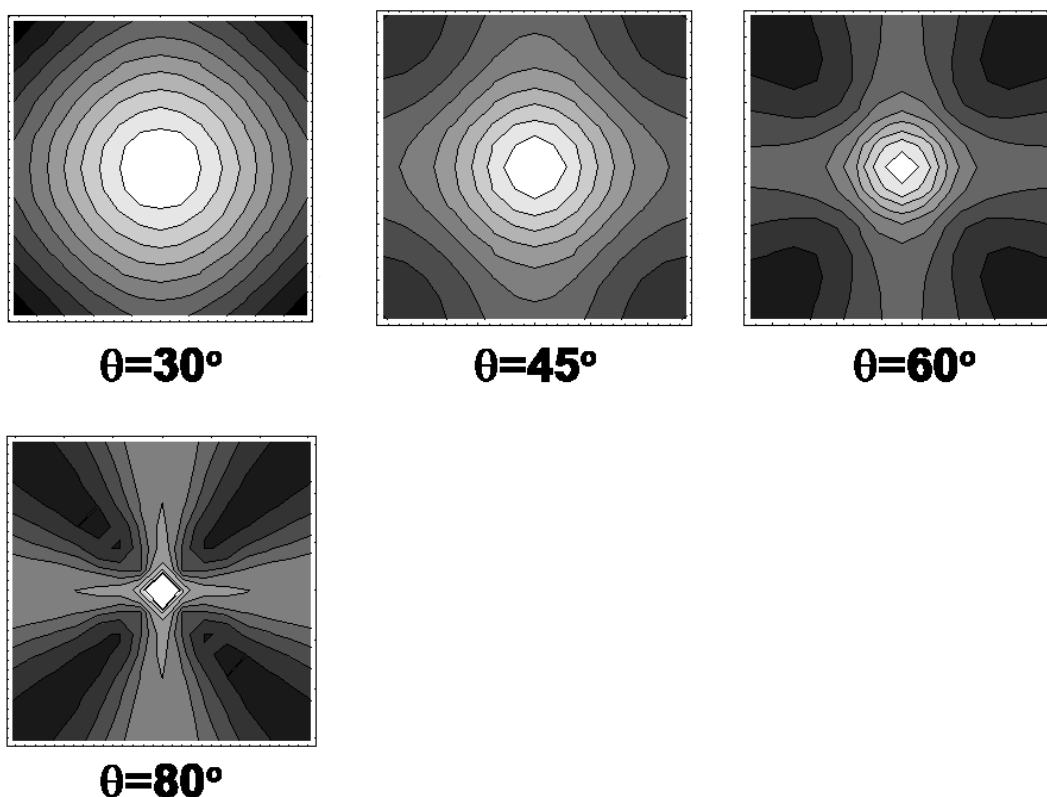


Figure 7.13. Calculated H_v SALS patterns based on optically anisotropic rod scattering showing the effect of radial scattering window on the pattern: $\varepsilon = 1$, $\omega = 45^\circ$, $L = 1 \mu\text{m}$. The scattering angles indicated apply to the corners of the calculated patterns.

Using these same four patterns, the effect of the length of the scattering rods was then investigated by allowing it to change while the other variables were held constant. If armed with a knowledge of the general features of Bragg's law ($n\lambda = 2d \sin \theta$) one expects that an increase in the length scale of a scattering body would force its corresponding scattered pattern to compress to smaller radial angles. The calculated patterns bear that out. The patterns shown in Figure 7.14

are the same as the previous patterns in all respects except for the length of the rods input into the model. In this case, the anisotropic rod length was simply doubled from 1 μm to 2 μm .

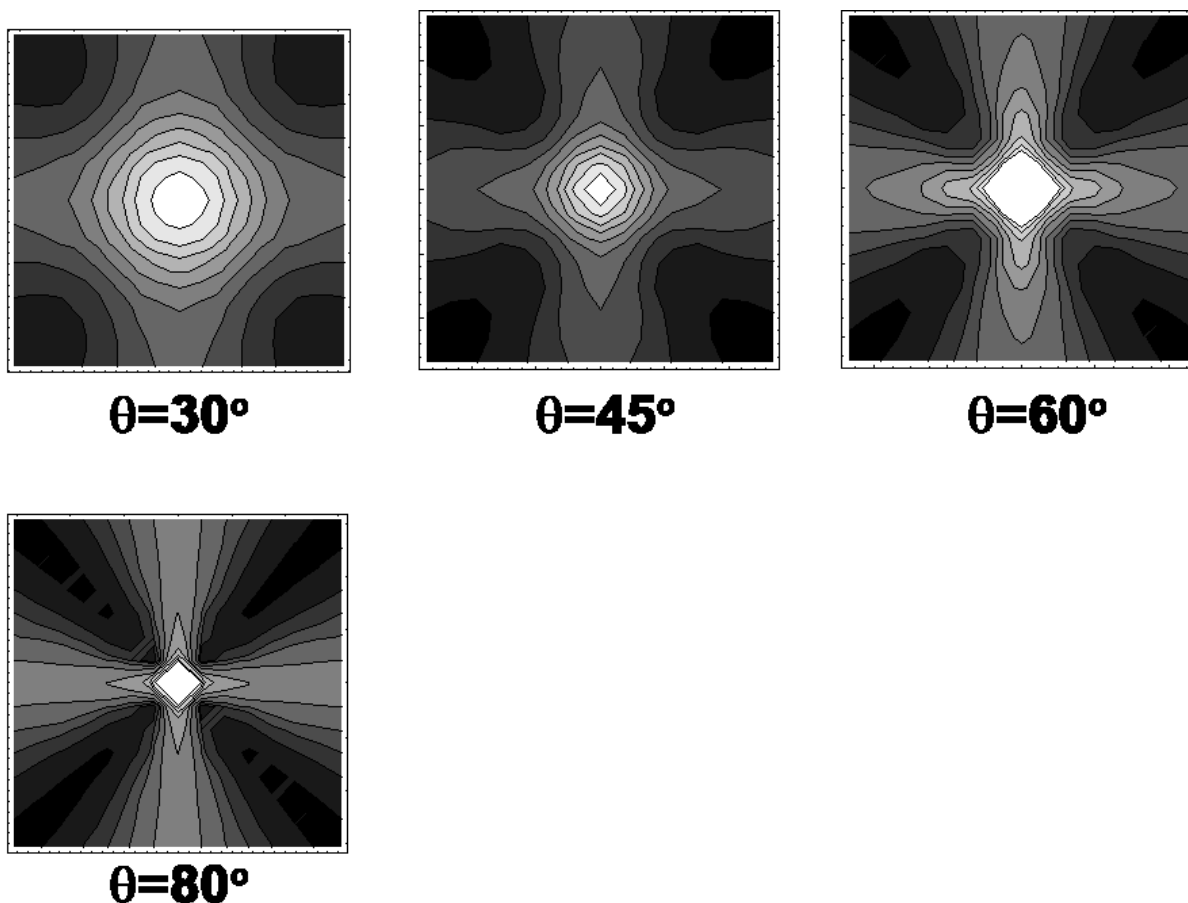


Figure 7.14. Calculated H_v SALS patterns based on optically anisotropic rod scattering displaying the effect of radial scattering angle window on the scattered pattern: $\varepsilon = 1$, $\omega = 45^\circ$, $L = 2 \mu\text{m}$.

Referring back to the previous two figures, one can see that the scattering patterns for each angle are essentially the same but that in the latter, the light is scattered at smaller angles. It is clear from this short calculation that there are observable differences in SALS patterns from changing the length of the rods in the model. Using this information, an estimate of the size of the scattering rods was obtained by predicting the scattered patterns for a series of rod lengths. Those predictions were then compared to actual photographed SALS patterns to roughly estimate the length of the scattering bodies in the polypeptide systems. The following group of calculated patterns (Figure 7.15) shows the results of this calculation. In this model, a scattering window of

θ from 0 to 6.7° was chosen for the series of calculations corresponding to the actual scattering angle range used during the experiment.

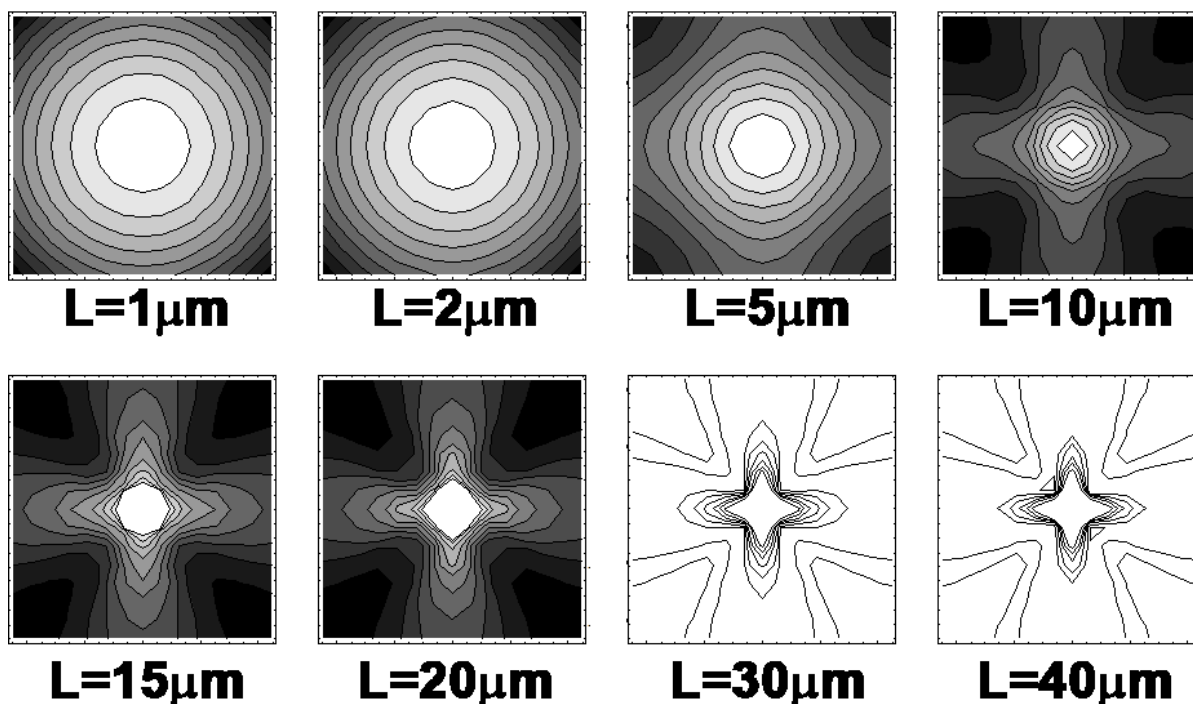


Figure 7.15. H_v SALS pattern calculations based on optically anisotropic rod scattering for various length scale scattering bodies. $\omega = 45^\circ$, $\varepsilon = 1$, varying L .

Again, it is clear that the size of the scattering body input into the model affects the resulting pattern. This result allows for a rough estimate of a length scale for the scattering body.

