SEGMENTED POLYURETHANES CONTAINING DIACETYLENE UNITS IN MULTIPLE MOLECULAR ENVIRONMENTS

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Submitted to the Department of Materials Science and Engineering in partial
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Abstract

A synthetic technique for synthesizing diacetylene unit containing polyesters in both hydroxylly functionalized prepolymer and high molecular weight forms was developed. Using this technique, several diacetylene unit bearing aliphatic polyesters have been synthesized and characterized to evaluate their thermal and chromic properties for use in segmented polyurethanes. These polyesters have shown thermochromic transitions near room temperature, and a few can be activated by body heat. The thermochromic transitions are dependent upon the melting transitions, which in turn are dependent upon processing as well as structure. The thermochromic transition of each polyester can be tuned to a desired temperature through processing and annealing sequences.

Using the diacetylene unit containing polyester macrodiols, several segmented polyurethanes were synthesized with additional diacetylene units incorporated into the hard segments as well. The resulting polydiacetylene chains in the two separate phases show well separated thermochromic transitions. Selective cross-polymerization of the hard segment diacetylene units has been demonstrated. By utilizing this technique, it is possible to dictate the relative levels of cross-polymerization in the hard and soft segments, thus adjusting the magnitudes of the thermochromic transitions in these phases.

The simultaneous orientation of the hard and soft segments and the mechanochromic transitions due to the polydiacetylene chains in the two separate molecular environments was observed. It has been found during this analysis that the majority of the soft segment crystallites orient transverse to the stretch direction, indicating the existence of chain folded lamellae or spherulites.

In segmented polyurethanes with diacetylene units present in the soft segments only, the resulting polydiacetylene chains become disordered in the highly stretched state (200-350% strain). The amorphous soft segment material undergoes strain induced crystallization, which supports additional diacetylene unit cross-polymerization transverse to the stretch direction only. The result is a material which absorbs light in different regions of the spectrum under different polarizations.

The effect of the cross-polymerization in the hard and soft segments on the dynamic mechanical properties has been studied. Cross-polymerization of the diacetylene units in the soft segments has been found to enhance the mechanical properties by increasing and extending the plateau modulus.

Thesis Supervisor: Dr. Michael F. Rubner

Title: TDK Professor of Materials Science and Engineering

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1. Introduction

The incorporation of diacetylene functionalities into polymer chains, called macromonomers, has been investigated for many polymer systems, such as polyamides [1-3], polyesters [4-13], vinyl methacrylates [13], carbonates [14], polyaromatics [15-17], and segmented polyurethanes [18-30]. The diacetylene units in these host polymer lattices can subsequently be cross-polymerized to form polydiacetylene chains, resulting in crosslinked polymers with optical properties closely linked to the local molecular environment surrounding the polydiacetylene chains. These systems have been used for such purposes as mechanical enhancement [1], strain determination [8,21-24], dielectric photoresists [31] determination of molecular orientation during deformation [29], and optical sensors for stress and temperature [27, 29].

In all of these previous studies, the diacetylene groups resided in either a homopolymer matrix, or one particular phase of a block copolymer, such as the hard segments of segmented polyurethanes. Because of this, their usefulness in terms of devices or probes was limited to the particular phase in which they were incorporated. In the case of thermochromism (change in color with temperature) for example, the melting range of the host matrix would solely determine the thermochromic transition of the polydiacetylene chains.

Recently, however, incorporation of diacetylene functionalities into polyester liquid crystalline monomers and polymers has been demonstrated [9,12]. Since these liquid crystalline systems exhibit two first order phase transitions, these separate transitions can be used to drive separate, distinguishable thermochromic transitions in the polydiacetylene chains [12]. In this way, one polymer system can have multifunctional capabilities.

Since the chromic transitions of the polydiacetylene chain are dictated by the local host polymer system, another way to achieve these multiple transitions is to incorporate diacetylene groups into separate local environments which are present in a single macromolecular structure. Segmented block copolymers are ideal for this, as there are many block copolymers which exhibit good phase separation and large differences in mechanical and thermal responses of the respective blocks.

More specifically, in this thesis work diacetylene groups have been incorporated into both the hard and soft segments of segmented polyurethanes (SPUs). A schematic of the proposed morphology is shown in Figure 1.1. Since these two separate phases usually have two separate melting ranges, the thermal response of the resulting polydiacetylene chains will be quite different. By modifying the molecular structure of the two phases, it is possible to create a multifunctional thermochromic device, with transitions occurring at desired temperatures. Of particular interest is the possibility of creating thermochromic devices with transitions at or near room temperature. These polymers could serve to sense changes in temperature for potential applications in the packaging industry or for use in novelty items.

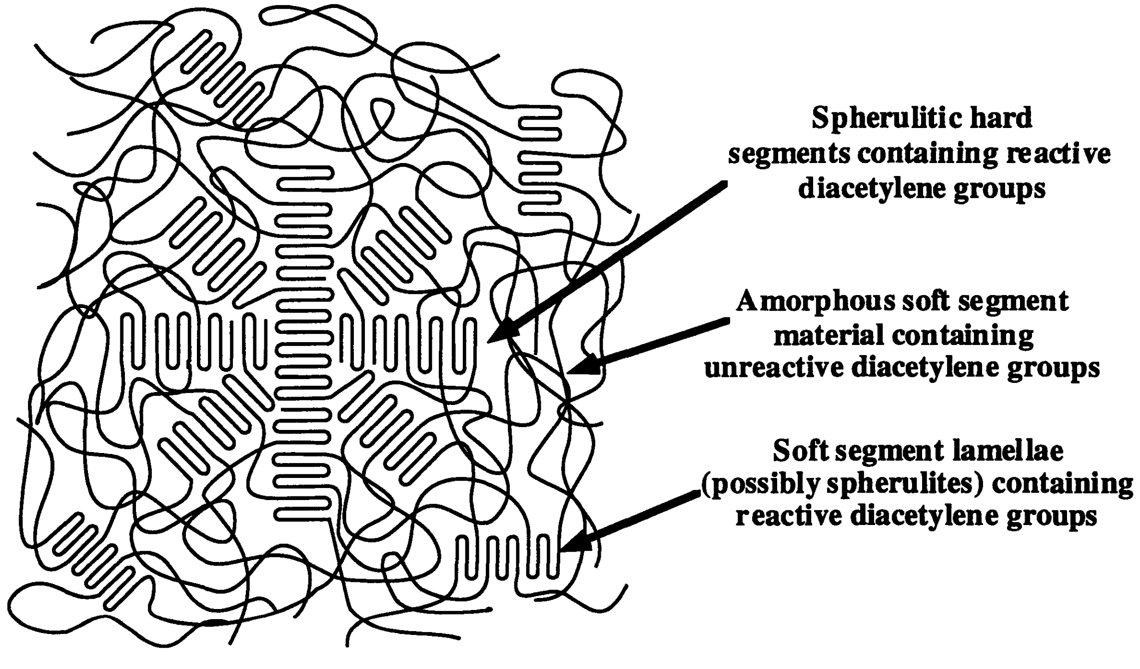

Figure 1.1 Proposed dual reactive diacetylene unit environment.

Additionally, since the two phases play different roles in the deformation process, the effect of the polydiacetylene chains on the mechanical properties will differ similarly. The polydiacetylene chains in a material can also serve as a molecular probe to investigate the stress and deformation on a molecular level. As the deformation mechanics of hard and soft segments differ substantially throughout the entire deformation process, the polydiacetylene chains can be used to probe the complex disordering and orientation processes.

1.1 Polydiacetylene Chains

Diacetylene units consist of two acetylenic groups connected by a single bond. When several of these diacetylene functionalities are packed together in the proper orientation, which must be within a specific distance-angle window (see Figure 1.2), the diacetylene units can be cross-polymerized to form a polydiacetylene chain. The distance and angle parameters (d and γ) necessary for this reaction to take place are generally in the range of 5 Å and 45^{o} respectively [32]. The cross-polymerization can be initiated by several means, such as heat, ultraviolet radiation, high energy irradiation, and pressure.

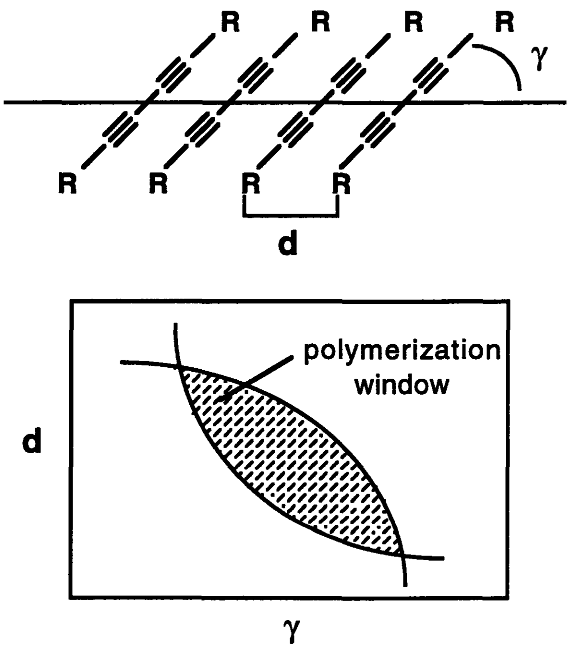

Figure 1.2 Geometric constraints for diacetylene unit cross-polymerization [32].

This reaction, which is referred to as topochemical, takes place in the solid state. Since there are no byproducts given off and the diacetylene units are already within the proper geometric bounds, the cross-polymerization results in only minor morphological changes. A schematic of this cross-polymerization is shown in Figure 1.3.

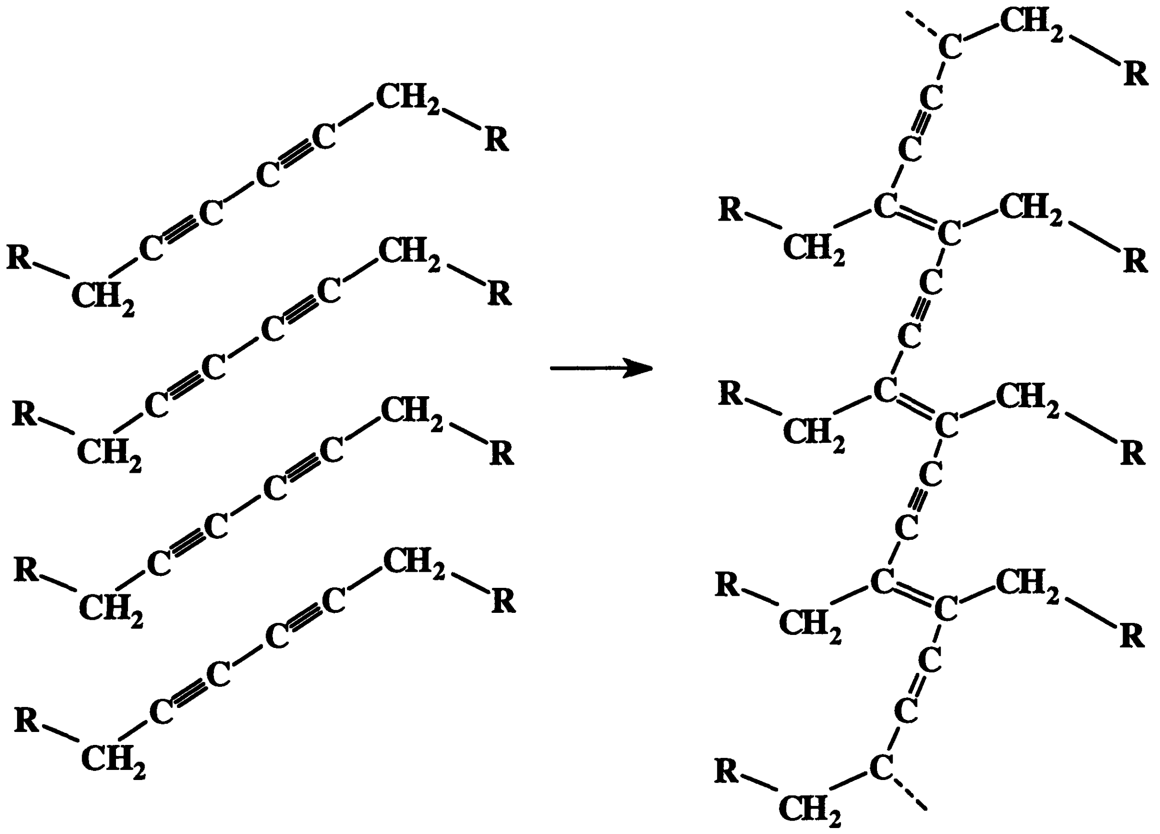

Figure 1.3 Diacetylene unit to polydiacetylene chain reaction.

The change from the diacetylene unit to the polydiacetylene chain is accompanied by the appearance of a distinct absorption in the visible region, usually between 450 and 650 nm. This is due to an excitonic transition in the highly conjugated system that is formed, which in turn depends upon the extent of electron delocalization.

Polydiacetylene chains which assume an extended or planar conformation will have a relatively large effective conjugation length over which the π bond electrons can delocalize. Large delocalizations correspond to a low excitation energy.

Therefore, changes in conjugation length in polydiacetylene chains will result in changes in the absorbed and observed colors. For more planar, or "ordered" polydiacetylene chains, the large delocalization results in an absorption band in the 600 to 650 nm range. As the order decreases, the absorption shifts to higher energies, usually between 450 and 500 nm.

The order of a polydiacetylene chain is effected by the conformation imposed upon it by the substituent (R) groups. These groups will largely determine the d and γ parameters for the diacetylene unit crystals. Additionally, factors which effect these R groups will in turn effect the polydiacetylene chain backbone. This disordering can be effected by either thermal disruption, solvation, or stress induced changes in the lattice structure. Additionally, shifts can arise from stretching of the existing crystalline lattice without any disordering of the crystal structure.

1.2 Segmented Polyurethanes

Segmented polyurethanes (SPU's) are a versatile class of polymers whose properties can be varied over a wide range, due both to chemical tailoring as well as post synthetic processing.

SPU systems can have properties that range from those of an ideal elastomer to those of a hard plastic. They are generally used for specialty purposes, as they are somewhat more expensive to produce than many other polymers which may be used as suitable substitutes. SPUs form a class of polymeric materials referred to as segmented block copolymers: their chemical structure is one in which two or more chemically different "blocks" are tied together to form the polymer molecule. The incompatibility of these blocks and their tendency to phase separate gives the SPUs their unique properties.