The variation in the contrast in the last two patterns in Figure 7.15 is due solely to the ability of the computer to resolve the range of contrast. By comparing the calculated patterns above to the photographed patterns seen previously, it is clear that the photographed patterns most resemble the calculated pattern corresponding to a rod length of about $10 \mu\text{m}$. In fact, the photographed patterns are in most cases similar to the calculated patterns with $L \geq 10 \mu\text{m}$. Based on the similarities between the model predictions by the computer routine and actual photographed patterns, it seems safe to say that the length of the scattering bodies in the polypeptide film samples are *at least* on the order of $10 \mu\text{m}$.

A final variable in the anisotropic rod scattering equation that can be studied with the computer simulation is the angle ω , the angle between the long axis of each rod and the direction

of maximum polarizability of the rod. The computer routine used was modified slightly to account for both positive and negative deviations from $\omega = 0^\circ$. For example, the pattern in Figure 7.16 is calculated by summing the results for the $\omega = +10^\circ$ and $\omega = -10^\circ$. Figure 7.17 shows a series of calculated patterns generated by summing the positive and negative deviations from $\omega = 0^\circ$.

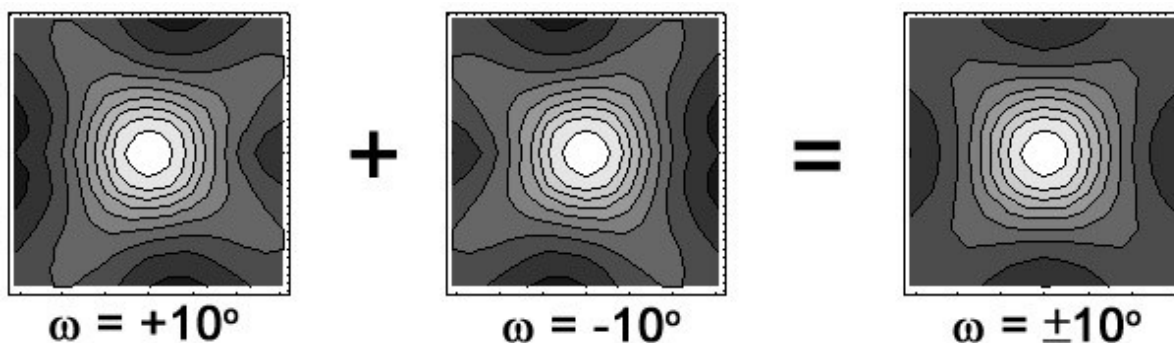


Figure 7.16. Calculated SALS patterns for rods oriented $\omega = +10^\circ$ and $\omega = -10^\circ$ to the angle of maximum polarizability sum to the patterns reported.

This pattern shows that if the optic axis were located at $\pm 10^\circ$ to the rod axis then the resulting SALS pattern would have lobes of intensity at $\mu = \pm 45^\circ$. We have already seen that the polypeptide patterns have scattered intensities at $0^\circ/90^\circ$. By varying the ω values input into the model and comparing those to the actual photographs as before, we conclude that the true ω values for the samples of this study lie between 30° and 60° and are most likely 45° .

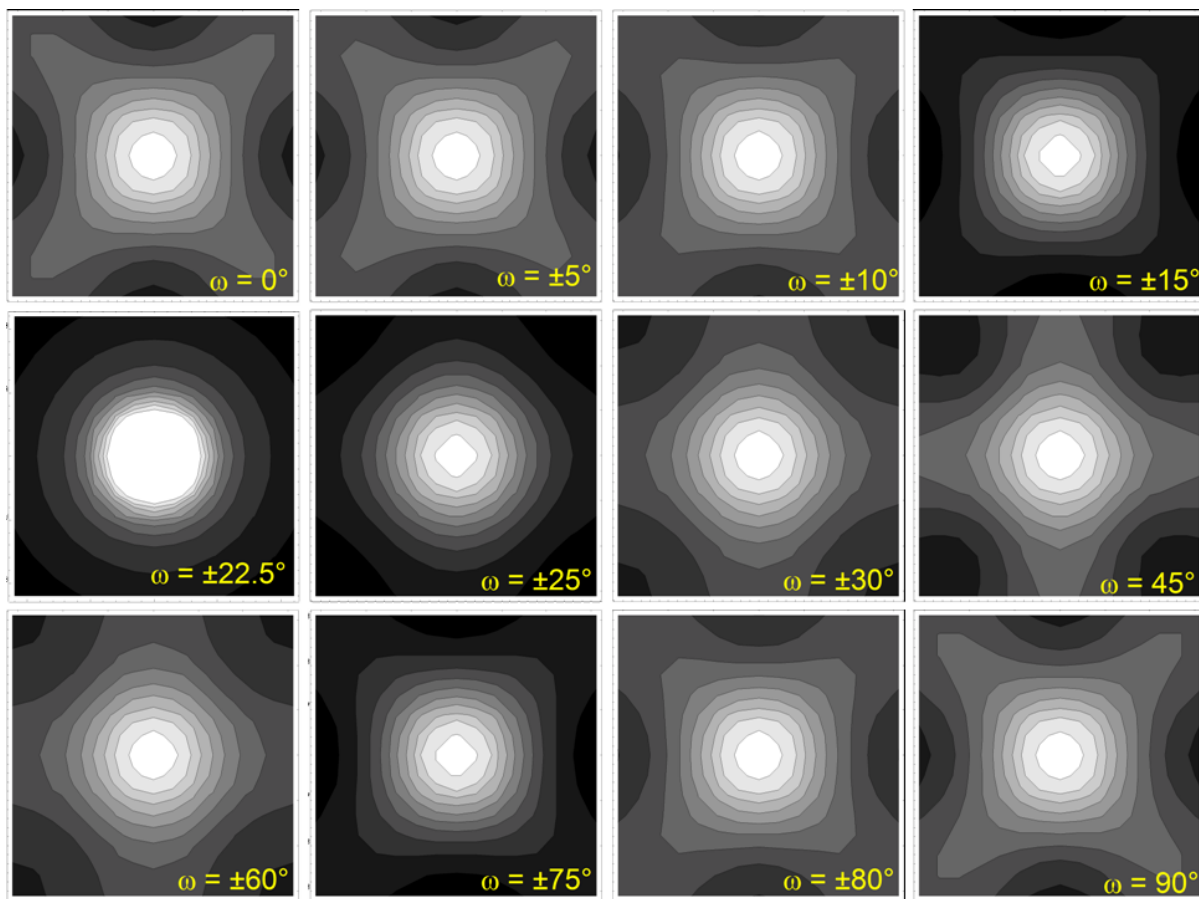


Figure 7.17. Calculated H_v SALS patterns calculated with varying ω values: $L = 2 \mu\text{m}$, $\theta = 30^\circ$, $\varepsilon = 1$.

Having seen evidence of the presence of optically anisotropic rods from SALS patterns and after gaining some understanding of their size from the indirect method of the *Mathematica*[®] modeling, microscopy techniques were used to evaluate whether the proposed structure exists in these samples. AFM scans were performed on each polypeptide sample produced in hopes of obtaining visual evidence of the proposed rod-like structure. The results of a typical AFM scan are shown in Figure 7.18. Figure 7.18 is a phase image produced from a PELG sample cast from a 5% chloroform solution. Differences in color of the scan are due to changes in the hardness of a particular region of the film. In these scans, lighter areas correspond to regions of harder material and darker areas correspond to regions containing softer material.

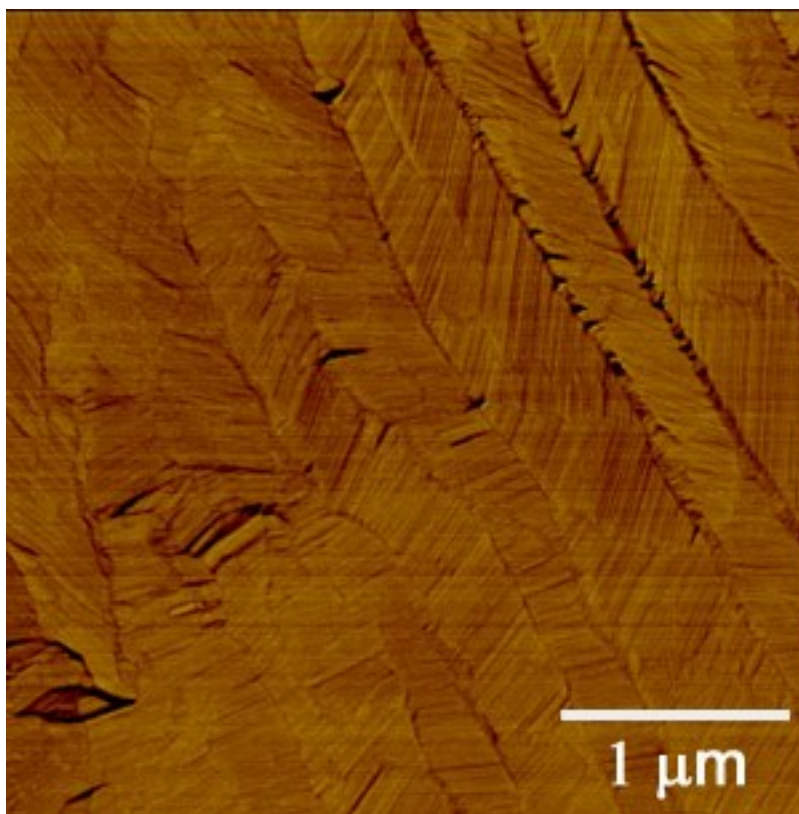


Figure 7.18. Phase image of AFM scan of PELG film cast from 5% chloroform solution.

Figure 7.19 is a height image from an AFM scan of a PBLG sample cast from a 5% chloroform solution. In this case, the lighter areas correspond to a point of higher elevation of the film whereas darker regions correspond to lower portions of the films.

Very clearly, a super-rod texture is visible in both height and phase images. Looking specifically at the phase image, a "herring-bone" pattern can be seen with band widths ranging from roughly 0.25–0.5 μm . There are clearly large bands running the entire length of the scans. Contained within each band there appears a finer structure, the majority of which have an apparent 45° tilt to the long axis of the larger bands. Alternating large bands have what appears to be alternating $\pm 45^\circ$ tilt in the finer structure, giving the overall phase image a herring bone texture. The finer, tilted structure in some places seems to be continuous across multiple bands having length scales $> 0.5 \mu\text{m}$.

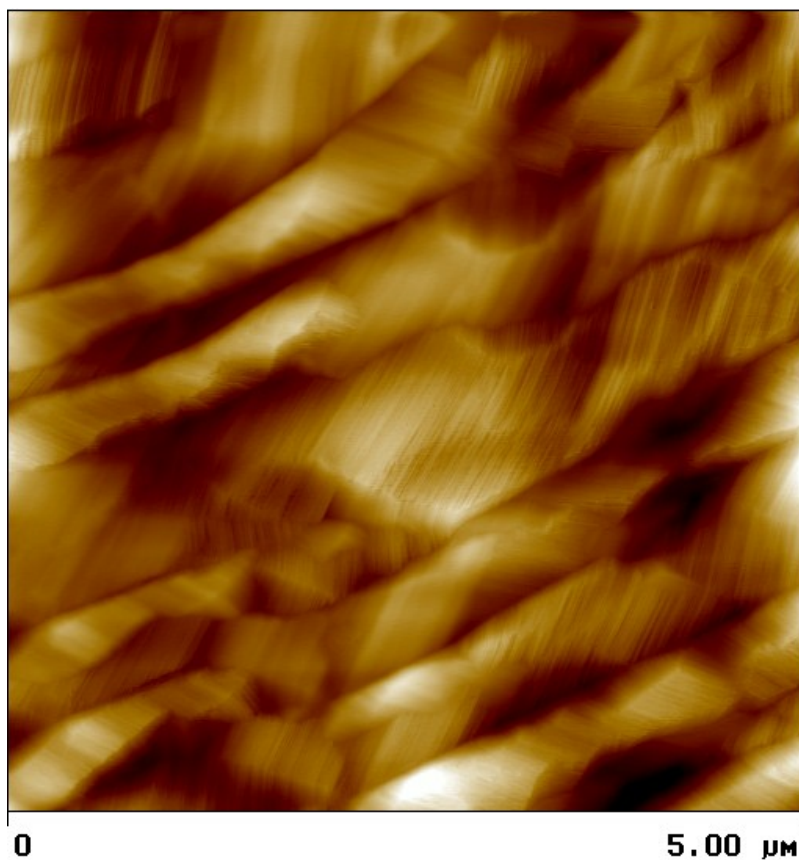


Figure 7.19. AFM height image of PBLG film cast from 5% chloroform solution.

This herring bone structure was seen for PBLG, PELG and some PnHxLG samples and was seen in films cast from both chloroform and 5% TCE solutions (Figure 7.20).

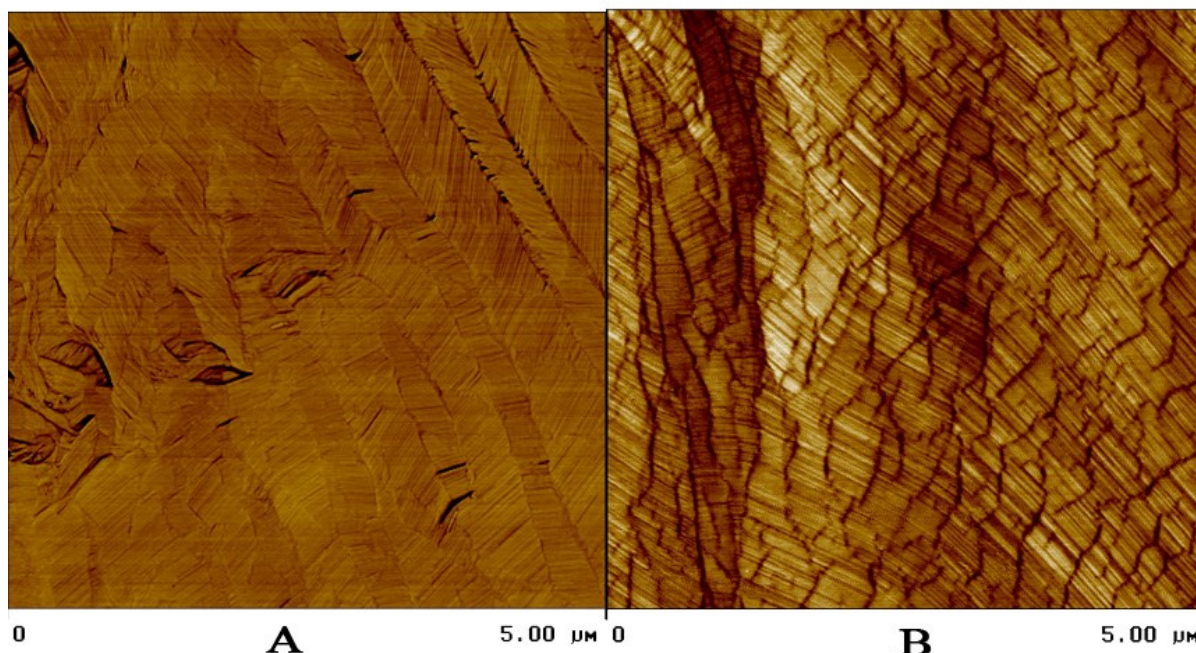


Figure 7.20. AFM phase images of A) PELG and B) PnHxLG samples cast from chloroform displaying the herring-bone pattern.

The length of the larger bands cannot be very accurately judged based on AFM results as the scans shown are only 5 μm in height and width. Based on the earlier SALS pattern calculations that the structure is most likely longer than 10 μm , one would not expect to see entire bands in one 5 μm AFM scan. On at least one occasion the scanning area of the instrument was moved along the length of the banded structure in order to obtain an estimate of the structures length. In that case, the bands were found to be in excess of 20 μm .

This herring-bone like structure seen with AFM was often observed using optical microscopy as well. Figure 7.21 is a POM micrograph taken of a PBLG sample cast from chloroform. It is apparent from the micrograph that there are localized differences in structure across the width of the film samples.

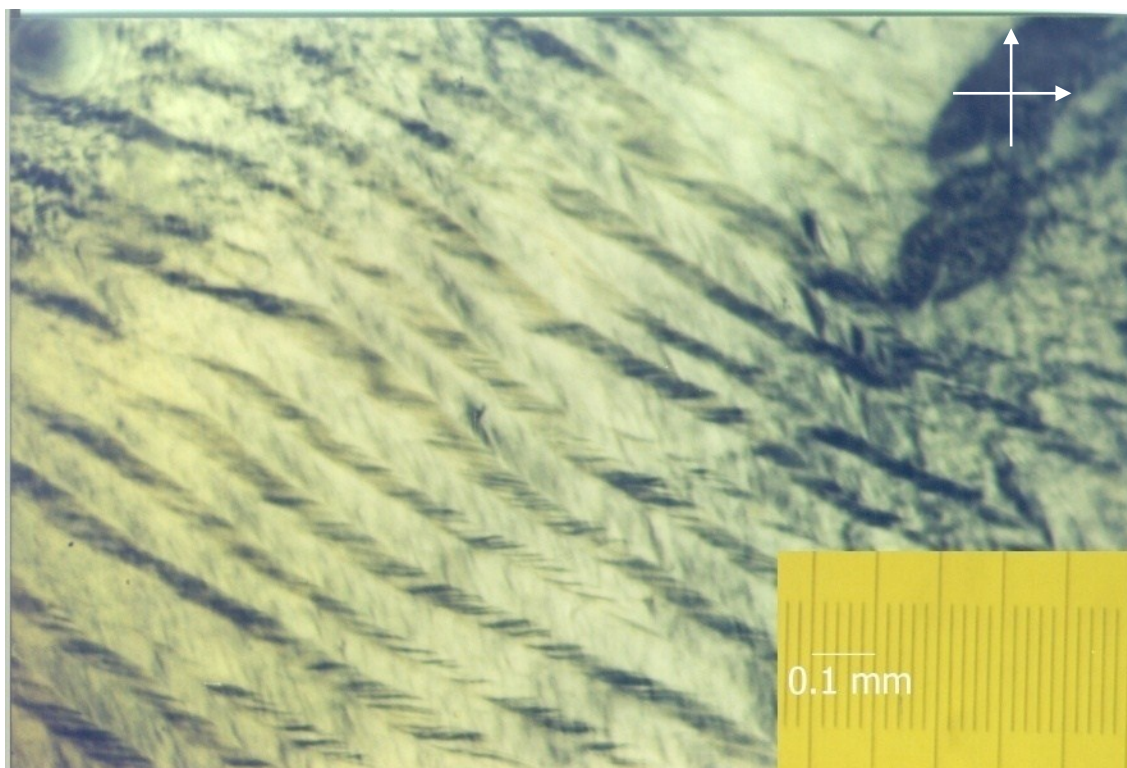


Figure 7.21. POM micrograph of a PBLG film sample cast from 5% chloroform solution.

The micrograph clearly shows a banded structure similar to that already seen in the AFM scans of Figure 7.18 and Figure 7.19. Still present is the apparent alternating $\pm 45^\circ$ tilt of a finer structure in each of the bands. The scale bar indicates that individual bands are roughly $50\ \mu\text{m}$ wide and run hundreds of μm in length. While some micrographs such as the one shown above display very clear banding, not all do. Though the micrograph in Figure 7.22 would not appear to contain the rod-like structure necessary to obtain a $0^\circ/90^\circ$ SALS pattern (there is no obvious rod-like structure from POM) it does in fact produce such a pattern as seen in Figure 7.23.

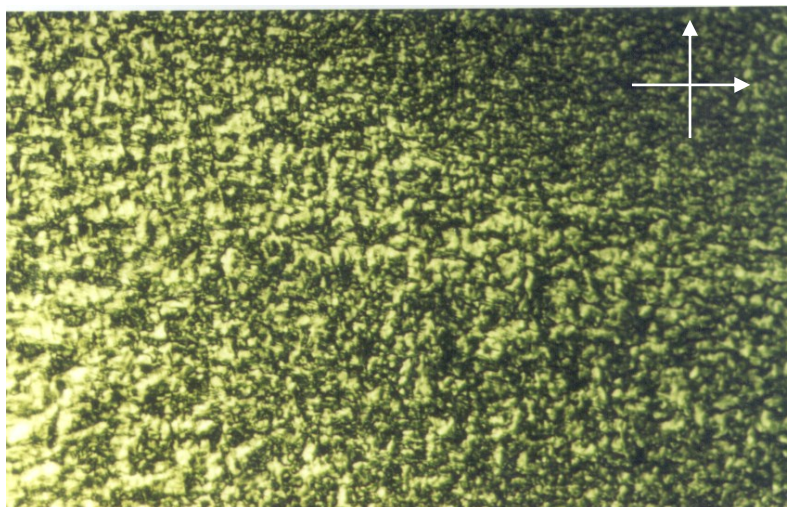


Figure 7.22. POM micrograph of a portion of PBLG film cast from 5% chloroform solution.

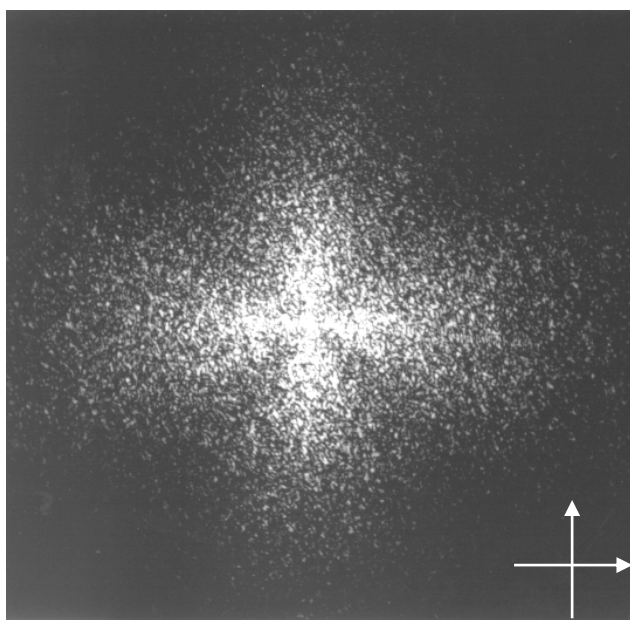


Figure 7.23. H_v SALS pattern taken from a portion of a PBLG film without obvious banded structure observed by POM.