Since SPUs are synthesized from a minimum of three different chemical precursors, there are a multitude of different properties which can be achieved through the variation of these constituents. Their unique phase separated morphology yields polymers which can combine the advantageous properties of the precursors, as well as generate new ones not possible with their homopolymers. Although there are numerous properties which can be created, SPU's are generally favored due to their processibility, high ultimate tensile properties, and their uncommonly good tear and abrasion resistance.

There are three basic "components" from which segmented polyurethanes (SPUs) are synthesized. The first is the "soft" segment, a prepolymer with a molecular weight in the range of 500 to 3000, which is functionalized with hydroxyl groups on the chain ends. Although numerous types of prepolymers have been successfully used in the production of SPUs, the most common are either polyesters or polyethers*. The prepolymers used have a wide variety of structures to yield properties for different purposes, but the majority are saturated chains with glass transition temperatures below room temperature to produce a product which is not brittle.

The other two components are a diisocyanate, and a "chain extender," which consists of either a low molecular weight diol, a diamine, or water**. These last two components make up what is termed as the "hard" segment of the system. In some cases, multifunctional components are used to effect crosslinking in the system, but this is more the exception than the rule.

There are two common ways in which SPUs are synthesized: the one shot and the two shot methods. In the two shot method, the prepolymer and twice its stoichiometric amount of diisocyanate are added to the reaction flask. The hydroxyl group and isocyanate react to form a urethane bond. This effectively end caps the prepolymer, and results in a difunctional diisocyanate. A stoichiometric amount of chain extender is then added, which connects the diisocyanate fragments into the final polymeric system. A schematic of this reaction is detailed in Figure 1.4.

In the one shot method, all of the components are added at the same time, which leads to a much more heterogeneous system on a molecular scale. Instead of regularly repeating hard and soft segments of equal lengths, several chain extenders might be linked before a soft segment is added or visa versa. The one shot method is more often used for processing conditions in which the reactor vessel will give the final shape of the product. This one shot method is also used for systems in which molar ratios of diisocyanate to chain extender to prepolymer are not 2:1:1, i.e. 3:2:1. In such a case, a two shot system would yield a somewhat random distribution of segments regardless of the order in which they are introduced. For this reason, there is no distinct advantage in using the two shot over the one shot method.

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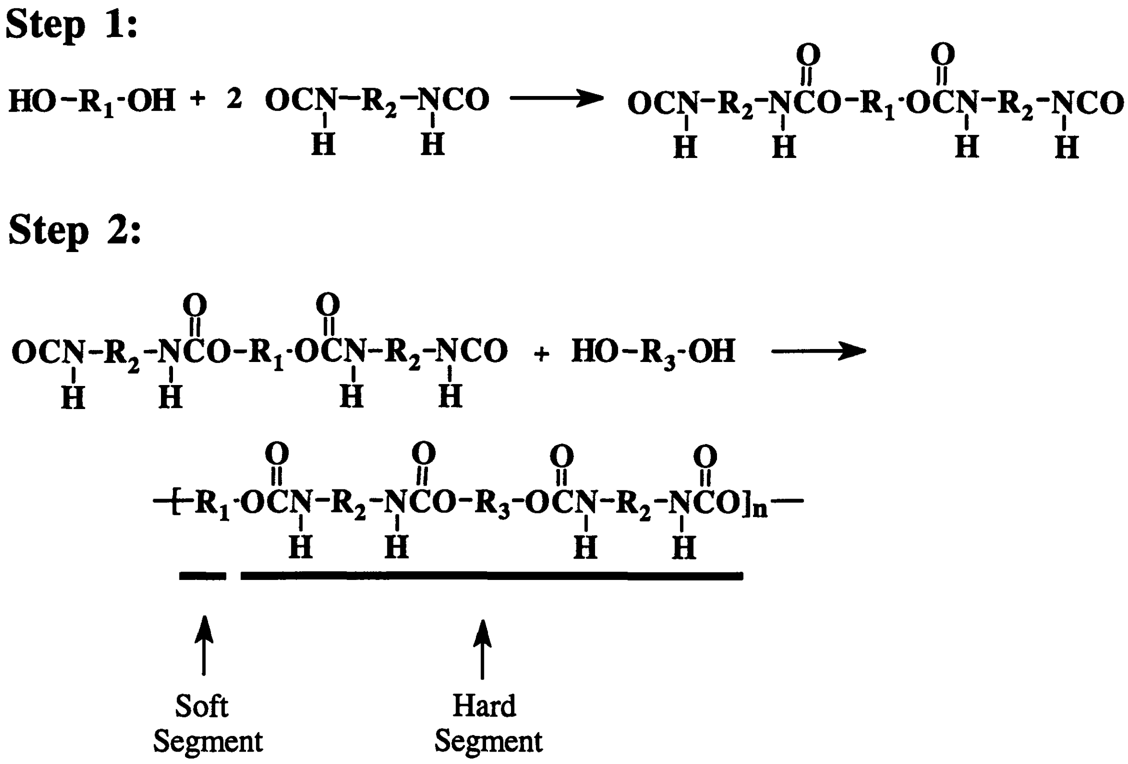
* Soft segments other than polyethers and polyesters have been successfully used, such as polydimethylsiloxanes, polybutadienes, and isoprenes, to name a few.

** Water was the "first" chain extender used in polyester soft segmented polyurethanes. It has been found that diols and diamines make for a product with better mechanical properties, and thus it is not used extensively anymore [46].



$$HO\text{-}R_1\text{-}OH + 2\ OC\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}CO \longrightarrow OC\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}\overset{O}{\overset{\|}{C}}O\text{-}R_1\text{-}O\overset{O}{\overset{\|}{C}}\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}CO$$

$$OC\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}\overset{O}{\overset{\|}{C}}O\text{-}R_1\text{-}O\overset{O}{\overset{\|}{C}}\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}CO + HO\text{-}R_3\text{-}OH \longrightarrow$$

$$-[\underbrace{R_1}_{\text{Soft Segment}}\underbrace{\text{-}O\overset{O}{\overset{\|}{C}}\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}\overset{O}{\overset{\|}{C}}O\text{-}R_3\text{-}O\overset{O}{\overset{\|}{C}}\underset{H}{N}\text{-}R_2\text{-}\underset{H}{N}\overset{O}{\overset{\|}{C}}O}_{\text{Hard Segment}}]_n-$$

Where: R_1 is the soft segment
R_2 is the diisocyanate unit
R_3 is the chain extender

Figure 1.4 Two shot segmented polyurethane synthesis.

SPU's obtain their unique physical properties from their phase separated morphology. Since the hard segments and soft segments are quite different chemically, with the hard segments being more polar, they tend to separate into two phases when cooled from the melt or cast from a solvent.

For ideal elastomers, it is desirable to have a highly extensible system which recovers fully even after extensions of up to 600%. To achieve this, it is necessary to have a polymer which is well phase separated, has well ordered and cohesive hard segments which are not continuous, and amorphous soft segments with a T_g well below room temperature.

During the deformation process, the soft segments are elongated while the hard domains remain rigid, which keeps the polymer from exhibiting irreversible flow. When the stress is released, the soft segments pull back into their original disordered form, and the original shape is recovered. It is often desirable to have the soft segments crystallize upon extension, as this adds to the cohesive strength of the polymer, which in turn increases its ultimate tensile strength [33, 34]. Any strain induced crystallization must be reversible for the polymer to fully recover.

This ideal morphology and its resulting properties are not always what one finds in a typical segmented polyurethane elastomer. There is inevitably some phase mixing, generally more so with polyester soft segments than with polyethers. This is because polyesters are more polar than polyethers and are therefore involved in more extensive hydrogen bonding with the hard segments [35].

The effects of this are numerous. The thermal properties can change dramatically, and can be seen as an increase in the soft segment T_g, a decrease in the hard segment T_g, or in extremely well mixed systems one single broad T_g for the whole system, a decrease in the degree of crystallinity in the hard segments, a decrease in melting point of the hard segments, and sometimes the addition of another set of thermal transitions due to this third "phase mixed phase."

The effects upon the mechanical properties are equally as numerous. Less ordered hard segments will yield polymers with lower ultimate tensile strengths, and sometimes higher strains to failure. Increased soft segment T_g's or extensively phase mixed systems can produce polymers which are leathery instead of elastic in nature. Finally, upon deformation, the phase mixed portions which don't have the cohesive strength of the hard segments nor the mobility and recovery of the soft segments will reorder themselves during the process and complete recovery will not occur. This restructuring of the phase mixed areas can take place at fairly low stresses, and is sometimes referred to as a hysteresis loss [35].

Additionally, some crystallinity in the soft segments may be present in the undeformed state, and it is quite common for many amorphous soft segments to crystallize over time, which can change their mechanical properties dramatically. Once again, this is seen more often in polyesters than the polyethers as the polyesters have a greater tendency to crystallize. In a very few cases, this crystallinity is slight, and does not effect the deformation process. In most cases, the material does not exhibit full recovery or ideal elastomeric properties. For small amounts of crystallinity, upon deformation the crystallites will rearrange themselves, and when the stress is released, these crystallites will not return to their original morphology, giving what is known as permanent set [33]. For large degrees of crystallinity, the crystallites will once again rearrange themselves during deformation, but without a significant amorphous fraction, no recovery will occur and the polymer will simply be going through a yielding process.

The wide variety of chemical components available for segmented polyurethane synthesis, compounded by the ability to change the morphology and molar ratios, yields a multitude of possible systems, the systematic study of which has merely just begun.

1.3 Diacetylene Unit Containing Polyesters

Polyesters were some of the first polymers to be investigated as hosts for diacetylene functionalities [11]. Patil and coworkers [36] investigated several aliphatic and aromatic polyesters by reacting 3,5-hexadiyne-1,6 diol with various diacid chlorides. The diacetylene unit reactivity to uv light was found to decrease with increasing the number of methylene spacers or the use of aromatic units. Lescano et al [10] studied four polymers of poly(10,12-docosadiyne sebacate) with different molecular weights. Although the effects of the different molecular weights were not discussed, the authors examined the reversibility of the thermochromic properties, and noted that proper annealing conditions would increase the degree of crystallinity, which in turn increased the degree of cross-polymerization which can take place. Ozcayir and Blumstein [9] investigated several diacetylene unit containing polyesters with various aromatic groups for their liquid crystalline properties. Both copolymerization and methyl substituted aromatic units were utilized to bring the transitions below the temperature at which thermally induced cross-polymerization occurred. Hammond and Rubner [12] also investigated several liquid crystalline diacetylene unit containing polyesters. They found that the conjugation length was dictated by the order of host polymer, whose first order thermal transitions (both crystal to liquid crystal and liquid crystal to isotropic melt) would drive separate thermochromic transitions in the polydiacetylene chains.

Lovell and coworkers [8] made several studies of low molecular weight aromatic polyesters for use as stress sensors. The polyesters were blended in different compositions with poly[ethylene-co-(vinyl acetate)] and crosslinked with heat. Using resonance Raman spectroscopy, the stress in the polydiacetylene chains was investigated as a function of the strain in the macroscopic structure. Fomin et al [4-6] have investigated several diacetylene unit containing polyester and copolyesters for potential use as third order nonlinear optical materials. Large increases in mechanical properties with irradiation were found. Additionally, one of the copolymer compositions demonstrated liquid crystallinity and was found to cross-polymerize while in the liquid crystalline state.

1.4 Segmented Polyurethanes Containing Diacetylene Units in the Hard Segments

The incorporation of diacetylene units into the backbone of these polymers yields a system which is not only unique in its own right, but also gives one an opportunity to study the properties of SPUs in general.

As the absorption spectrum of a polydiacetylene chain is directly coupled to the electronic states, and these states are highly dependent upon the host environment, changes in the absorption are indicative of changes in the host environment. Shifts can be due to stress, temperature, pressure, or crystallographic changes. Detecting these changes can give insight into the morphology and mechanical behavior of SPUs.

Additionally, because of the shifts in the visible range due to temperature and deformation (thermochromism and mechanochromism), polydiacetylene chains can be used as devices themselves to detect temperature and stress levels.

Previously, extensive research has been done on the incorporation of diacetylene units in the hard segments of segmented polyurethanes [18-30]. It has been found that these polymers, depending upon their particular molecular structure, exhibit mechano and/or thermochromic transitions [27, 29]. Since the response of the polydiacetylene chain to strain and/or temperature is extremely sensitive to its molecular environment, small changes in the chemical or morphological surroundings can cause vastly different effects [27]. The anisotropic absorption of the polydiacetylene chains due to their extended linear structure was utilized to determine the orientation of the conjugated chains during mechanical deformation [29].

This in turn yielded information about the orientation and deformation of the hard segment lamellae, which are oriented perpendicular to the polydiacetylene chains. Discussion of the detailed results of these orientation and deformation studies is presented in Chapter 4, as they are used for comparison with the soft segment polydiacetylene chains.

The incorporation of diacetylene units into host polymers has proved to be useful in terms of producing both devices and analytical systems. Due to the multitude of properties and functions of monomeric components and polymers available today, it is apparent that the addition of diacetylene functionalities to these will continue to produce polymers with as yet unimagined properties and uses.

2. Experimental Procedures

2.1 Synthetic Procedures

5,7 dodecadiyne-1,12 diol

5,7-dodecadiyne-1,12 diol was synthesized by oxidative coupling of 10-undecyne-1-ol as described by Hay [37]. After the reaction was completed, a solution of 5N HCl was added until the mixture reached a pH of 1. The 5,7-dodecadiyne-1,12 diol was extracted three times using an ether-water extraction. The ether fraction was dried by stirring overnight with $MgSO_4$. The majority of the ether was removed by rotovap, after which the remaining oil was dried overnight in a high vacuum. The resulting yellow solid was dissolved in ether, and then filtered out after recrystallizing at approximately -15 ^oC. This recrystallization process was repeated until the precipitate had a defined melting temperature, as observed in a mel-temp apparatus, between 49 and 51 ^oC.

10,12 docosadiyne 1,22 diol

This material was synthesized by the same method as 5,7-dodecadiyne-1,12-diol. After the reaction was completed, a solution of 5N HCl was added until the mixture reached a pH of 1. The resulting mixture was poured into 5 times its volume of methanol. The precipitate was filtered off with a buchner funnel, and then repeatedly washed with deionized water and filtered until the water which was removed had a pH equal to that of the fresh deionized water. The precipitate was then dried overnight in a high vacuum, and purified by multiple recrystallizations from acetone.

Polyesters

Polyesters were synthesized by a modified version of the method as described by Korshak and Vinogradova [38]. The desired stoichiometry of diol and diacid (1:1 for high molecular weight polymers) was added along with 2.0% by weight p-toluene sulfonic acid, and toluene into a three necked flask to make a 15% polymer in toluene solution. A soxhlet extractor system with sodium metal (to remove the water) placed in the thimble was attached to the middle neck. Chunks of glass were place in the thimble along with the sodium to adjust the retention volume, so that the polymer concentration never exceeded 25%. The entire reaction was refluxed and stirred for 24 hours under a blanket of dry nitrogen.

At the termination of the reaction, the entire mixture was precipitated in a beaker of methanol, and recovered in a buchner funnel. The recovered polyester was washed repeatedly with methanol to remove any remaining catalyst or monomers. The polymer was then dried under high vacuum overnight.

Polyester macrodiols were synthesized by adding a stoichiometric excess of the diacetylene diol. The quantity of this excess was first calculated using the equation:

$$P_n = 1+r/1-r; \quad r = [\text{diacid}]/[\text{diol}] \qquad \textbf{Equation 2.1}$$

where P_n is the degree of polymerization. Experimentally, it was found that the calculated stoichiometric imbalance produced a prepolymer with approximately one half the desired molecular weight. The cause of this discrepancy is not known. In other words, to produce a prepolymer of a defined molecular weight, twice the stoichiometric imbalance calculated by Equation 2.1 is used. Typical yields were 85 - 90%. Determination of molecular weight and end group functionalization is described in Section 2.2.

It should be noted that this synthetic technique is the only one which has been found to produce both high molecular weight polyesters, and functionalized prepolymers (>99% hydroxyl termination, when an excess of diol is used). Typical direct esterification techniques involve heating to high temperatures in bulk, which results in the cross-polymerization of the diacetylene units. Using acid chloride synthetic techniques, we were not able to obtain molecular weights over 10,000 g/mol, and functionalization over 95% was extremely difficult. Fomin et al [6] have used oxidative coupling of bisacetylenic diesters to achieve polyesters with weight average molecular weights as high as 73,000 g/mol. However this technique, as well as interfacial polymerization techniques are not able to produce functionalized prepolymers for use in segmented polyurethanes.

Segmented Polyurethanes

The polyester macrodiol is dissolved in hot toluene at a concentration of 5.5 ml/g. prepolymer (this quantity of toluene is used to both dissolve and later wash through the prepolymer). An equal quantity of toluene is added to a three necked flask along with a small scoop of dibutyltin bis(2-ethylhexanoate) and hexamethylene diisocyanate (HDI) in 2.05 molar equivalents as compared to the prepolymer. The toluene/dibutyltin bis(2-ethylhexanoate)/HDI mixture is stirred using a mechanical stirrer and heated to 70°C. The prepolymer solution is then added to an addition funnel which is attached to one of the side necks. The prepolymer solution is then added dropwise over an hour, and the entire solution is then refluxed at 80 °C for three hours. The heat is then turned off, a stoichiometric amount of chain extender equal to that of the prepolymer is added and washed through with a minimal amount of toluene, and the mixture is stirred overnight. In the morning, the solution is heated to 60 °C for 3 hours. The solution is then cooled and precipitated in a beaker of methanol. The precipitate is filtered off using a buchner funnel, washed in methanol, and filtered again. The resulting polymer is dried overnight under high vacuum.

During all synthetic procedures, glassware is flamed under vacuum to remove water, and all reactions are carried out under a blanket of dry nitrogen. All liquids were fractionally distilled, and all solids were rigorously dried using high vacuum.

2.2 Characterization techniques

Polyester end group analysis

Acid number determination was performed according to standard techniques with a standardized potassium hydroxide solution [39] using a thoroughly dried synthesized polyester macrodiol in its entirety. The resulting solution was back titrated with an equimolar amount of HCl, and washed thoroughly with water and then methanol, to remove the KCl and residual indicator. The recovered polymer was then dried overnight under high vacuum. Since this procedure subjects the polymer to a wide variety of chemicals and conditions, the acid number found for the subject polymer (.05) was assumed to be consistent with those of future polymers, and the procedure was not repeated on subsequent polyesters.

A thoroughly dried one gram quantity is used for an hydroxyl number titration following a standard technique [40] with the following adjustments:

-due to the small amount of prepolymer used, the normality of the standardized KOH solution was .1, not 1.

-as many of the prepolymers were slightly cross-polymerized, and gave a slightly pink color after the acetylation step, a mixed indicator solution of phenolphthalein and thymol blue was used instead of just phenolphthalein.

-the indicator solution was not pH adjusted.

-the destruction of the residual acetic anhydride with water was performed after the heating step, which is proper, as the addition of the water before the heating step in the reference is a typographical error.

The molecular weight and functionality of the prepolymers was determined according to the proper equations [40].

Infrared Spectroscopy (IR)

IR was performed on a Nicolet 510P fourier transform infrared spectrophotometer. Samples of both monomers and polymers were prepared by dissolving the material in tetrahydrofuran and evaporating on a NaCl plate. IR was used to both confirm chemical structures, and to investigate the relative quantities of hydrogen bonding in the segmented polyurethanes, which gives insight into the degree of phase separation and packing order [41]. IR spectra of all synthesized monomers and polymers was in agreement with expected results. Segmented polyurethanes demonstrated well defined, phase separated hard segments as characterized by hydrogen bonding.

Differential Scanning Calorimetry (DSC)

A Perkin Elmer DSC7 with liquid nitrogen subambiant capabilities was used to determine melting phenomenon in both the polyesters and segmented polyurethanes, as well as the effects of annealing, casting procedures, and irradiation. In almost all cases, the heating rate employed was 10 °C/min., with the exception being the heating rate studies to study the in situ recrystallization effects. Typical sample weights for cast films were 10 mg., while the spin coated samples, which were scraped off of glass slides, were approximately 3 mg. Melting peak areas of the polyesters were used to make qualitative comparisons of degrees of crystallinity, while the separation or lack thereof in the segmented polyurethanes was used to investigate phase separation.

Dynamic Mechanical Analysis (DMA)

DMA was carried out on a Seiko Instruments DMS 200 with a liquid nitrogen cooling system. Multiple measurement frequencies of 1, 2, 5, 10, and 20 Hz were used in each test. The heating rate used was 2 °C/min.. Polyesters films were prepared by dissolving the polymers in tetrahydrofuran at a concentration of 80 mg/ml. and evaporating the solution overnight in a glass casting dish. The resulting films were then removed and dried under high vacuum. Segmented polyurethane solutions were prepared in a 50/50 mixture of toluene and tetrahydrofuran at a concentration of 80 mg./ml and cast in glass casting dishes overnight. Results were instrumental in determining the glass transition and melting temperatures, as well as the small strain properties and the effects of electron beam radiation on each of these properties.

Ultraviolet and Visible Spectroscopy (UV-Vis)

Absorption spectra were obtained using an Oriel InstaSpec™ II. For thermochromic studies, polyester samples were prepared by spin coating from THF on glass slides. Segmented polyurethanes were cast on glass slides from a 50/50 mixture of toluene and tetrahydrofuran at a concentration of 80 mg./ml. When necessary, polyesters were annealed in a sealed chamber immersed in a heated water bath. Samples were heated using a Mettler hot stage.

For mechanochromic studies, samples were prepared using the same method as that used for DMA studies. Mechanochromic tests were performed by clamping the sample in a manual stretching rig, marking a measured length on the sample, and using the distance between the two marks to determine the strains.

Cross-Polymerization

Poly(ester-diacetylene) thin films for optical studies were cross-polymerized using a low pressure mercury arc lamp emitting 254 nm radiation. Films for mechanical studies were cross-polymerized by electron beam radiation, as this process penetrates the full thickness of the polymer film.

3. Polyester Synthetic Considerations, Characterization, and Thermochromic Effects

3.1 Introductory Remarks

As diacetylene units have been successfully incorporated into the hard segments of SPUs, it was necessary to determine how to incorporate them into the soft segments as well. Typically, soft segments for SPU's have consisted of polyester or polyether macrodiols, although specialty polymers have been used such as siloxanes and branched alkanes. However, synthesizing a polyether or other chain growth type polymer with diacetylene functional groups is not a readily tractable problem. Diacetylene unit containing diols are easily synthesized from available materials, making polyesters the material of choice for the soft segments.

To incorporate these diacetylene unit containing polyesters into segmented polyurethanes, they must be synthesized in the molecular weight range of 1000 to 4000 g/mol and functionalized with hydroxyl groups, which, as was noted in Chapter 2, is possible using the developed synthetic technique. Since the properties of the macrodiols, such as melting point and glass transition temperature, depend largely upon the molecular weight, it is necessary to synthesize high molecular weight versions of these polyesters for comparative purposes. Additionally, knowledge of the homopolyester glass transition temperatures (T_g's) will aid in determining the extent of phase mixing in the segmented polyurethanes.

This chapter investigates several high molecular weight diacetylene unit containing polyesters. Their properties, such as glass transition temperature, absorption spectrum, and degree of crystallinity, and the effects of cross-polymerization upon these properties, will aid in determining which chemical formulations are the best for use in the dual environment diacetylene unit containing segmented polyurethanes.

3.2 Structural Design of Soft Segments

The mechanical and thermal properties of an SPU are mainly determined by the chemical structure, although processing can have a dramatic effect as well. These properties will in turn dictate the optical properties and transitions of the polydiacetylene chains. By changing different components, is possible to produce a variety of effects, such as minimal hysteresis, or complete permanent set (a polymer with no recovery), or various crystalline cohesive strengths which will determine melting temperatures and mechanical integrity.

The following sections detail the molecular design considerations which are involved in choosing the proper structural components.

3.2.1 Ideal Elastomers

Ideal elastomers are polymers which are not only elastomeric, but exhibit a minimal amount of permanent set. In other words: a system which fully recovers its original dimensions after a large deformation process, typically 300 to 700 percent. To achieve this, the soft segment must conform to several standards, which have been mentioned previously, and are outlined below.

1) The glass transition temperature of the soft segment *in the segmented polyurethane system** must be sufficiently below room temperature for it to be deformed to any large degree. If the T_g is close to or above room temperature, the resulting SPU will be leathery or brittle, respectively.

2) The degree of crystallinity in the soft segment must be small enough to allow mobility of the majority of the soft segment. If not, the material will have only limited extensibility [34]. It should be noted that some crystallinity is allowable, as long as it does not disrupt the large scale deformation mechanics. For small amounts of crystallinity, there will be some inherent hysteresis in the polymer due to reordering of these crystallites during deformation. After the crystallites are reordered, the polymer will not exhibit further hysteresis, and will function as an ideal elastomer.

3) Any strain induced crystallization should be limited in scale until large extensions are reached, otherwise the material will stiffen at low strains. Additionally, any crystallization which occurs must be reversible to allow the system to regain its original dimensions.

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* The T_g of the prepolymer alone can differ considerably from that of the prepolymer in the SPU. This is because for low molecular weight polymers T_g is partially dependent upon molecular weight, due to the effects of the chain ends. The restriction of the chain ends in the final polymer product, as well as any phase mixing effects, can raise T_g significantly.

As was noted before, it is found that most polyether systems meet the three criteria expressed above, while most polyesters do not. For aliphatic polyester systems, it is difficult to pass both criteria 2 and 3 due to inherent crystallinity in the soft segments and extensive phase mixing between the hard and the soft segments.

Although the semicrystalline nature of polyester soft segments is usually the cause of their downfall in terms of a fully recoverable polymer, it will serve as a boon in terms of the proposed polyester-diacetylene system. As mentioned before, for the diacetylene units to polymerize, they must be ordered within certain geometric bounds. It has been found that polyester systems in general meet this geometric criterion successfully [6-11,36]. The difficulty involved will be in designing a polyester system in which the diacetylene unit cross-polymerization may take place, yet the crystallinity is not too great to retard elastomeric behavior.

3.2.2 Nonideal Elastomers

Although the properties of ideal elastomers could prove to be quite useful, non ideal elastomers, i.e. ones which don't exhibit full recovery or any recovery at all, may have unique and valuable properties of their own. Previous work has been done on poly(diacetylene-urethane) systems which are glassy and not elastomeric [21-23]. Since there is no long range mobility, stress is transferred to the polydiacetylene chains in the hard segments at extremely small strains, and can be accurately measured by Raman spectroscopy. These materials can therefore be used for small strain detection systems.

However, these polymers are brittle, which limits the types of applications in which they can be used. In the preliminary stages of this thesis, a poly(diacetylene-urethane) system was synthesized which has a highly crystalline soft segment (results not shown). When heated above the soft segment melting point, it can be drawn to fully extend the soft segments, and then cooled in place. Due to its crystalline nature, it cannot retract. Once it is in its stretched form, small strains transfer stress to the hard segments, so that it exhibits mechanochromism at low extensions. This polymer, unlike the glassy polyurethanes, is still above the Tg of the soft segments, and can be twisted, folded, etc... However, its major drawback is that it must be drawn first, so that it cannot be used if simply applied as a coating to another material.

Highly crystalline diacetylene unit containing soft segment materials would overcome this problem of prestretching. Even if they are too crystalline to be highly extensible, they will still be useful for detecting small strains without any prior processing.

Additionally, extensibility will have no impact upon a material's thermochromic ability. To have a polymer which is sensitive to two distinct temperature ranges, it will simply be necessary to have the thermal transitions of the hard and soft segments well separated, so that they do not significantly overlap.

3.2.3 Reduction and Control of Crystallinity

There are several ways in which crystallinity in polyester systems can be retarded, if not destroyed completely. Several of these methods are as follows: using odd numbered methylene spacers in the diol and/or the diacid components to reduce the packing efficiency of the crystal lattice [42,43], increasing the percentage of ester groups which increases the quantity of carbonyl oxygens which are difficult to pack in a crystal* [34,42,43], use of a component which includes additional ether groups [43], copolymerization with a small amount of isophthalic acid which destroys the linearity of the polyester and therefore impedes crystalline packing, decreasing the molecular weight of the prepolymer [43-46], the use of aromatic instead of aliphatic diisocyanates [45], quenching the segmented polyurethane from the melt to avoid crystallization of the soft segments [45], using the segmented polyurethane system above the melting temperature of the prepolymer [33], addition of plasticizers [46], copolymerization with different length diols and diacids to destroy the regularity and therefore the crystallizability of the system [33,34,42,43,47], and the use of diols and/or diacids with pendent branches, such as 1,3 propane diol which greatly reduces, if not destroys any crystallinity [33,34,43].