The SALS pattern indicates that a rod-like structure must exist in the film though it is not clear from its optical micrograph that it would. The pattern also implies that the rod-like structure has no net orientation and that the rods are randomly oriented in all directions in the plane of the film. However, other samples or even different portions of the *same* sample (Figure 7.24) sometimes showed a very different structure. The two optical micrographs shown in this figure are of the same portion of the PBLG sample. However, Figure 7.24B shows the POM

micrograph of the sample following the insertion of a full waveplate into the light path which caused a visible shift in the color spectrum. This shift further emphasizes the orientation of rods optic axes. The distinct banded structure also shows the localized nature of the structure of solution cast films. The micrographs in Figure 7.22 and Figure 7.24 were taken from the same film sample.

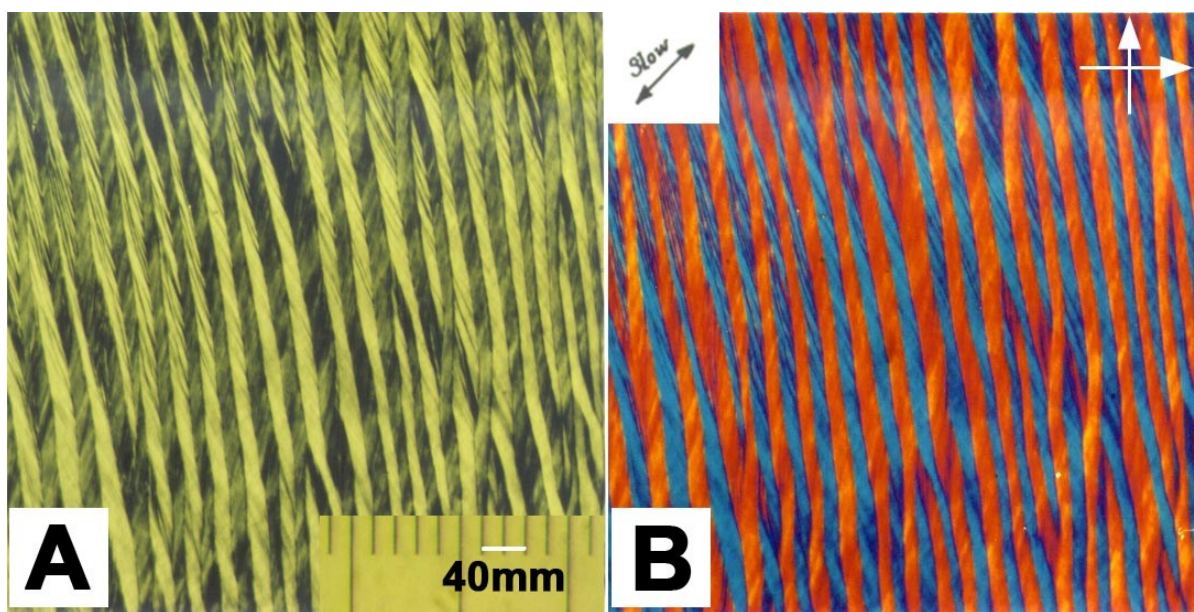


Figure 7.24. A) POM micrograph of PBLG film cast from 5% chloroform solution; B) The same structure as seen with the use of a waveplate.

The micrograph in Figure 7.24B was obtained with a full waveplate in the light path of the microscope oriented as shown in Figure 7.25. Given the orientation of the waveplate and the color change of the POM pattern shown in Figure 7.24, conclusions can be drawn regarding the orientation of the optic axis of the polypeptide molecules. With a full waveplate inserted into the light path of the microscope, structure with an optic axis perpendicular to the slow direction of the waveplate will appear blue, whereas structure with an optic axis parallel to the slow direction of the waveplate will appear yellow or red.



Figure 7.25. Full waveplate orientation used in POM.

Given that, it is apparent that the optic axis of the polypeptide chains lies parallel to the finer banded structure inside each super rod. Figure 7.26 provides a graphic example of this conclusion.

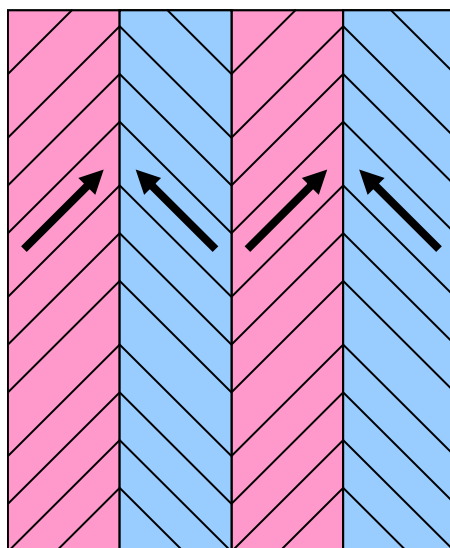


Figure 7.26. Graphical representation of location of optic axes (dark arrows) in the polypeptide films.

Again in Figure 7.24, as in Figure 7.21, there appears to be a very obvious twisting or banded structure similar to that seen with the AFM. It also appears that the finer structure inside each band lies *ca.* 45° to the long axis of the larger bands. This was also seen in the AFM though on a very different scale. Note the length scale superimposed on the micrographs. These large banded structures appear to be hundreds of microns in length, a result not contradicted by the

AFM scans. However, using polarized optical microscopy, the band's thicknesses in the POM are on the order of 20 μm , much larger than the 0.5 μm band width evident in the AFM though admittedly, the pictures were produced by imaging different areas of the sample.

Given what appears to be a highly ordered banded structure from POM, one might expect that the SALS patterns display a have significant difference from those observed thus far. SALS pattern computer model calculations were also performed while varying the orientation parameter, ϵ , Figure 7.27 shows the effect of changing from a random collection of rods, $\epsilon = 1$, to a collection with a preferred orientation, $\epsilon = 2$.

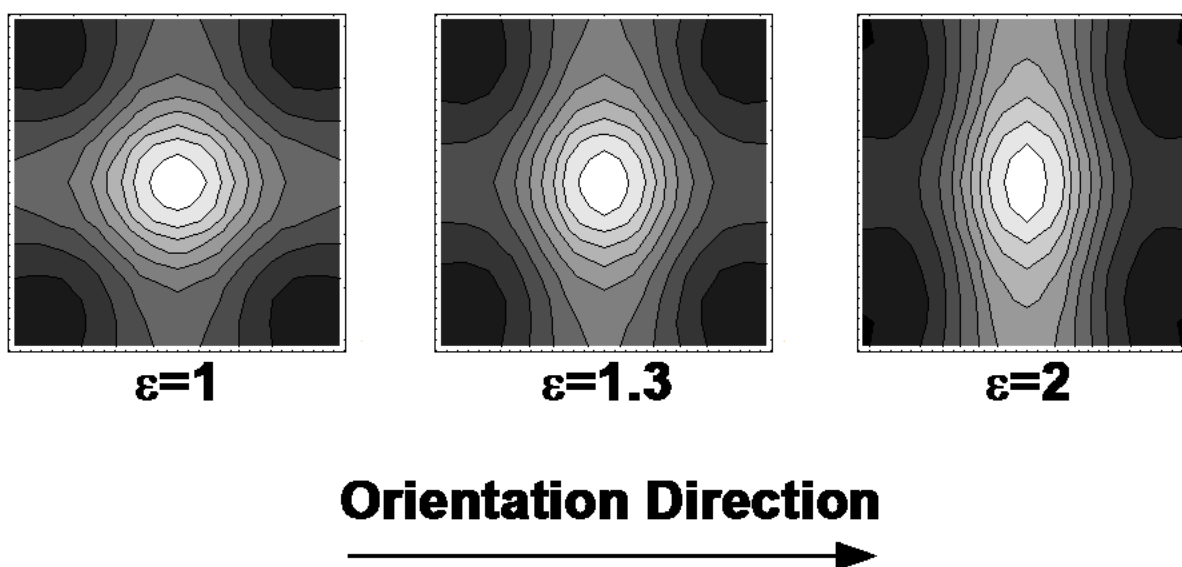


Figure 7.27. SALS H_v pattern calculations of optically anisotropic rod scattering as a function of orientation parameter: $L = 5 \mu\text{m}$, $\omega = 45^\circ$. *The rod axis increasingly aligns in the horizontal direction with respect to the images shown.*

Clearly, as the orientation parameter is increased, there is a marked change in the calculated scattering pattern. Two of the lobes, 0° and 180° to the vertical, are elongated while the other two, 90° and 270° , are diminished to smaller angles. By the time ϵ takes on a value of 2, these latter two lobes have almost completely vanished. Given what appears to be a very high level of order in the banded region of the PBLG film in Figure 7.24A, a SALS pattern would be expected to show similarities to the last picture in Figure 7.27. Figure 7.28B shows the photographed SALS pattern of the very region shown in optical micrograph of Figure 7.24A.

This SALS photograph clearly displays a pattern in keeping with a highly ordered structure [145] though the full reason for the origin of the texture is not clear.

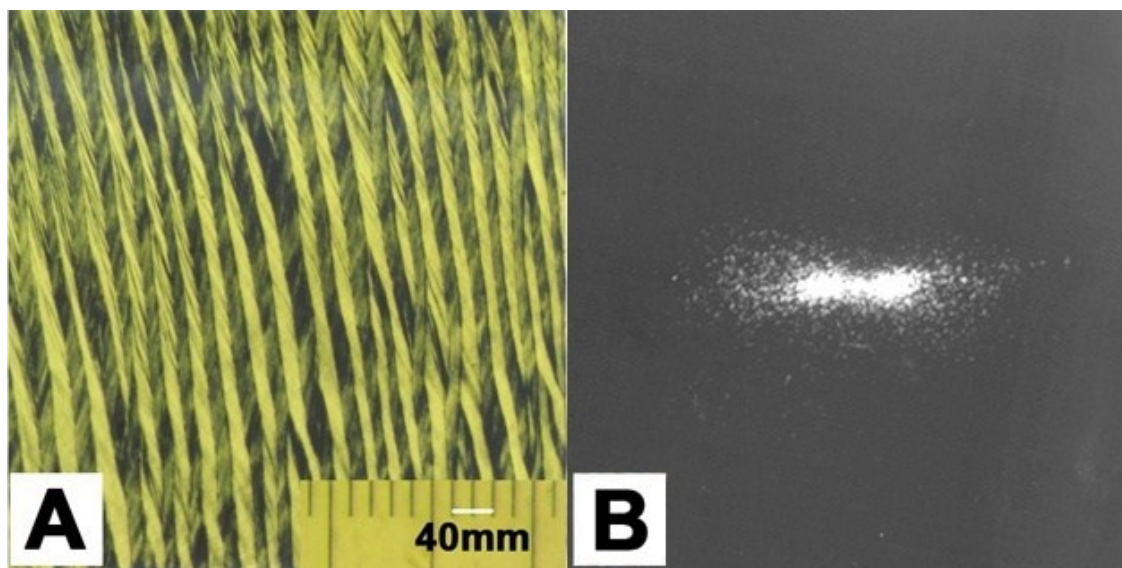


Figure 7.28. A) POM of PBLG film cast from 5% chloroform solution. B) H_v SALS photograph taken of a portion of the sample that showed a banded structure similar to that shown in (A).