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* Although an increase in ester concentration will reduce crystallinity in the polyester, it has been reported to increase the permanent set due to increased crystallinity upon extension [33].

3.2.4 Reduction and Control of T_g

There are several factors, both intra and intermolecular, which affect T_g. The intramolecular considerations are of course all chemical in nature. To obtain a polymer with a low glass transition temperature it is desirable to have no bulky substituents [34,47], flexible bonds such as ether linkages, no bulky pendent groups or disubstituted carbons which can sterically hinder movement, and monosubstituted alkyl chains which effectively plasticize the polymer by increasing free volume [48]. For polyethers, an increase in the ether to methylene ratio serves to lower T_g.

In the case of polyesters, an increase in the ester to methylene ratio increases T_g [42,47,49].

Intermolecular interactions in SPU's are mainly due to the effects of the hard segments upon the soft segmental mobility. An increase in the prepolymer molecular weight serves to decrease the soft segment T_g, since a larger percentage of the prepolymer is not restricted by the rigid hard segments [42,44].

Additionally, a broadening in the T_g with increasing prepolymer length will be observed due to increased phase mixing between the two segments. Reduced hard segment percentage will also reduce T_g as it reduces the restriction of the soft segments and the amount of phase mixed hard segments [44]. However, the extent of the hard segment percentage effects are highly dependent upon the type of hard segment used [50]. Annealing of a polymer can increase and broaden the T_g in some cases as this increases the degree of crystallinity in the soft segments which restricts mobility [44,45]. Lastly, the use of diisocyanates which yield a more ordered hard segment and creates less phase mixing will keep from raising the T_g of the soft segment. Examples are the use of hexamethylene diisocyanate instead of diphenylmethane, or diphenylmethane instead of dimethyldiphenylmethane [45,49].

Designing an elastomeric soft segment is not as simple as following a few of the previous suggestions. Although these findings serve as general guidelines, they do not serve as steadfast "rules" for the production of elastomers. In many cases, the use of branches and asymmetrically substituted phenyl rings to destroy crystallinity succeeds, yet the bulkiness or stiffness of these units raises T_g too much for the system to be elastomeric.

A complete analysis of all of the polyester combinations would be quite impossible due to the infinite number of variations. To this point, only a few combinations can be ruled out.

For the diacetylene unit containing diol, only a few synthetic components are readily available. Of these, those which the hydroxyl group is attached to a secondary or tertiary carbon would be best avoided due simply to their reduced reactivity (approximately an order of magnitude less) with isocyanates [42]. This leaves six diacetylene unit containing diols to work with: those with 1, 2, 3, 4, and 9 methylene spacers between the acetylene unit and the alcohol functionality, and 2,8 diene-4,6-decyne diol, a diacetylene unit containing diol with two double bonded groups.

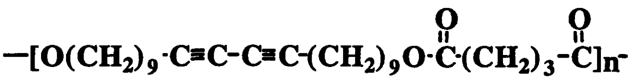
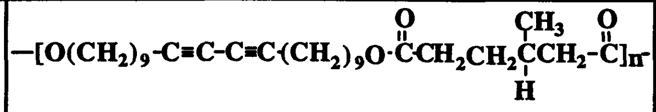
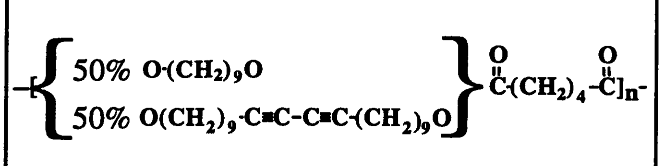
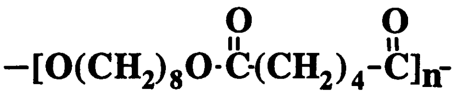
It should be noted that polyesters which are not reactive are not necessarily going to be unreactive in a segmented polyurethane system. Furthermore, amorphous polyesters may crystallize upon extension in a segmented polyurethane system, thus allowing polymerization to take place. This fact may yield a poly(diacetylene-urethane) system which exhibits an order-disorder transition upon relaxation from the stretched state. In fact, it may be possible to polymerize a system in the stretched state, and have it exhibit disorder by both relaxation *and* further stretching.

3.3 High Molecular Weight Diacetylene Unit Containing Polyesters

Several high molecular weight diacetylene unit containing polyesters have been synthesized to investigate the role of the structure on the properties of interest (Table 3.1). The role of the spacer length in the diacid component was changed to control the degree of crystallinity, change the melting points, and vary the optical absorption. Since extensive work has been done on the effects of different diacid precursors upon the thermal properties of polyesters [38,43], we were able to selectively choose ones which would give us the desired melting ranges for use in the multifunctional segmented polyurethanes. In a more severe measure to reduce the melting point and degree of crystallinity, we synthesized both a copolymer system and a polyester whose diacid component spacer contains an asymmetric methyl group. Additionally, one non-diacetylene unit bearing polyester was synthesized for comparative purposes, as will be discussed later. The polyesters are named by first listing the abbreviation for the diacid component used, followed by the abbreviation for the diol component.

The molecular weights of all of these polyesters were quite high (see Table 3.1); high enough so that we can disregard molecular weight effects upon the melting temperature, T_g, and the crystalline structure. All of the polyesters formed good films when cast, and, with the exception of 3A-10,12 which has a very low degree of crystallinity, all were rather tough.

Table 3.1 Polyester structures and properties.

Polymer (diacid component)	**Structure**	**Mn***	**Mw***	**PDI**
MA-10,12 (malonic)	 $-[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_1-\overset{O}{\overset{\Vert}{C}}]_n-$	52,500	80,900	1.54
SA-10,12 (succinic)	 $-[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2-\overset{O}{\overset{\Vert}{C}}]_n-$	46,300	93,600	2.02
GA-10,12 (glutaric)	 $-[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_3-\overset{O}{\overset{\Vert}{C}}]_n-$	66,700	98,100	1.47
AA-10,12 (adipic)	 $-[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}]_n-$	77,700	108,800	1.40
3A-10,12 (3-methyl adipic)	 $-[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\overset{\Vert}{C}}CH_2CH_2\underset{H}{\overset{CH_3}{C}}CH_2-\overset{O}{\overset{\Vert}{C}}]_n-$	48,700	71,800	1.48
AA-1,8/10,12 (adipic) copolymer	 $-[\left\{\begin{array}{l}50\%\ O-(CH_2)_9O\\ 50\%\ O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\end{array}\right\}\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}]_n-$	44,100	80,800	1.83
AA-1,8 (adipic) no diacetylene units	 $-[O(CH_2)_8O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}]_n-$	53,600	91,800	1.71

*Molecular weights in polystyrene standards

3.3.1 Thermal Transitions

In order to determine the T_g's of the polyesters, DMA was carried out on the cast films using a testing frequency of 1 Hz. The results of the DMA are shown in Figure 3.1. The lower temperature peak corresponds to the glass transition temperature. A larger glass transition tan δ peak reflects a larger amorphous fraction contributing to the softening at T_g.

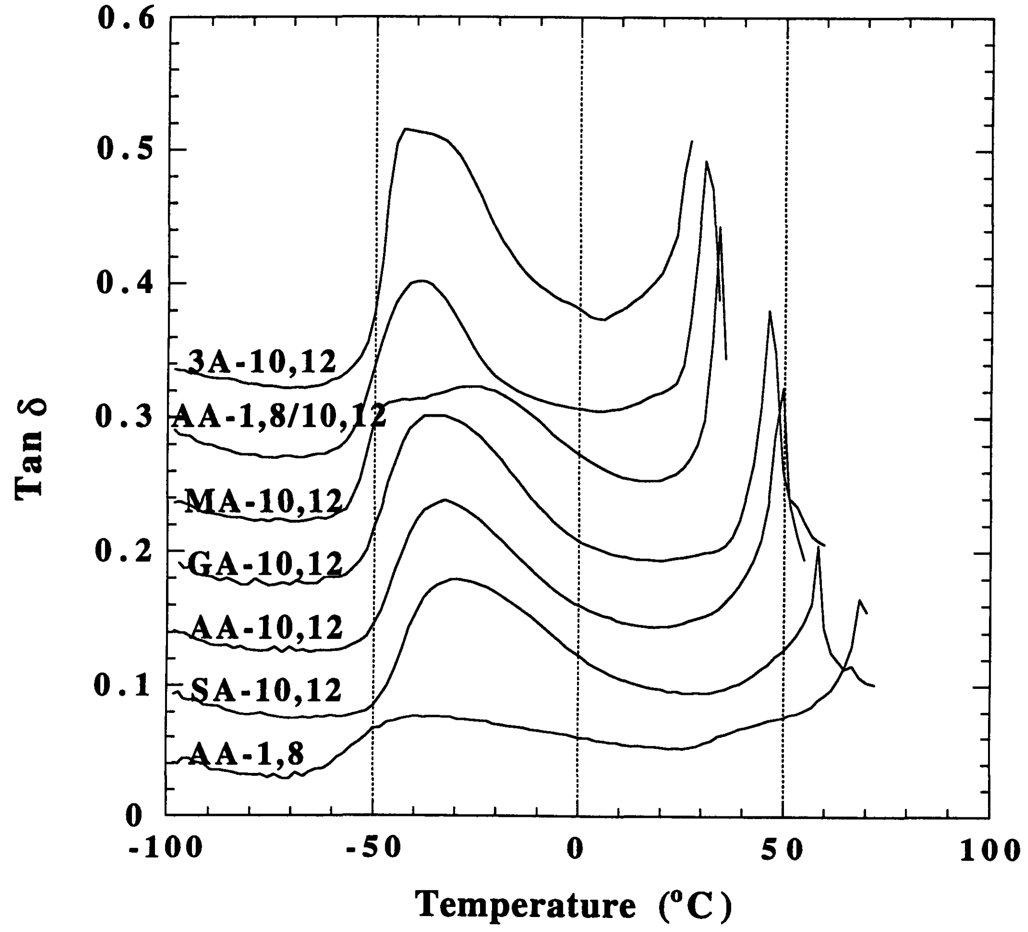


Figure 3.1 Tan δ at 1 Hz. Results offset vertically for clarity.

All of the T_g's as evidenced by the temperature for the peak in tan δ are in the range of -60 to 10 °C. These Tg's are sufficiently low enough for use in elastomeric segmented polyurethanes. The tan δ for MA-10,12 at T_g shows two distinct peaks, which is mostly likely due to two separate distributions of soft segment material. The higher transition is probably due to amorphous material which is closely influenced by surrounding crystalline material. This type of behavior has been observed in poly(ethylene terephthalate) (PET) by Vigier et al. [51], who attributed the two amorphous regions to amorphous material dispersed between the crystalline lamellae of the spherulites, and material dispersed between the spherulites themselves. The other polyesters, however, only show one broad T_g peak, which is most common for a homopolymer.

The sharp increase in tan δ at higher temperatures is due to the mechanical failure of the sample as it melts. When comparing the T_g peak area to the high temperature failure point, it becomes evident that the higher melting materials have a higher degree of crystallinity. For 3A-10,12 and AA-1,8/10,12, this is not surprising, as their structural aspects which reduce their melting points also serve to reduce the degree of crystallinity. It appears that the molecular aspects of the other polyesters which serve to increase the melting temperatures also increase the degrees of crystallinity.

This increase in crystallinity with melting temperature is most likely responsible for the slight increase observed in T_g for the diacetylene unit containing materials. A higher degree of crystallinity restricts the amorphous fraction, which serves to increase the temperature at which the large scale segmental motion can take place.

The mechanical failure temperatures as determined by DMA, which are determined by the melting of the sample, follow closely to the melting temperatures as found by the peak of the melting endotherm as determined by DSC (see Figure 3.2). The melting range covered by these different diacetylene unit containing structures (21-55 ^{o}C) is sufficiently below that of the thermochromic segmented polyurethane hard segments (90-120 ^{o}C) investigated in other work, which should ensure that a composite system will have two distinct thermochromic transitions. Additionally, even though the heats of fusion for these particular polymers are not known, the different DSC melting peak areas detailed in Table 3.2 indicate the same trend in the degree of crystallinity with structure.

Detailed results from Figures 3.1 and 3.2 are presented in Table 3.2. The variation in melting temperatures with the number of diacid component methylene spacers is in accordance with other aliphatic polyesters [43]. The increase in melting temperatures from 1 to 3 to 4 spacers is due to the decrease in ester group concentration and the odd/even spacer effect. The unusually high melting point for SA-10,12 has been noted for some aliphatic polyesters using succinic acid and is most likely due to a crystal packing anomaly.

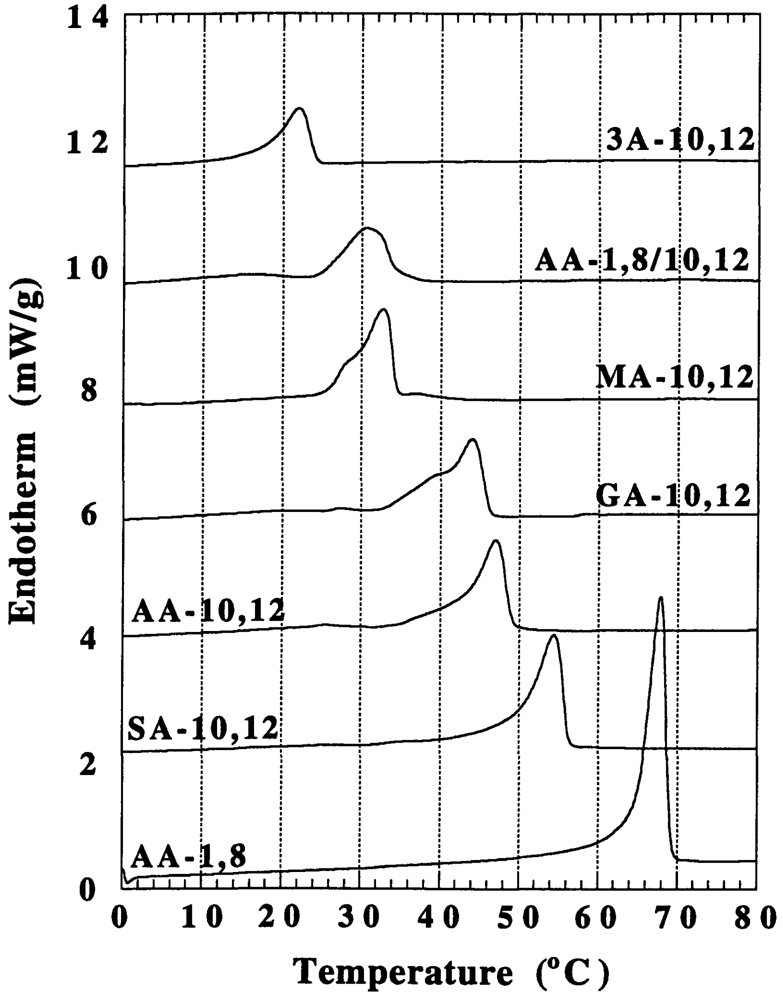


Figure 3.2 DSC thermograms of as cast polyesters. Thermograms offset vertically for clarity.

The use of a comonomer and an asymmetric pendant group to create polymers with low melting points proved successful. AA-1,8/10,12 and 3A-10,12 have the lowest melting temperatures of all the polyesters, as well as the least amount of crystalline material. The pendant methyl group reduces the melting point of 3A-10,12 25 °C as compared to AA-10,12. The addition of the comonomer in AA-1,8/10,12 reduces the melting point by 16 °C when

Table 3.2 Polyester transition temperatures and properties.

Polyester	**Tan δ Peak for T_g (°C)**	**Tan δ Peak for Mechanical Failure (°C)**	**DSC T_m Peak (°C)**	**DSC T_m Peak Area (J/g)**
3A-10,12	-42	27*	21.9	27.3
AA-1,8/10,12	-38	32	30.6	31.3
MA-10,12	-43, -26	34	32.7	42.9
GA-10,12	-36	45	44.0	49.5
AA-10,12	-33	49	47.0	51.4
SA-10,12	-29	58	54.4	60.8
AA-1,8	-38	70	67.9	80.4

*Sample failed before an actual peak was reached

compared to AA-10,12. Addition of a comonomer to any of the other polyesters should serve to reduce their melting points similarly.

3.3.2 Thermal Processing Effects

The melting temperature of these polymers was found to be dependent upon processing as well as chemical structure. When spin coated, many of the polymers show reduced melting peaks due to smaller and defect laden crystallites formed during the spin coating process. The polyester GA-10,12 is used to demonstrate this phenomenon in Figure 3.3. The first thermogram in Figure 3.3 details what appears to be three melting peaks, as seen at a heating rate of 10 °C/minute. The lowest temperature endotherm (peak I) gives the actual melting behavior of the material as spin coated. The apparent higher multiple endotherms (peaks II and III) are actually crystalline material which has recrystallized during the DSC scan. This type of behavior has been documented for poly(ethylene terephthalate) (PET) [52,53,54] and this has been confirmed by performing scans at different rates. When the material is heated at 50 °C/minute, only peak I remains. At this fast heating rate, the polymer does not have time to continually recrystallize into a higher melting forms.

The thermograms shown below the spin coated sample demonstrate how similarly processed samples can be modified by annealing after spin coating. As the annealing temperature is increased, the crystallites

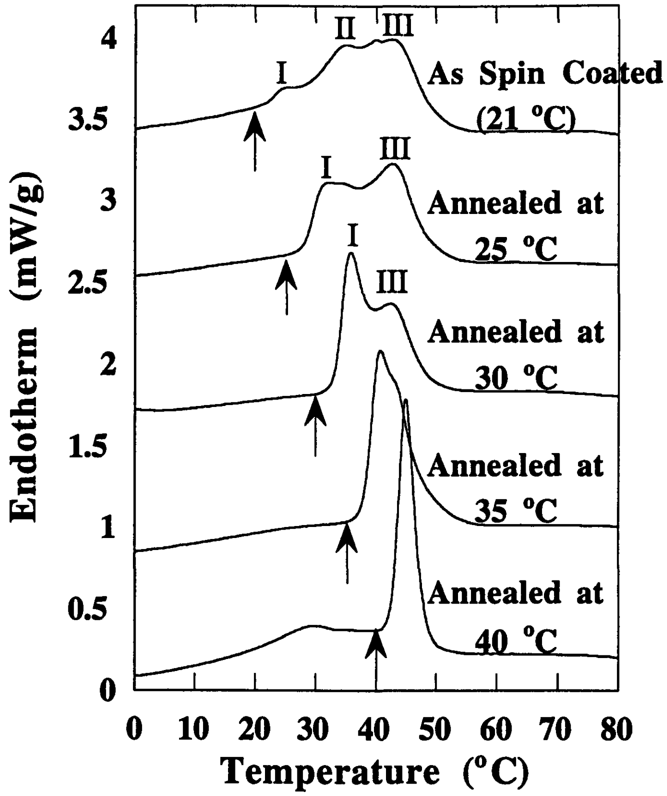


Figure 3.3 Effects of annealing upon spin coated GA-10,12. Thermograms offset vertically for clarity.

formed during the spin coating process are continually perfected, most likely due to crystal thickening and fold-surface smoothing, which has been observed for PET [55,56]. As will be shown later, the change in color with temperature of the polydiacetylene chains is directly linked to the melting of the host crystallites. By using processing to dictate the melting temperatures, the temperature of the thermochromic change can be specified.

3.3.3 Optical Characteristics

The visible absorption of a polydiacetylene chain is dictated by the planarity of the conjugated backbone. This ordering is in turn defined by the geometry of the host crystalline lattice.

The differences in the crystalline packing due to varying chemical structures is expected to greatly effect the absorption spectra, just as it did the thermal properties. Indeed, when the polyesters films are irradiated with uv light, we find this is so (see Figure 3.4). For one and two methylene spacers (n=1,2) in the diacid component (MA-10,12 and SA-10,12), λ max is positioned around 650 nm, yielding a blue colored polymer. When n=3 (GA-10,12), λ max blue shifts to 530 nm, yielding a purple colored polymer. For n=4 (AA-10,12), λ max remains at 530 nm, while the absorption in the higher wavelength region is decreased, yielding a reddish polymer.

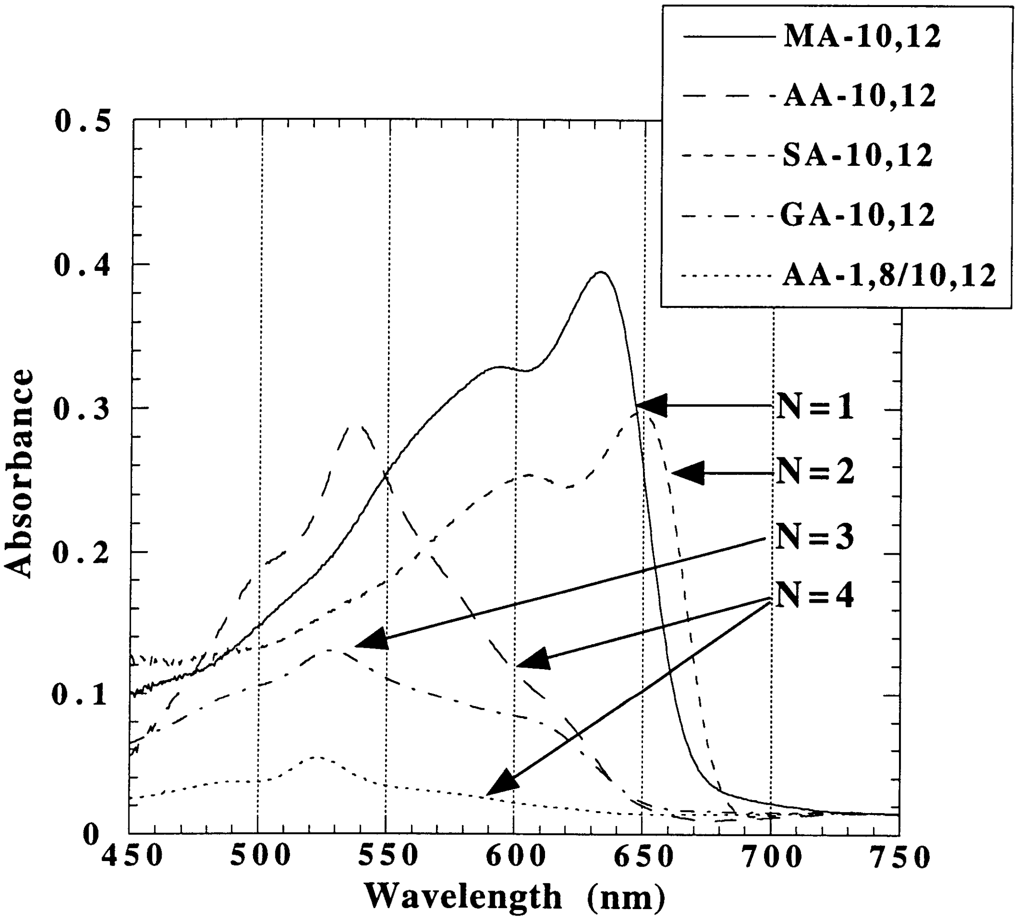


Figure 3.4 Absorption spectra of spin coated samples. Samples were exposed to uv light for 2 minutes.

Apparently, for the polyester structures studied, the fewer methylene spacers provide a better molecular environment for the support of highly ordered polydiacetylene chains. The opposite effect has been reported for polyesters [14] and polyamides [3] which use sebacic (n=8) and succinic (n=2) acid monomers, where λ max shifted to higher wavelengths with the use of sebacic acid. However, as the optical effects of using sebacic acid were not studied here, it is not possible to identify a trend as to which acid component spacer lengths will provide the best packing environment for the polydiacetylene chains.

This variation in the absorption spectra will prove useful when designing the dual-functional segmented polyurethanes. It may be desirable to either try to match the absorption characteristics of the soft segments to those of the hard segments, or have them absorb in separate spectral ranges.

Since these seemingly small variations in chemical structure result in dramatic changes in absorption, it is curious to note that AA-1,8/10,12 (n=4), which contains a rather large amount of non diacetylene unit bearing diol comonomer, does not shift the absorption as compared to the n=4 (AA-10,12) homopolyester. Even more intriguing is the fact that this large amount of copolymer does not effect the relative distributions of the resulting polydiacetylene chains. In other words, one might expect that by using a 50/50 diol mix in the synthesis, there would be a large distribution in the perfection of the diacetylene unit bearing crystallites. This would effect the absorption spectra of the polydiacetylene chains which are formed, resulting in a broad, ill defined absorption peak. Instead, the polydiacetylene chains which form in the copolymer have the same distribution as those in the n=4 homopolyester, indicating that the two diol components may be phase separating into two separate crystalline domains.

As shown in Table 3.2, the copolymerization process resulted in a 16 °C depression in the melting point as compared to the homopolyester. This strongly suggests that for a given spectral absorption range, we can vary the melting temperature to any desired temperature by introducing a comonomer.

For 3A-10,12, there is no absorption data presented, as this polyester does not show any cross-polymerization upon exposure to UV light, even when the polymer is exposed at lower temperatures to promote crystallization of the polyester. It is unknown why this polyester is not reactive to uv light, while it will cross-polymerize upon exposure to electron beam radiation.

The vastly different melting temperatures due to different chemical structures and processing regimes should drive different thermochromic transitions in the supported polydiacetylene chains. The effects of different processing conditions on the thermochromic transitions are probably most dramatic for MA-10,12, which is discussed below.

Figure 3.5 shows the thermochromic shift of MA-10,12, when processed by melting, then quenching in liquid nitrogen, then exposing to UV radiation for 2 minutes. Figures 3.6 and 3.7 show the thermochromic shifts of as spin coated EM after exposure to UV radiation for 2 and 20 minutes, respectively. The changes in the transition temperatures and the broadening of the transition are not surprising in light of the DSC data presented in Figure 3.8. Quenching produces smaller crystallites with reduced melting points, and thus a lower transition. Increasing the level of cross polymerization of the polyester by increasing the irradiation time form 2 to 20 minutes tends to

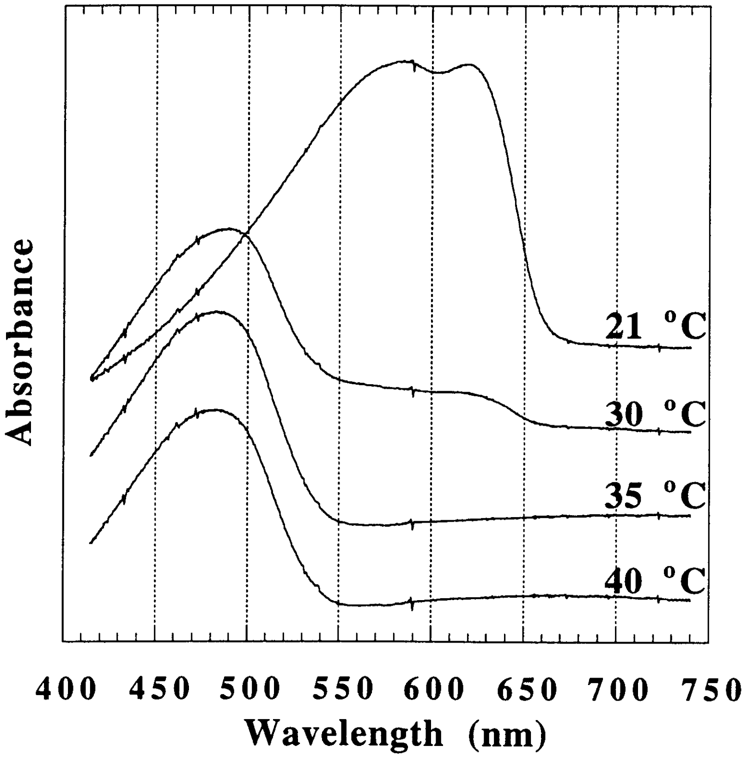


Figure 3.5 Absorption spectra for quenched MA-10,12 as a function of temperature. UV irradiation time: 2 minutes.

restrict the melting process of the host polyester lattice, driving it to higher temperatures and decreasing the amount of true melting dissociation which can take place. Similar trends are seen for the other samples.