To this point, the main results presented have been for films cast from *ca.* 5% solution concentrations of chloroform, though it was noted that often the results were similar for samples cast from TCE. When the solution concentration was varied downward from 5% however, differences in morphology became evident. These differences were most noticeable in the AFM scans of films cast from solution concentrations 1% and lower. Lower concentration solutions had a much higher solvent content than did higher concentrated solutions. When films were cast onto glass slides without the use of a saturated environment, the evaporation of solvent progressed at a higher rate for low concentration solutions. That higher evaporation rate caused a perceptible change in film structure as seen using the AFM (Figure 7.29), just as it did in the SALS results earlier.

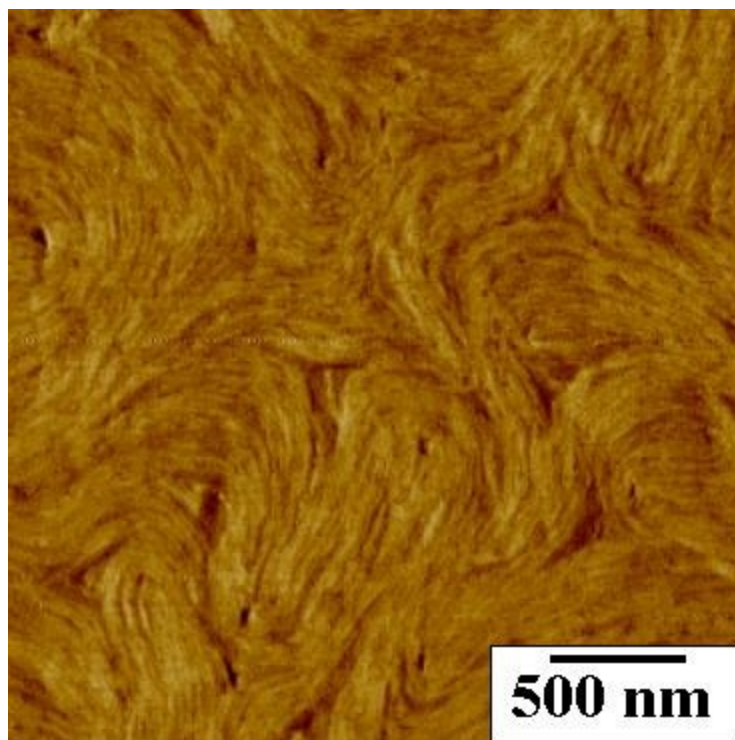


Figure 7.29. AFM phase image of fast cast PBLG film cast from 0.5% chloroform solution.

A question recurs; are differences in structure due to concentration or is it the differences in evaporation rate alone which affects the structure? Contrast Figure 7.29 with the image seen in Figure 7.19. These two AFM scans were carried out on the same material, PBLG, using roughly the same doctor blade drawing speed during film casting. The only difference between the two samples was the concentration of the solution from which they were prepared. They were each produced without solvent saturated environments and are thus “fast-cast” films. Because it was cast from a much less concentrated solution (0.5%) and likely may not have been given time to attain what might be its thermodynamically desired state, the film in Figure 7.29 has a very different structure than the film cast from the higher concentrated solution.

This same effect of solvent concentration is seen in PELG films as well. Figure 7.30 shows an AFM scan of a PELG fast-cast sample from *ca.* 0.5% chloroform solution. Note here the contrast between the structure seen in Figure 7.30 and the structure of the PELG film cast from 5% solution (Figure 7.18). For both PBLG and PELG, the faster solvent evaporation rate has a noticeable effect on the resulting film structure.

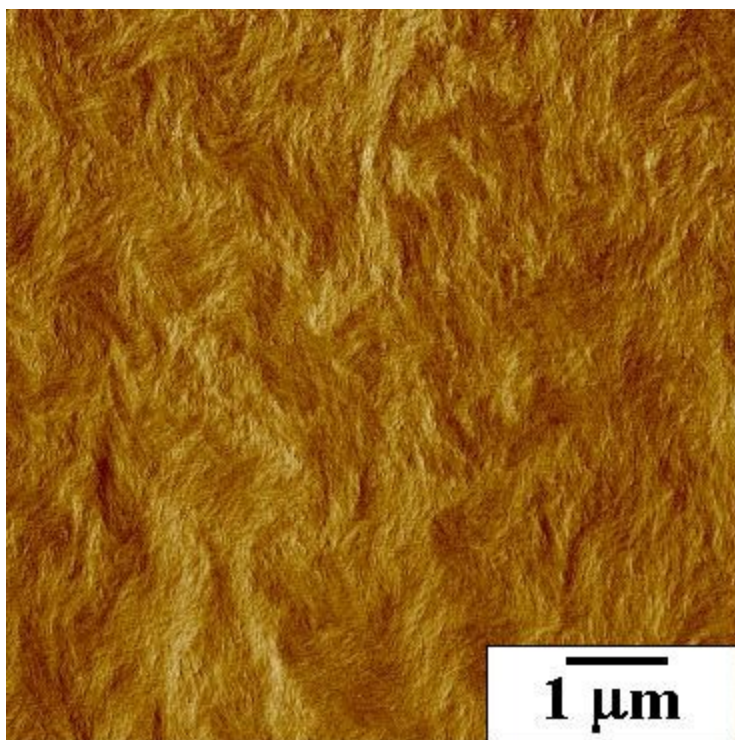


Figure 7.30. AFM phase image of fast cast PELG film cast from 0.5% chloroform solution.

Clearly the fast cast films lack the long range order present in the slower cast films in that there is no evidence of large bands or rod-like textures present. Some order does exist in these films but it is short-range order at best. If we consider the structure of the 5% films to be the thermodynamically desired structure, the faster solvent escape from the samples cast from lower concentrations is apparently “locking in” a structure that is less favored due to kinetic limitations. When the solvent evaporation rate is slowed by the use of a solvent saturated environment, long-range order can be restored in many cases leading to the so called "slow cast" films.

It is clear that the banded structure can develop in the films prepared from lower concentrations if the kinetic limitations are removed. When films were cast in solvent saturated environments as was the sample in Figure 7.31, the apparent thermodynamically desired structure can be induced. Here there is an unmistakable banded structure, again having a finer banded structure contained within it although it does not seem as well developed as those shown in Figure 7.19. We can therefore conclude that variation in structures seen at different concentrations is greatly influenced by evaporation rate and not a concentration effect alone.

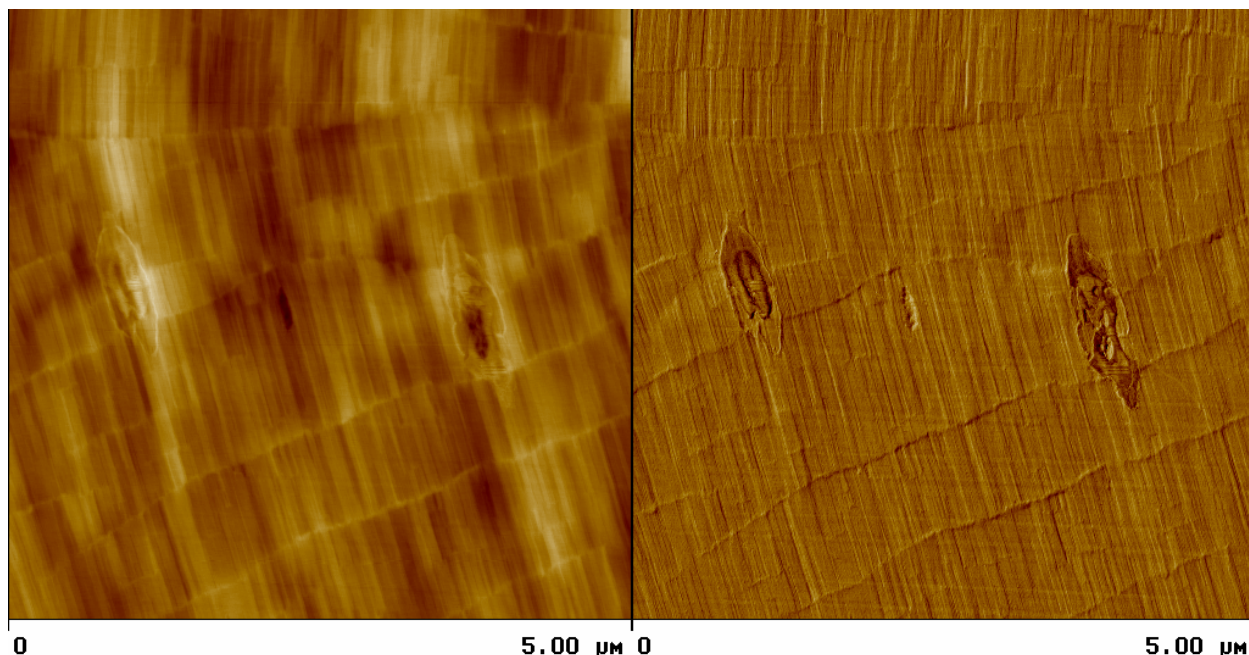


Figure 7.31. AFM image of PBLG film cast from 0.5% chloroform solution under a saturated chloroform environment.

In addition to AFM, SEM was used to characterize the surface of the polypeptide films. The film surfaces of samples cast from 5% chloroform solution did not show a banded structure similar to those seen thus far. Instead, those micrographs only showed a “pitted surface structure”, perhaps due to the quick evaporation of solvent from the fast cast films. One example of such a film is provided in Figure 7.32. However, when the samples were fractured in liquid nitrogen, a fiber-like structure was evident beneath the surface of the films (Figure 7.33).