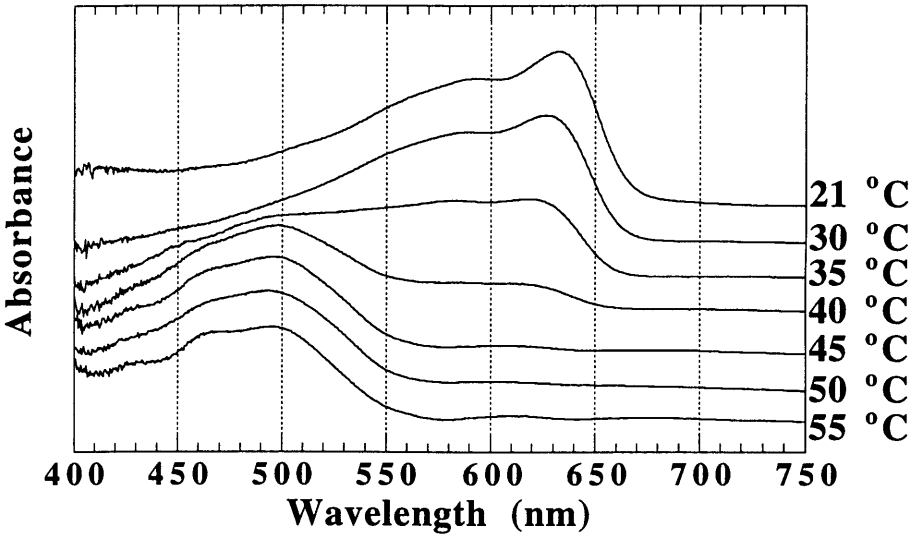


Figure 3.6 Absorption spectra for spin coated MA-10,12 as a function of temperature. UV irradiation time: 2 minutes.

For certain applications it is desirable to have a thermochromic material whose transition is irreversible (the host lattice has no "memory"). A material with an irreversible transition could be used for indicating the highest temperature seen in a particular environment. In other cases, it is desirable to have a material with a reversible transition.

Rubner has shown that in segmented polyurethanes with polydiacetylene chains in the hard segments, the thermochromic transitions were reversible to extended temperatures [27]. This was due to the ability of the hydrogen bonds to keep the hard segments from completely dissociating. At still higher temperatures, the hydrogen bonds are broken and the color change becomes irreversible. Since the polyesters have no hydrogen bonds, there is no mechanism to ensure the memory of the host polyester lattice. However, when extensively cross-polymerized, the polydiacetylene chains themselves can act as crosslinks to stabilize the polyester crystallites.

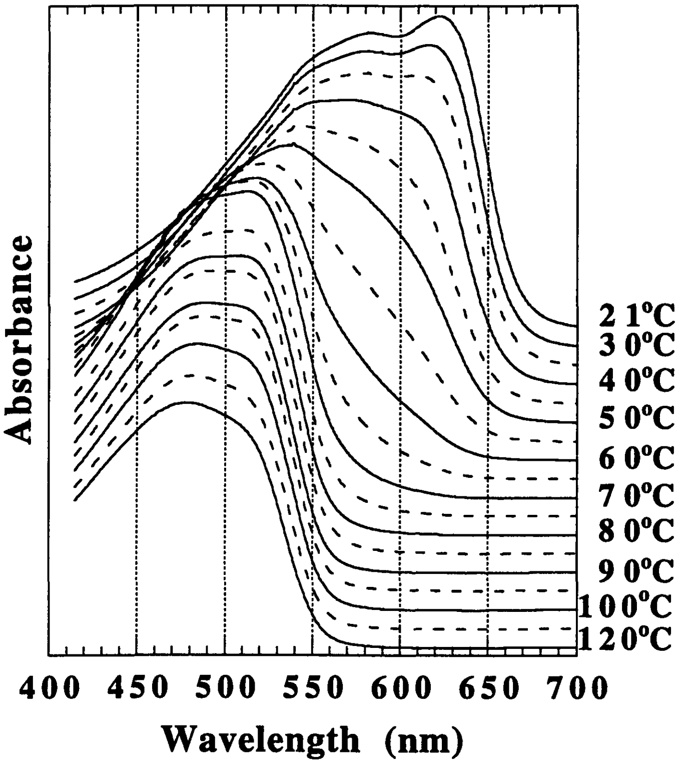


Figure 3.7 Absorption spectra for spin coated MA-10,12 as a function of temperature. UV irradiation time: 20 minutes.

Figure 3.9 shows the spectra for MA-10,12 at room temperature after being heated to a certain temperature. A comparison between Figures 3.5 and 3.9 indicates that for small amounts of cross-polymerization, there is no memory in these systems in terms of polydiacetylene chain order, which is to be expected from a phenomenon driven by melting. A comparison of Figures 3.7 and 3.10, however, shows that for increased levels of cross-polymerization, there is some recovery of the original color. For this material, even though the host polyester lattice is effectively melting, much of the material is dominated by polydiacetylene chain lattice. These crosslinks help to hold the material together and prevent permanent disorganization of the material. At higher temperatures, the ability of the polydiacetylene chains to hold the lattice in a semi ordered fashion is overcome, and no return to the original absorption is observed.

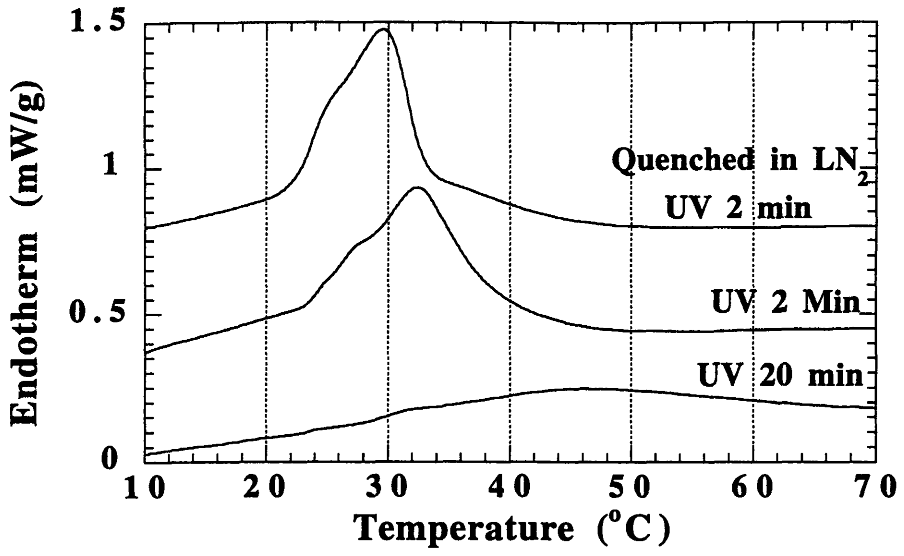


Figure 3.8 DSC thermograms of irradiated polymers.

All of the diacetylene unit containing polyesters demonstrated these variations in thermochromic activity with processing and cross-polymerization conditions. Table 3.3 gives a summary of several of these thermochromic transition ranges. DSC data on these samples have shown melting endotherms in the same ranges where the thermochromic transitions take place, once again indicating that color changes are driven by the melting of the host crystalline lattice. It can be seen that by melting and quenching one of the polyesters, the transition temperature can be reduced, whereas by increasing the polymerization time, the transition temperature can be raised. Additionally, by quenching to reduce the melting temperature, and then annealing to increase it to a desired temperature, the transition range for one particular polyester can be varied systematically over a wide range.

It should be noted that the thermochromic transition of the quenched sample occurs below body temperature, so that exposing a film of this polymer to body heat causes an irreversible color change from purple to yellow. Since the melting temperature of the polymer can be adjusted over a wide range by annealing, the thermochromic transition can be correspondingly moved to any desired temperature range. Additionally, since we are able to adjust the maximum possible melting temperature through

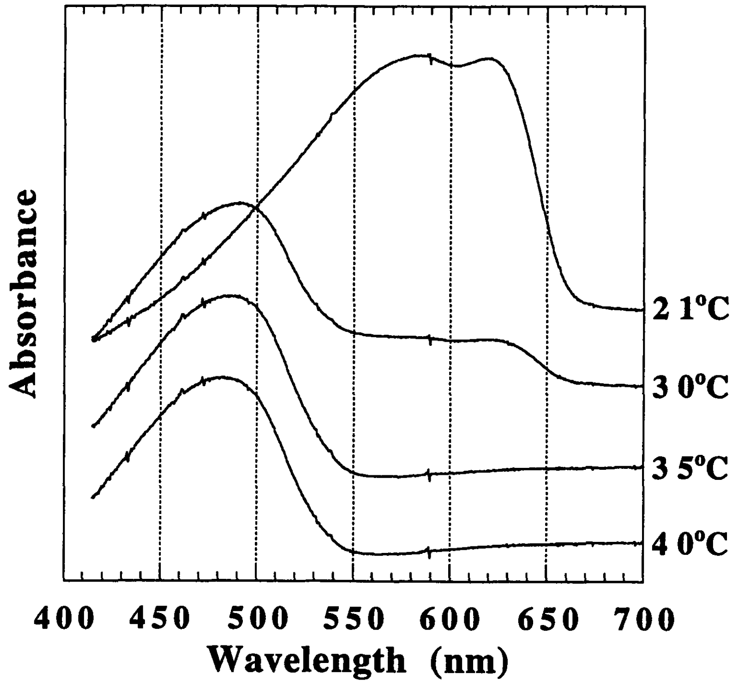


Figure 3.9 Absorption spectra for quenched MA-10,12 at room temperature after heating to various temperatures. UV irradiation time: 2 minutes.

chemistry, we are able to create a thermochromic device with its transition *at any temperature* from 25 °C to 60 °C. As all of these transitions occur at temperatures well below that of typical hard segment melting temperatures, these polymers should be well suited as soft segments in dual thermochromic segmented polyurethanes.

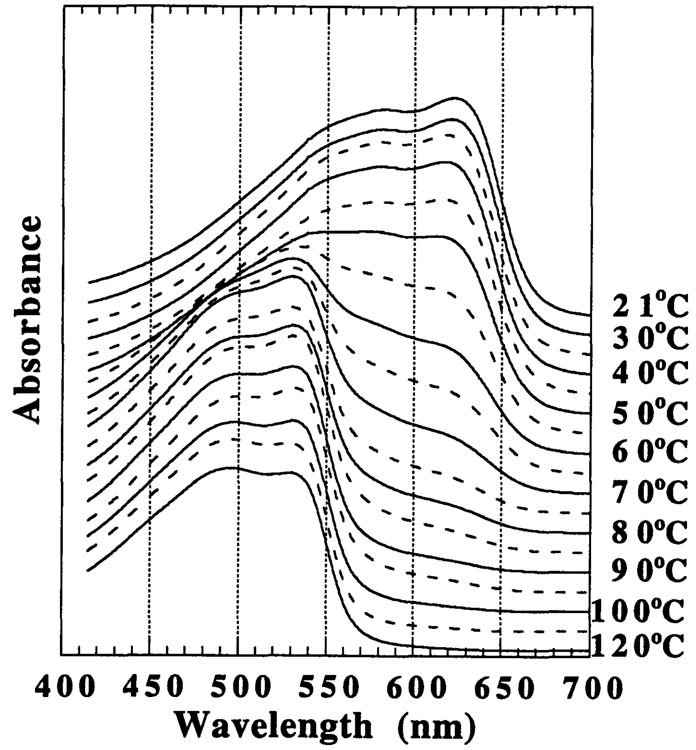


Figure 3.10 Absorption spectra for spin coated MA-10,12 at room temperature after heating to various temperatures. UV irradiation time: 20 minutes.

Table 3.3 Melting and thermochromic transition ranges.

Polymer	Conditions	Thermochromic Transition Range (°C)
AA-1,8/10,12	As spin coated, uv for 2 min.	30-45
MA-10,12	Quenched, uv for 2 min	21-32
MA-10,12	Annealed at 27.5°C, uv for 2 min.	30-45
MA-10,12	As spin coated, uv for 20 min.	35-65
MA-10,12	As spin coated, uv for 200 min.	25-65
GA-10,12	Annealed at 38°C, uv for 2 min.	40-50
AA-10,12	Annealed at 39°C, uv for 2 min.	40-50
SA-10,12	Annealed at 49°C, uv for 2 min.	50-60

3.3.4 Mechanical Effects of Cross-Polymerization

Since the cross-polymerization process is one which crosslinks the host polymer, it is expected that the mechanical properties should be greatly effected. For all of the diacetylene unit containing polyesters, there are three fundamental changes which occur upon cross-polymerization. The first of these is the increase in the melting point and the extension of the rubbery plateau. This is exactly what would be expected by increasing the crosslink density in a previously uncrosslinked homopolymer [57], with the exception that in this case, all of the crosslinking is taking place in the crystalline regions, leaving the amorphous domains uncrosslinked.

The second and third changes which are apparent are a decrease in the storage modulus directly after the T_g, and the dramatic increase in the height and area of the tan δ at T_g. Both of these indicate a decrease in the degree of crystallinity in the polyester. These three effects are detailed for MA-10,12 in Figures 3.11 and 3.12. The extension of the melting temperature, as well as the decrease in modulus directly after T_g and the increased T_g tan δ peak area are clearly demonstrated. By performing multiple experiments, we have found that these three effects are consistent, while the apparent variations in modulus below T_g are due to the difficulty in determining the cross sectional area of the test specimen.

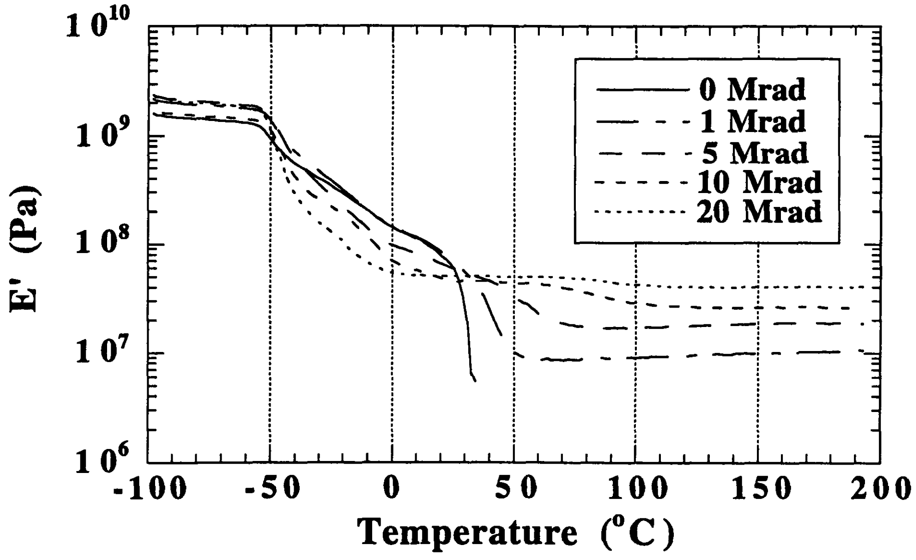


Figure 3.11 Storage modulus for MA-10,12 as a function of irradiation.