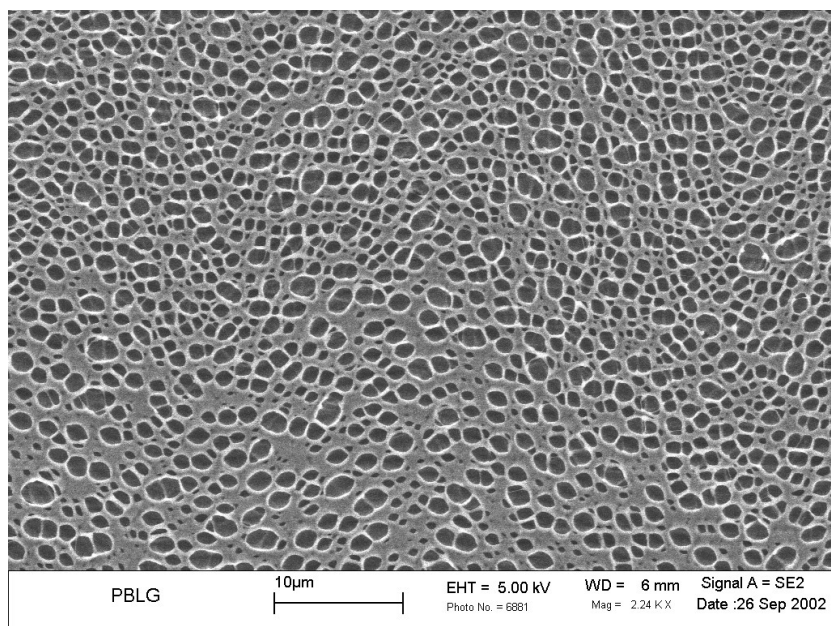


Figure 7.32. SEM micrograph of the film surface of a PBLG sample cast from 5% chloroform solution.

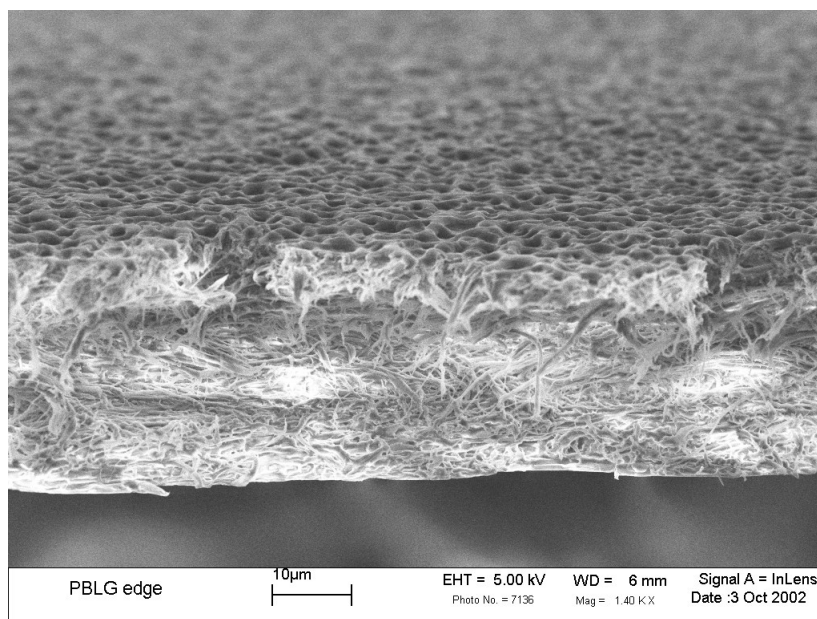


Figure 7.33. SEM micrograph of the fracture edge of a PBLG film sample fast-cast from 5% chloroform solution. Note that the sample was fractured after being submerged in liquid nitrogen.

This SEM micrograph reveals a fibrous structure in the bulk material. Although the top surface does not show any evidence of the banded structure observed with POM, the bulk of the material shows that a fibrous structure with a high aspect ratio is present. POM was able to

discern the banded structure because it is a technique that can detect the bulk structure, i.e. the polarized light propagates *in* the sample as it does with SALS. Therefore, the surface texture had minimal effect on SALS and POM. In addition, the silicone oil coating used in the SALS technique to minimize surface effects would have filled the pits seen in the SEM. The AFM, although generally thought of as purely a surface technique, actually images the structure deeper than the surface depending on tapping strength used. Hence, AFM too was able to distinguish a banded structure beneath the surface.

Considering that the exteriors of these films appear to display evidence of a fast evaporation of solvent (pitting), a film cast in a solvent saturated environment (with its slower evaporation rate) might be expected to show a different surface structure. That does in fact occur. Figure 7.34 shows the surface of a PBLG sample cast from a 0.5% solution in a chloroform saturated environment.

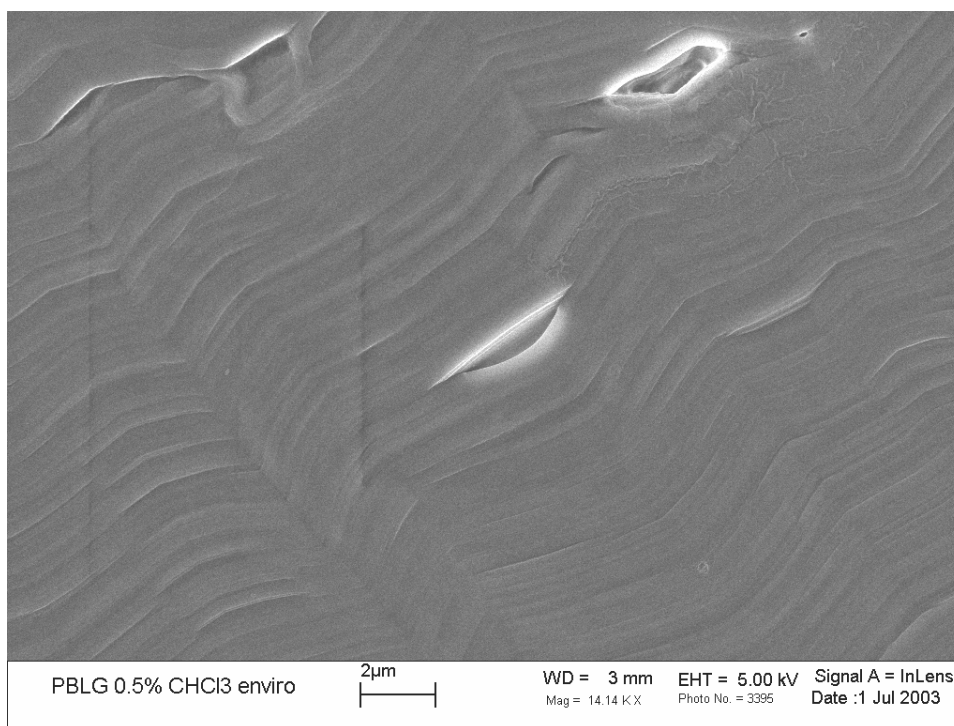


Figure 7.34. SEM micrograph of the surface of a PBLG film sample slow-cast from 0.5% chloroform solution in a chloroform saturated environment.

Not only does the micrograph lack the pitted texture of the films cast from 5% solutions, but it also shows distinct evidence of the reemergence of the banded structure previously seen with both POM and AFM. The films slow cast under solvent saturated environments now show

banded structure with each of these three microscopy techniques. It is perhaps expected that these films should also display the $0^\circ/90^\circ$ SALS patterns as previously calculated and measured. Figure 7.35 shows a SALS pattern taken from a PBLG cast from a different solution, 0.5% TCE, under a saturated environment. Indeed, the SALS photograph also confirms the existence of the anisotropic rod microstructure.

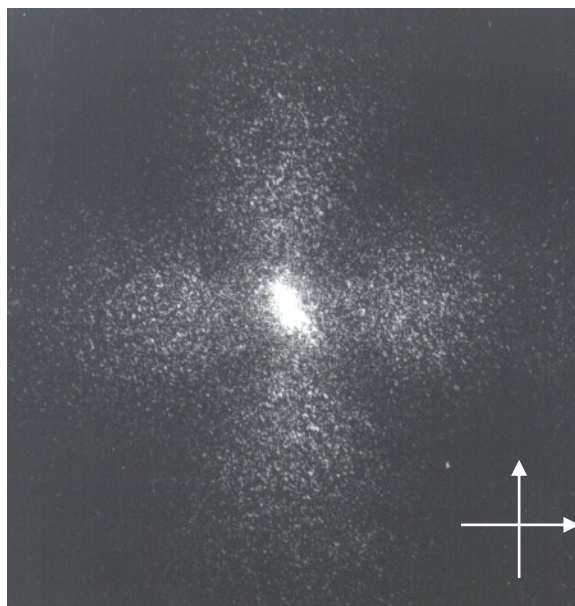


Figure 7.35. SALS photograph of PBLG film sample cast from a 0.5% TCE solution under a solvent saturated environment.

Based on the techniques discussed thus far, a rod-like structure clearly exists. However, the structure of the rods themselves is unclear. Past work on polypeptides suggests that the structure is likely semicrystalline or at least contain LCP or both. To confirm this, WAXS was run on several samples including PBLG, PELG, and PMLG solution cast films from different solvents. The sharp diffraction rings in the WAXS patterns presented in Figure 7.36a–f indicate that indeed, these materials are semicrystalline or liquid crystalline.

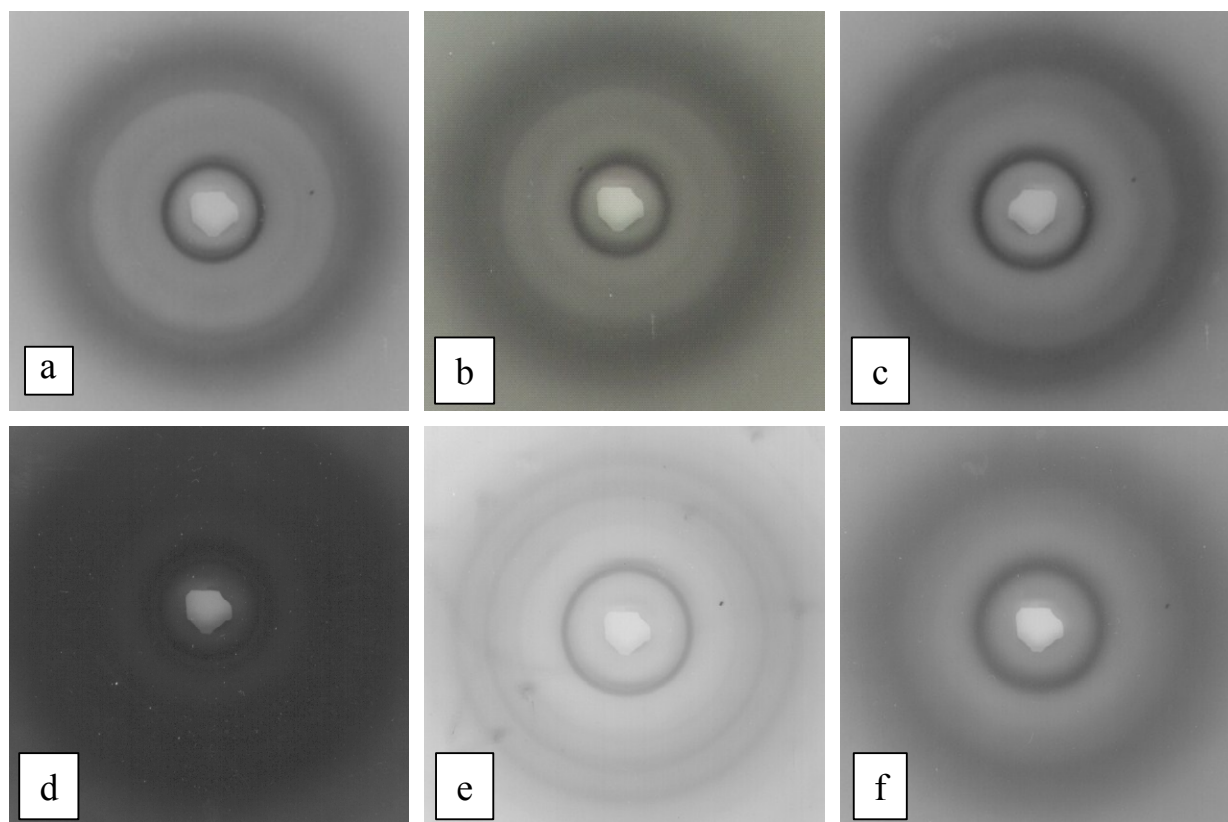


Figure 7.36. WAXS diffraction patterns of various polypeptide solution cast films: a) PBLG in CHCl_3 ; b) PBLG in TCE; c) PELG in CHCl_3 ; d) PELG in TCE; e) PMLG in CHCl_3 ; f) PMLG in TCE.