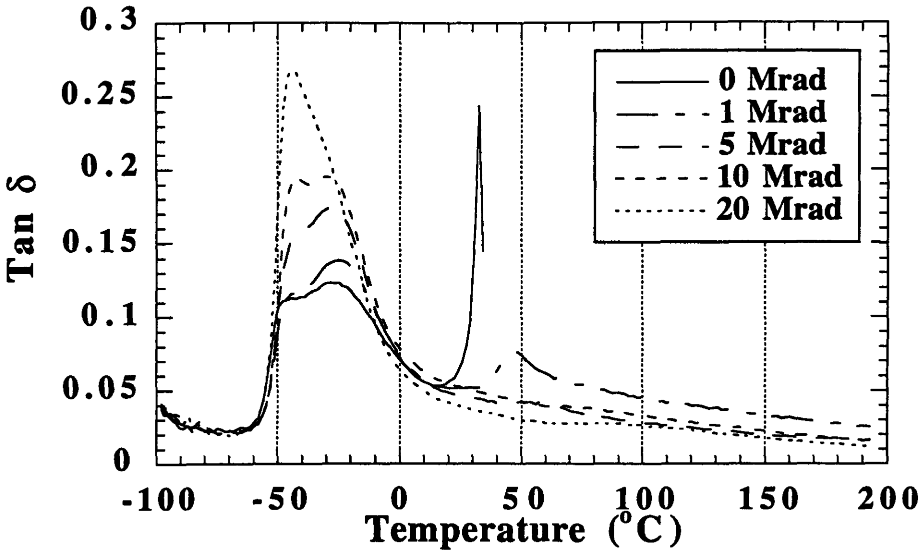


Figure 3.12 Tan δ for MA-10,12 as a function of irradiation.

There are two possible reasons for the decrease in crystallinity with irradiation.

Although the cross-polymerization reaction usually results in little or no change in the crystalline lattice, there have been several documented examples of this crosslinking distorting the host lattice. Kaiser et al have detailed an example where the cross-polymerization of diacetylene monomers distorts the crystalline lattice to an extent that the reaction become self limiting [58]. Studies on diacetylene unit containing polyamides [2] and polyesters [5] have shown a decrease in crystallinity upon cross-polymerization, and attribute it to the distortion of the host crystalline lattice.

Conversely, Kaiser et al [58] also showed examples of the cross-polymerization which does not disrupt the original lattice structure. Kuhling et al [14] have remarked that cross polymerization in certain diacetylene unit containing polyester and polycarbonate systems does not change the degree of crystallinity, although no evidence is presented.

Another possible explanation for the apparently large decrease in crystallinity is the distortion and melting of the polyester crystallites by the heat of the incident electron beam. Although several of the polyester samples were irradiated on ice blocks, they can still experience a significant rise in temperature. Such potential changes in temperature were not systematically investigated. If the heat from the electron beam were to either melt the host polyester crystallites, or simply distort them during the cross-polymerization, then the resulting cross-linked network would have an increased amorphous fraction.

It is not possible to determine the exact nature of this amorphization. However, since the melting temperatures of these polyesters are close to room temperature, and the increase in amorphous content is quite significant, one is led to believe that melting of the crystalline material by the electron beam is at least partially responsible.

Figure 3.13 shows the DMA data for AA-1,8 (no diacetylene units), which is unaffected by the radiation under similar conditions. This indicates that all of the radiation induced changes in the diacetylene unit containing polymers are due to the polydiacetylene chains being formed, and not crosslinking or chain scission in the ester bonds.

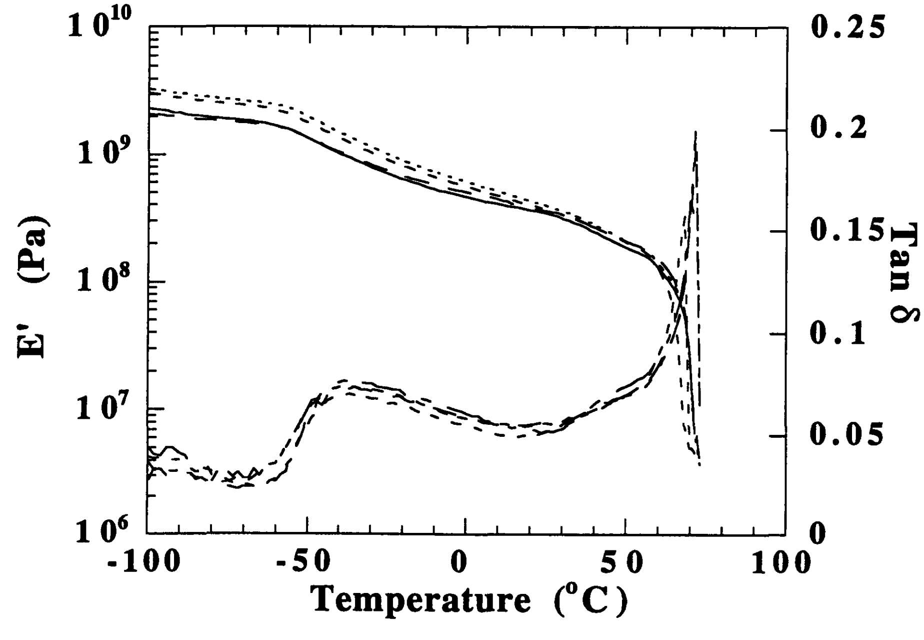


Figure 3.13 E' and Tan δ for AA-1,8 as a function of irradiation.

When incorporated into the segmented polyurethanes and cross-polymerized, the diacetylene unit containing polyesters should have similar effects upon the mechanical properties. After irradiating, it is expected that the segmented polyurethane will exhibit enhanced high temperature properties due to the crosslinks introduced in the soft segments.

3.4 Concluding Remarks

Several diacetylene unit containing polyesters of high molecular weight have been synthesized and characterized in terms of their small-strain mechanical, thermal and optical properties.

By increasing the irradiation dosage on cast films of these polyesters, it is possible to extend the rubbery plateau, enhancing its mechanical properties in a manner similar to that of other crosslinking studies. It is expected that these polyesters will impart the same mechanical enhancements to a segmented polyurethane system when incorporated as soft segments.

It has been found that when the diacetylene units are cross-polymerized to form polydiacetylene chains, the thermochromic transitions are driven by the melting of the polyester crystallites. Several methods of controlling the melting temperature and degree of crystallinity have been utilized, which include changing the number of methylene spacers in the acid component, using an asymmetric acid component to interfere with crystalline packing, copolymerization with a non diacetylene unit bearing diol to reduce long range crystalline order, extent of cross-polymerization, and thermal processing by way of quenching and subsequent annealing.

By using these methods, a series of polymers has been developed with thermochromic transitions ranging from room temperature up to 60 ^{o}C. This is considerably lower than the thermochromic transitions of previous diacetylene unit containing segmented polyurethanes. By incorporating these polyesters into the soft segments of similar segmented polyurethanes, we should be able to make a polymer which has two separate tunable thermochromic transitions due to the two different molecular environments. Additionally, it is hoped that the diacetylene units in the soft segment crystallites will serve as molecular probes for use in investigating soft segment crystallite orientation and deformation processes.

4. Dual Environment Diacetylene Unit Containing Segmented Polyurethanes

4.1 Thermochromic Properties

4.1.1 Molecular Design Considerations

All of the diacetylene unit containing polyesters show promise for use both as stand alone functional materials, and as prepolymers for use in segmented polyurethanes. For incorporation into the segmented polyurethanes studied here, the most promising of these polyesters was chosen by the following criteria.

In the synthesis of dual thermochromic transition systems, there are several molecular design parameters which must be satisfied. The first is a distinct separation between the two transitions. As the thermochromic transitions for polydiacetylene chains have been shown to be driven by the melting of the host crystalline lattice, it is necessary to chose components that will have different melting temperatures as well as demonstrate a good degree of phase separation. All of the polyesters described in Chapter 3 have melting temperatures which should be well below that of typical segmented polyurethane hard segments. However, SA-10,12 (which uses succinic acid as the diacid component) has a fairly high melting temperature (54 ^{o}C) compared to the others, and would not be the material of choice.

Secondly, the absorption spectra of the polydiacetylene chains in the hard and soft segments should be as narrow and well defined as possible, so that shifts in the absorption due to disordering can be easily determined. Polyester GA-10,12 (from glutaric acid) has the broadest absorption of the homopolyesters, and is therefore less desirable than the others.

Thirdly, the absorption peaks in the two phases should be chosen wisely to give the desired color changes. Previous research has found that the hard segment chemistry which we have chosen, hexamethylene diisocyanate and 5,5 dodecadiyne-1,12 diol, produced polydiacetylene chains which absorb strongly in the red region, yielding a blue polymer [27]. From the absorption data for the available polyesters, we can choose a polyester which either appears blue also (MA-10,12), or one that appears red (AA-10,12 or AA-1,8/10,12).

Lastly, the diacetylene units should be fairly reactive to uv light. As AA-10,12 is more reactive than AA-1,8/10,12, it is the preferred choice.

This leaves us with two apparent materials of choice: MA-10,12 and AA-10,12. These two polyesters have been incorporated as soft segments in several segmented polyurethanes; some with and some without additional diacetylene units in the hard segments.

The polymers are named in the following way: diisocyanate-chain extender/soft segment diacid component-soft segment diol component-soft segment molecular weight. For instance, the polymer with a hard segment of HDI and 1,8 octane diol and a soft segment from 10,12 docosadiyne-1,22 diol and adipic acid of 5850 g/mol would be referred to as HDI-1,8/AA-10,12-5850, where AA stands for adipic acid. The polymer with an HDI and 5,7-dodecadiyne-1,12 diol hard segment with a malonic acid containing soft segment is named HDI-5,7/MA-10,12-5550.

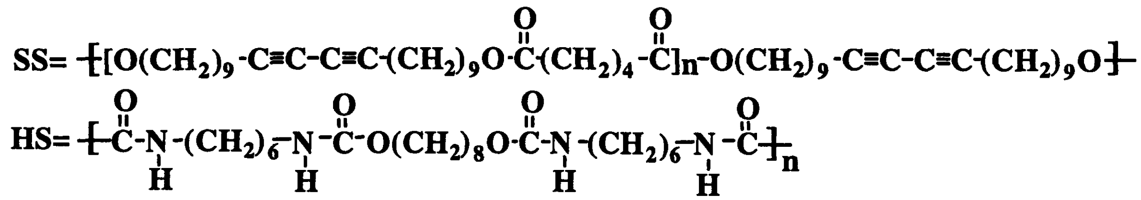
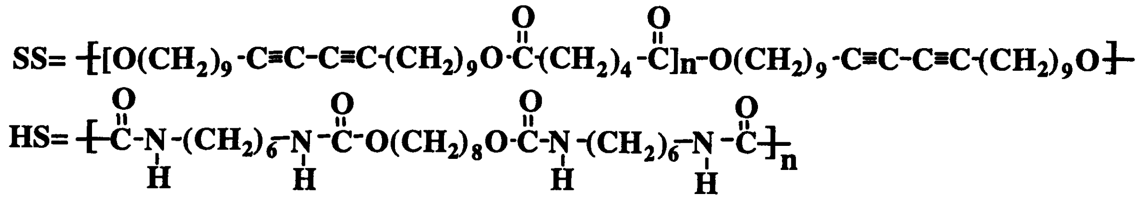
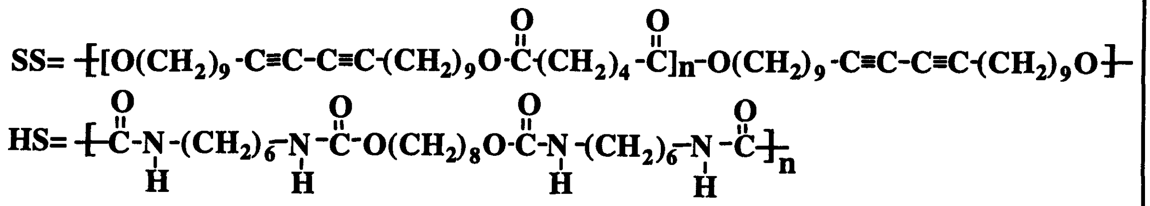
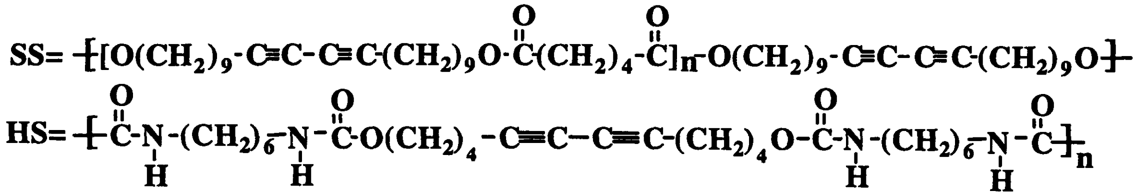
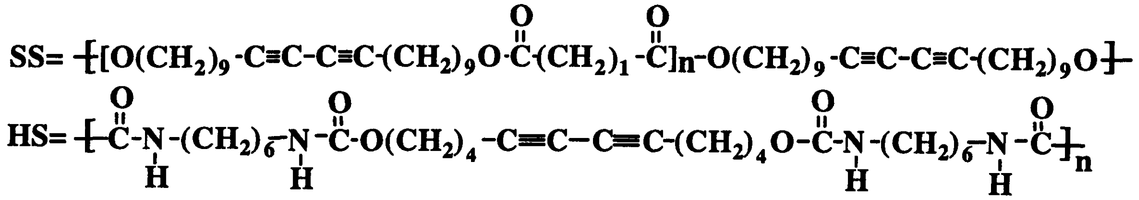
The names and hard and soft segment structures of the segmented polyurethanes synthesized for thermo and mechanochromic studies are given in Table 4.1. Molecular weights of these polymers are given in Table 4.2. The names and hard and soft segment structures of the segmented polyurethanes synthesized for selective cross-polymerization and dynamic mechanical studies are presented in Table 4.3.