Though Figure 7.36d does not show up well, it has a sharp diffraction ring. The other five samples each show very sharp rings as well and are semicrystalline or liquid crystalline. There does not appear to be an azimuthal dependence on the scattered intensity, indicating that there is no net orientation in the samples in the beam direction on the microscopic level. The results from other techniques indicated that there is indeed a net orientation in some portions of the solution cast films. However, each of those other techniques (AFM, SAXS, POM, and SALS) measured structure on a much larger length scale.

Once more it should be mentioned that the banded structure was not the only one found in the film samples. The whole of the sample actually contained a number of different structures. Selected areas of these films are also presented here to provide a more complete view of the films' properties. Figure 7.37 shows a region of the film often called a fan-shaped texture for its obvious similarities to handheld fans. Both smectic and cholesteric phases are known to display this type of structure and are common in liquid crystalline systems.

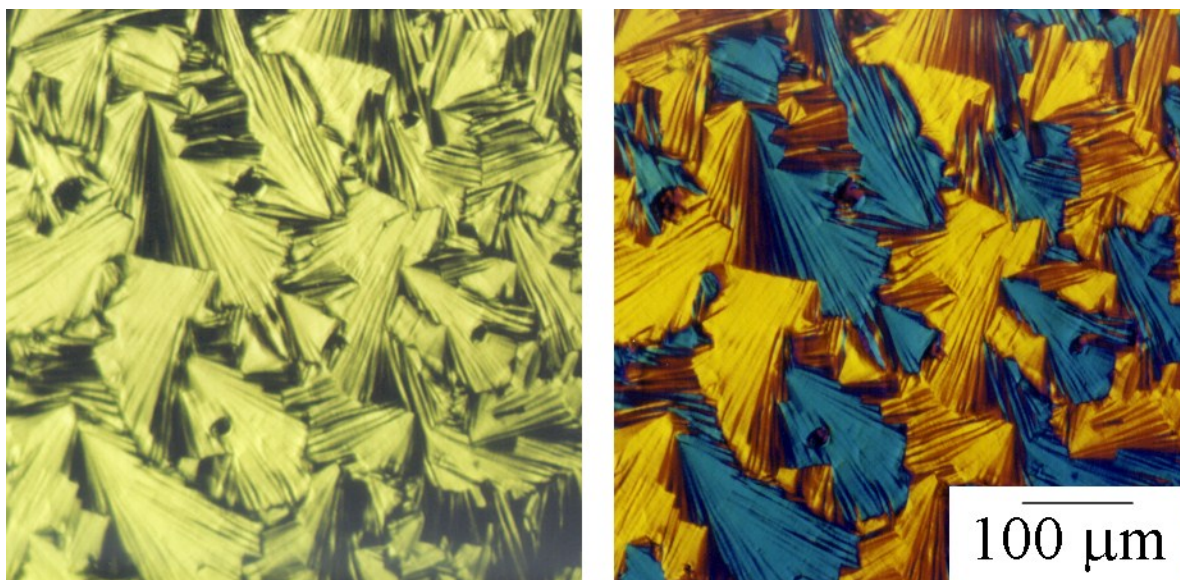


Figure 7.37. Fan structure observed in PBLG film cast from 0.5% chloroform solution under a solvent saturated environment. A) without waveplate; B) with a waveplate (Figure 21) inserted into the light path.

Optical micrographs of comparable morphological structures as noted by POM are also evident in other materials can be found in the literature, though a particularly good reference covering a range of materials and structures was published by Demus and Richter [167]. Two examples of fan-shaped structures from other nonpolymeric materials are provided in Figure 7.38. So it is clear now that the polypeptide solvent cast films discussed can take on a number of different structures as we have witnessed the highly ordered banded structure, a schlieren structure that showed no obvious order, and a fan structure. The banded structure may be attributable in part due to a mechanical orientation of the polypeptide chains. This occurred during the casting process as a shearing force developed during the drawing of the doctor blade across the glass slides.

A recent study by Oka et al. on the effect of concentration on poly(L-glutamate) phase behavior may shed further light on the different structures we have seen in this study [168]. They investigated at a series of poly(L-glutamates) in *m*-cresol including some of those we have studied including: PBLG, PMLG, and PELG. Though the solvent and temperatures were different for their study as compared to this one, they were able to produce phase diagrams for the entire concentration range of 0–100 vol% by following the d_{100} spacing with WAXS. Most importantly, they showed that over a critical concentration range between 40-50%, a phase

transformation occurred from a mix of isotropic and columnar phases to pure columnar phase. While they did not mention the rate of solvent loss, it is apparent that as solvent left a given system, phase transformation took place during film casting at ambient temperatures. This same effect of concentration on phase behavior is likely present in our systems and the kinetics of solvent loss in the slow versus fast cast films may be responsible for “locking in” the structures as was mentioned previously.

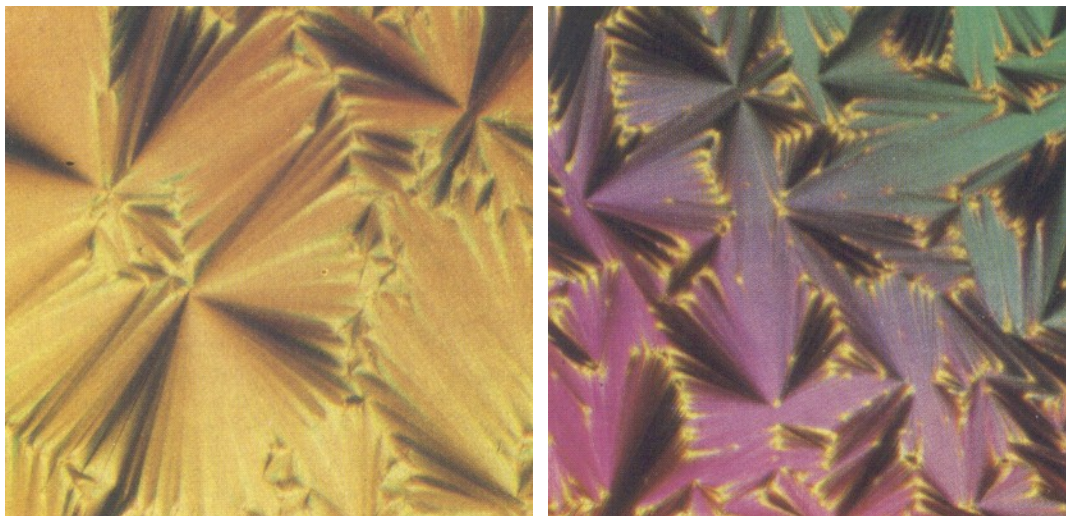


Figure 7.38. Fan-shaped texture of 4-n-Butyloxy-4'-n-butanoyl-biphenyl [167].

So it is clear now that the polypeptide solvent cast films discussed can take on a number of different structures as we have witnessed the highly ordered banded structure, a schlieren structure that showed no visible ordering, and a fan structure. The banded structure may be attributable in part due to a mechanical orientation of the polypeptide chains. This occurred during the casting process as a shearing force developed during the drawing of the doctor blade across the glass slides. This could cause the initial alignment of the chains. Based on previous work by Worley, Linton and Samulski [162], by Tobolsky and Samulski [169], and by Wilkes [144], orientation of the polypeptide chains can be induced in ways other than the application of a mechanical shearing force, e.g. using a magnetic field. The work by Worley et al. used magnetic fields up to 8 kG while Wilkes' studies used fields up to 25 kG. An attempt was made here to produce a similar alignment in the rod-like packing to that already documented. However, rather than a magnetic field, the PBLG solution was cast in the presence of an electric field. The experimental set-up schematic and POM micrograph shown in Figure 7.39 indicate

that structure and orientation similar to that previously seen was induced in the sample. Just as in the mechanical drawing case, the direction of the driving force for orientation (in this case the electric field) is orthogonal to the long axis of the oriented rods.

This caused the initial alignment of the chains. Based on previous work by Wilkes [144], orientation of the polypeptide chains can be induced in ways other than the application of a mechanical shearing force—using a magnetic field in that case. An attempt was made to produce a similar alignment in the rod-like packing to that already documented. However, rather than a magnetic field, the PBLG solution was cast in the presence of an electric field. The experimental set-up schematic and POM micrograph shown in Figure 7.39 indicate that structure and orientation similar to that previously seen (Figure 7.28a) was induced in this sample. Just as in the mechanical drawing case, the direction of the driving force for orientation (in this case the electric field) is orthogonal to the long axis of the oriented rods.

Once again there is a visible banded structure that develops. However, in this case it is a result of electrical rather than mechanical forces. In earlier POMs (Figure 7.24A, Figure 7.37a) a structure was observed inside the large banded regions that was aligned roughly 45° to the bands long axis. Upon close inspection of the micrograph in Figure 7.39, the finer structure is also seen in this sample. Thus the electric field work produced very much the same structure as seen in the mechanically sheared solvent cast films.

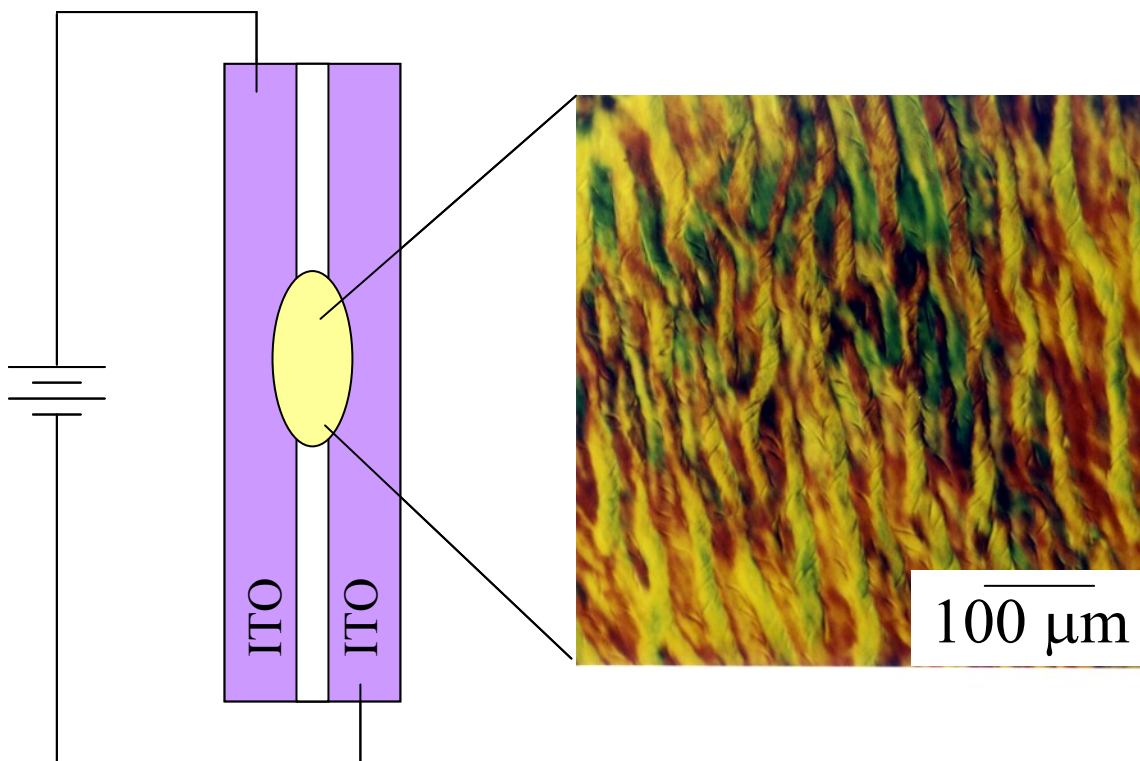


Figure 7.39. Schematic set-up and POM micrograph of a PBLG film cast from 15% chloroform solution in a D.C. electric field with the orientation shown.

In light of the work done here as well as that of Oka et. al., a better understanding of the effects and kinetics of solvent loss on the phase behavior of poly(L-glutamate)s is warranted. Specifically, controlled experiments could be done using our materials (PBLG, PELG, and PMLG) and our solvents (chloroform, TCE and formic acid) to determine the exact phases present in the solid state and to determine if in fact the kinetics of solvent loss are truly preventing a thermodynamically preferred state from developing. In addition, work should also be done to understand the cause of the pitted surface of the fast cast PBLG film.

7.7. CONCLUSIONS

A series of polypeptides films, PBLG, PELG, and PMLG, were cast from solutions of chloroform, TCE and FA. The PBLG films cast from chloroform and TCE were predicted to have an optically anisotropic rod-like structure based on the combination of SALS pattern

exposures and SALS pattern modeling using an optically anisotropic rod scattering model. That combination of model and experiment also predicted that the direction of maximum polarizability lies at 45° to the long axis of the rod molecule and that the length of the rod structure would be in excess of $10\text{ }\mu\text{m}$. AFM and POM confirmed that the predicted microstructure was in fact observed for films cast from 5% solutions. The rod-like structure spanned the order of hundreds of microns in length and was seen to be roughly $0.5\text{ }\mu\text{m}$ in width via AFM. Conversely, the width of the banded region in the optical micrographs and SEM was observed to be on the order of $20\text{ }\mu\text{m}$. Nevertheless, when portions of the films containing highly oriented bands (as seen with POM) were isolated and their SALS patterns photographed, a four-lobed pattern also developed. This was in good agreement with the predicted SALS profiles.

Films fast-cast from much lower solution concentration, that is 0.5% solutions, were found to have very different microstructures due to the shorter time period of solvent evaporation. It was strongly believed that the quick loss of solvent in these samples imposed a kinetic limitation on structure formation which prevented the thermodynamically favorable rod-like structure from fully forming. Instead, a wispiest, shorter range ordered structure developed. When the lower concentration solutions were slow-cast in a solvent saturated environment, the previous banded, rod-like microstructure reemerged. This structure was again confirmed with POM, AFM, SEM, and SALS. The large banded structure witnessed with POM, AFM and SEM also displays a much finer tilted structure inside each large band. The use of a waveplate in the POM indicated that the molecular axis of a polypeptide chain lies in the same direction as the finer tilted structure (Figure 7.26).

Films were also oriented by casting them into an electric field. Clearly the electrical orientation produced a banded structure as seen in the POM.

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APPENDIX A

MATHEMATICA® CODE FOR SALS PATTERN CALCULATIONS

This section defines all the variables used in the scattering equation. It defines the variable a in terms of both the radial scattering angle, θ , and the azimuthal scattering angle, μ . β is the angle measured between the tilt of the scattering rod and the z-axis. ω is the angle between the long axis of the rod and the direction of maximum polarizability of the rod. The value of k is set to $2\pi/\lambda$, here chosen for a He-Ne laser. The variables that follow are all adjustable so that they may be changed to model different scattering systems. SFD is the sample to film distance, here set to roughly 15 inches. $window$ defines the size of the scattering window and is the maximum radial scattering angle θ in the x and y directions. δ is a variable which measures the anisotropy of the rod doing the scattering, $\delta = \alpha_l - \alpha_t$. ϵ is a distribution function which defines the degree of orientation of the rod assembly. At $\epsilon = 1$, there are equal numbers of rods associated with all values of β . ρ is the scattering power of a rod per unit length per unit incident field strength at $\beta = 0$. L is the length of the scattering rod. θ defines the scattering angle between the scattered and incident wave. Note that all values are in nanometers.

Clear “*”

$$\alpha = -\text{Sin}\left[\beta + \frac{\pi}{2} - \mu\right]\text{Sin}[\theta];$$

$$\beta' = \beta + \omega;$$

$$k = 2\pi / 632.8;$$

$$SFD = .381 * 10^9; \quad (* \text{ roughly 15 inches} *)$$

$$window = 6.7 \text{ Degree};$$

$$xMax = yMax = SFD \text{ Tan}[window];$$

$$rMax = xMax / \text{Sin}[45 \text{ Degree}];$$

$$\delta = 4;$$

$$\omega = \rho;$$

$$\epsilon = 1;$$

$$\rho = 1;$$

$$L = 10000;$$

$$\theta = \text{ArcTan}[r/\text{SFD}];$$

This is the definition of the integrand of the H_v scattering intensity equation. There are constants outside of the integral that are not taken into account in this expression. Note that when the substitutions above are made, the resulting expression depends only on values of r , μ , and β . Because we will integrate with respect to β , we will be left with r and μ and we can then plot our solutions using polar coordinates.

$$H_v = \left(\varepsilon^{-2} \cos[\beta]^2 + \varepsilon^2 \sin[\beta]^2 \right)^{-1/2} \delta^2 \sin[\beta']^2 \cos[\beta']^2 \left(\frac{\sin\left[\frac{kaL}{2}\right]}{\frac{kaL}{2}} \right)^2$$

This is the integrating step of the routine. Because *Mathematica*[®] doesn't want to integrate the $\sin^2(\cos(x))$ term we must use a numerical integration. This means substituting in real values for r and μ and letting the program integrate the remaining expression which is in terms of β . Rather than calculating smooth curves defined over all values of r and μ , we will have discrete values of H_v at user defined increments of r and μ . We will have to use an interpolating function to determine values of H_v for intermediate values of r and μ that are not calculated explicitly. The first four statements define the domains of the r and μ values which will be substituted into the expression. These values can be changed as long as one restriction is noted. Looking at the output equation above, we see that we cannot chose to integrate using the value $r = 0$ because of the denominator.

Here, the value of $r_{\text{Max}} = 0.22 \times 10^9$ corresponds to an angle θ of roughly 30° . This integrating step is responsible for the majority of the computation time. It can be controlled to a degree by changing the size of the increments (r_{Inc} and μ_{Inc}) that are used in the integration. Smaller values for these increments means greater accuracy but longer computing time.

$$r_{\text{Min}} = .001 * 10^9;$$

$$\mu_{\text{Min}} = 0;$$

$$\mu_{\text{Max}} = 2\pi;$$

$$r_{\text{Inc}} = .001 * 10^9;$$

$$\mu_{\text{Inc}} = \pi/36;$$

```

Timing[
  solHv=Table[
    NIntegrate[Hv, {β, 0, π}],
    {μ, μMin, μMax, μInc},
    {r, rMin, rMax, rInc}
  ];
]

```

At this point we have a very large number of computed H_v intensities (not shown), each corresponding to a discrete pair of values (r , μ) that we solved with in the previous step. This next step produces an interpolating polynomial function so that an intensity can be calculated using any values of r and μ in the domain defined above. We will then have essentially what we wanted, H_v scattered intensity as a continuous function of r and μ . Rather than finding an exact solution by integration, we have found an approximate solution for all values of r and μ by doing a numerical integration and interpolating for intermediate values. The quality of the approximation can be increased using smaller increments $rInc$ and μInc .

```
approxHv = ListInterpolation[solHv, {{μMin, μMax}, {rMin, rMax}}]
```

These next few steps manipulate the data so that they can be plotted. The first statement defines the maximum values for the x-y plot based on the maximum value of r . We want to plot over a range of $\pm x$ and $\pm y$ values. However, the interpolating polynomial is not defined for values of $r < rMin$. This corresponds to very small values of x and y . In order to generate a graph, we must define the intensity at those very small values rather than calculate them. The next few statements define intensities in this region as equal to the intensity at $rMin$. This step also defines the conversion of the coordinate system from Cartesian coordinates to polar coordinates which will be used in the plotting command.

```
mu[x_, y_] := ArcCos[x/Sqrt[x^2 + y^2]] /; Sqrt[x^2 + y^2] > rMin
```

```
mu[x_, y_] := 0 /; Sqrt[x^2 + y^2] <= rMin
```

```
R[x_, y_] := Sqrt[x^2 + y^2] /; Sqrt[x^2 + y^2] > rMin
```

```
R[x_, y_] := rMin /; Sqrt[x^2 + y^2] <= rMin
```

Finally, we can plot the data. This plotting command is actually carrying out a number of procedures. It first takes the values of x and y that the user has chosen (depending on the choice of r_{Max}) and transforms them into polar coordinates. These coordinates are then plugged into the interpolating function and the intensity is calculated. This intensity is then multiplied by the terms in the Hv scattering equation which were not inside the integral in the complete scattering equation. This produces the final scattering intensity. The data are then plotted and contours of equal intensity are drawn.

```
ContourPlot[ $\rho^2 L^2$ *approxHv[mu[x,y], R[x,y]], {x, -xMax, xMax}, {y, -yMax, yMax}];  
Plot3D[ $\rho^2 L^2$ *approxHv[mu[x,y], R[x,y]], {x, -xMax, xMax}, {y, -yMax, yMax}];
```