Naming schemes and structures of polymers from other sources used for comparative purposes can be found in their respective references. In all of these segmented polyurethanes, as noted previously, the stoichiometric ratio of hard to soft segments, 1:1, was kept constant.

It is important to understand the molecular weight effects that incorporating the diacetylene unit containing polyesters into segmented polyurethanes will have upon the thermal and optical properties: will they be well phase separated, and will the morphological restrictions dictated by the hard segments effect the optical properties of the soft segment polydiacetylene chains?

To study this, a series of three segmented polyurethanes was synthesized in which the molecular weights of the soft segments were varied while keeping the stoichiometric ratio of hard to soft segments equal. All three polymers had diacetylene unit containing soft segments synthesized from 10,12 docosadiyne 1,22 diol and adipic acid. The hard segments contained no diacetylene units, and were composed of hexamethylene diisocyanate chain

Table 4.1 Segmented polyurethane structures for use in thermo and mechanochromic studies.

Polymer Name and Structure
HDI-1,8/AA-10,12-1320  $SS= \left[[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{C}-(CH_2)_4-\overset{O}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\right]$ $HS= \left[\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}-O(CH_2)_8O-\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}\right]_n$
HDI-1,8/AA-10,12-2960  $SS= \left[[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{C}-(CH_2)_4-\overset{O}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\right]$ $HS= \left[\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}-O(CH_2)_8O-\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}\right]_n$
HDI-1,8/AA-10,12-5850  $SS= \left[[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{C}-(CH_2)_4-\overset{O}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\right]$ $HS= \left[\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}-O(CH_2)_8O-\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}\right]_n$
HDI-5,7/AA-10,12-4820  $SS= \left[[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{C}-(CH_2)_4-\overset{O}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\right]$ $HS= \left[\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}-O(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_4O-\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}\right]_n$
HDI-5,7/MA-10,12-5550  $SS= \left[[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{C}-(CH_2)_1-\overset{O}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O\right]$ $HS= \left[\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}-O(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_4O-\overset{O}{C}-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{C}\right]_n$

extended with 1,8 octane diol. Because the stoichiometric ratio of hard to soft segments was kept constant while the soft segment molecular weight is varied, the segmented polyurethane with the longest soft segment length has the largest volume fraction of soft segment material. The structures of these three materials, HDI-1,8/AA-10,12-1320, 2960, and 5850, are given in Table 4.1

Table 4.2 Segmented polyurethane molecular weights, given in polystyrene standards, of segmented polyurethanes for use in thermo and mechanochromic studies.

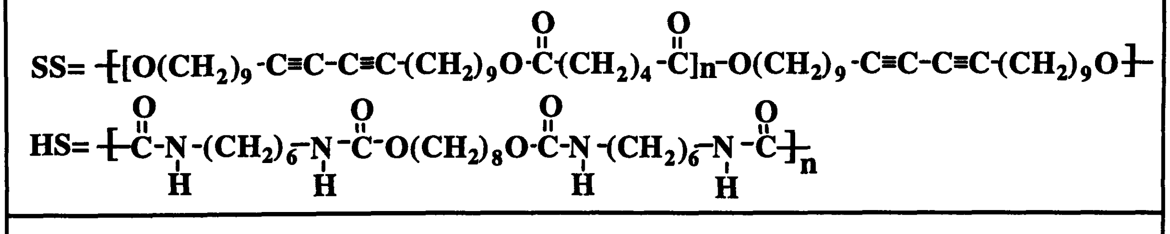
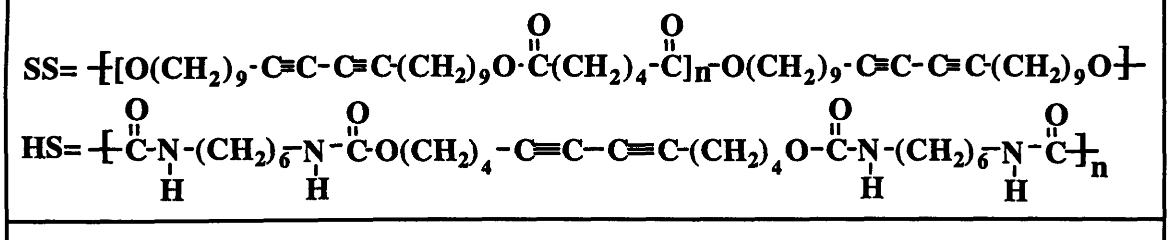
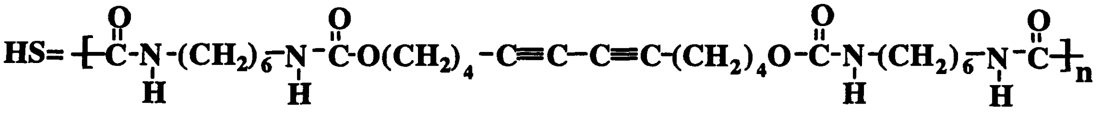
Polyurethane	M_n	M_w	PDI
HDI-8/AA-10,12-1320	15,430	33,600	2.18
HDI-8/AA-10,12-2960	18,610	35,950	1.93
HDI-8/AA-10,12-5850	23,620	48,990	2.07
HDI-5,7/AA-10,12-4820	30,590	66,791	2.18
HDI-5,7/MA-10,12-5550	35,000	62,340	1.78

In order to study the effect that varying soft segment lengths has upon the phase separation of the hard and soft segments, DSC thermograms of these three polymers cast from a 50/50 solution of THF and toluene were obtained. These thermograms are shown in Figure 4.1.

The two polymers with the highest molecular weight soft segments, 2960 and 5850, show two distinct endotherms which can be attributed to the melting of the hard and soft segments. The differences in the relative soft and hard endotherm peak areas for these two segmented polyurethanes is in accordance with the relative differences in their hard and soft segment volume fractions. The material that has the largest soft segment volume fraction, HDI-1,8/AA-10,12-5850, also shows the largest soft segment melting peak area. Additionally, crystallization in the soft segments may be more retarded for HDI-1,8/AA-10,12-2960 due to the disordering effects of the hard segments. This type of behavior has been shown for other polymers, where decreasing soft segment molecular weights serves to prevent crystallization in the soft segments [59,60,61].

DMA tests (not shown) gave T_g's for HDI-1,8/AA-10,12-2960 and 5850 of -25.8 and -31.0 ^oC respectively. These values are somewhat higher than that

Table 4.3 Segmented polyurethane structures for use in selective cross-polymerization and dynamic mechanical studies.

Polymer Name and Structure
HDI-1,8/AA-10,12-1710  $SS= -\!\![O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{\overset{O}{\Vert}}{C}-(CH_2)_4-\overset{\overset{O}{\Vert}}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\!\!$ $HS= -\!\!\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-O(CH_2)_8O-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-\!\!\!_n$
HDI-5,7/AA-10,12-1670  $SS= -\!\![O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{\overset{O}{\Vert}}{C}-(CH_2)_4-\overset{\overset{O}{\Vert}}{C}]_n-O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\!\!$ $HS= -\!\!\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-O(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_4O-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-\!\!\!_n$
HDI-5,7/commercial polyester-1050 **SS= Commercial polyester macrodiol, no diacetylenes**  $HS= -\!\!\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-O(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_4O-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{H}{\vert}}{N}-(CH_2)_6-\underset{\underset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-\!\!\!_n$

found for the homopolyester: -33.4 °C. The slight increase in T_g in these segmented polyurethanes as compared to the homopolyester is probably due to both the restrictions placed upon the soft segments by the hard segment domains and phase mixed hard segment material dispersed throughout the soft segments. The higher T_g of HDI-1,8/AA-10,12-2960 as compared to HDI-1,8/AA-10,12-5850 is most likely due to increased phase mixing. Several studies have shown that an increase in hard segment content serves to raise T_g due to increased phase mixing [61,62]. Nevertheless, the two well defined DSC endothermic peaks clearly show that the material is, on a whole, well phase separated.

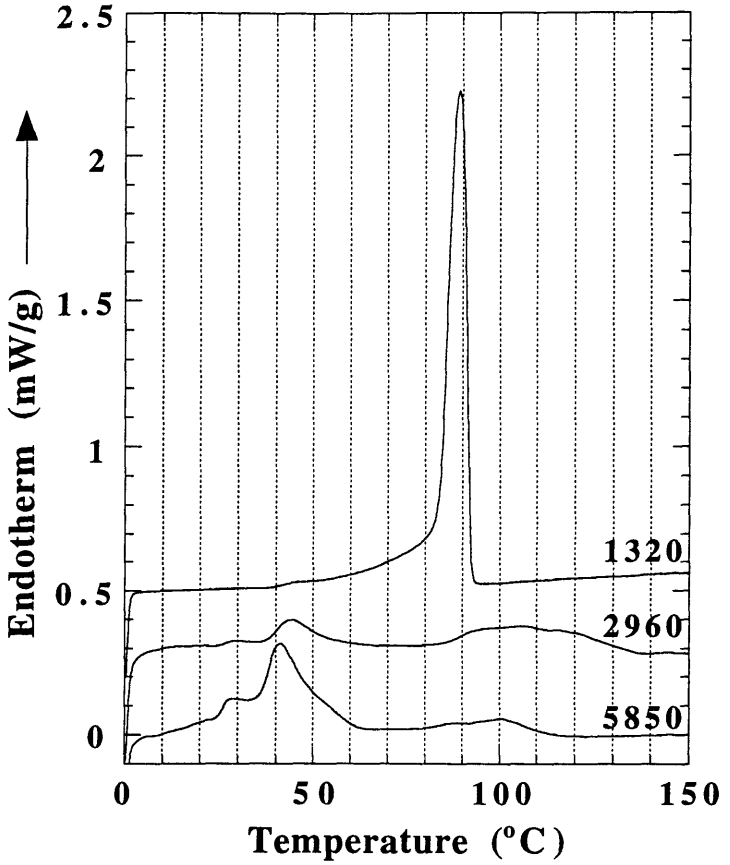


Figure 4.1 DSC thermograms of segmented polyurethanes with varying soft segment molecular weights. Molecular weights of the soft segments are listed for each curve. Thermograms are offset vertically for clarity.

On the other hand, the DSC thermogram for the segmented polyurethane with the smallest soft segment length, HDI-1,8/AA-10,12-1320, shows only one distinct endotherm. The temperature of this transition is situated between the endotherms of the hard and soft segments shown for the other two segmented polyurethanes. This seems to indicate that this material is not exhibiting a phase separated morphology. The cast film of this material was crumbly and brittle, so that DMA could not be performed. Because of this, it is not possible to clearly state that polymer is completely phase mixed. It is possible that there is a second amorphous phase present.

To further study the effects of soft segment molecular weight on the molecular environment of the diacetylene units, the optical properties of the resulting polydiacetylene chains were examined. When spin coated films are cross-polymerized for 2 minutes with uv light, all of the three segmented polyurethanes appear reddish to the naked eye. Absorption spectra for these polymers along with that of the homopolyester AA-10,12 are shown in Figure 4.2. The polydiacetylene chains in HDI-1,8/AA-10,12-2960 and 5850 show absorption spectra nearly identical to the homopolyester, while polydiacetylene chains in HDI-1,8/AA-10,12-1320 yield a fairly undefined absorption spectra, characteristic of a large distribution of conjugation lengths.

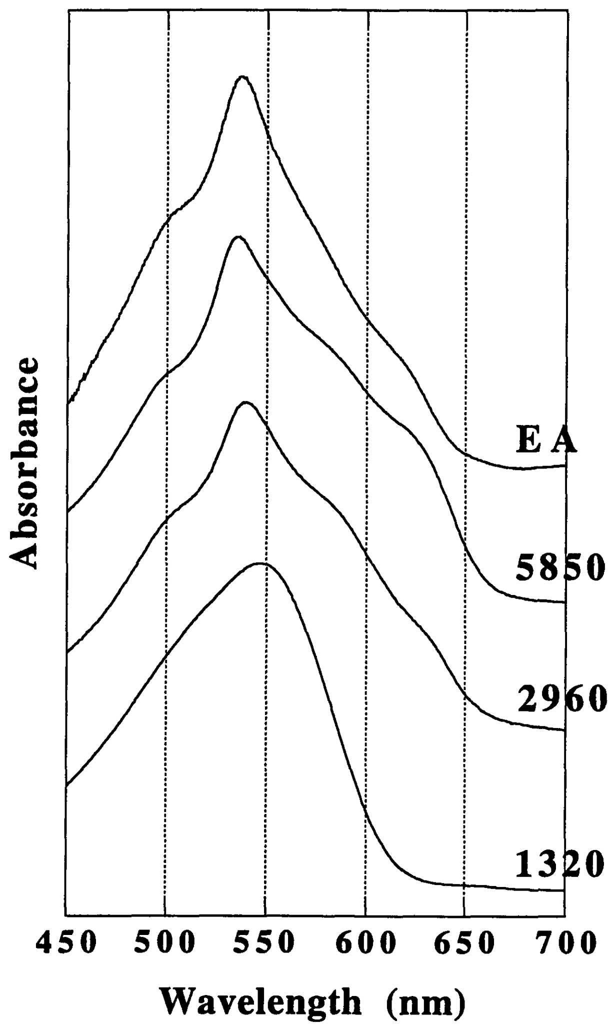


Figure 4.2 Absorption characteristics of cross-polymerized 10,12 docosadiyne 1,22 adipate in both homopolyester form (AA-10,12), and as varying molecular weight soft segments (5850, 2960, and 1320 g/mol) in segmented polyurethanes.

When samples of the three segmented polyurethanes cross-polymerized for 2 minutes with uv light are studied for their thermochromic properties (data not shown), HDI-1,8/AA-10,12-2960 and 5850 have color changes between 25 and 55 °C, which corresponds to their soft segment melting endotherms shown in Figure 4.1. HDI-1,8/AA-10,12-1320 has it's thermochromic transition between 80 and 95 °C, corresponding to its large single endotherm.

It is clear from these results that HDI-1,8/AA-10,12-2960 and 5850 provide a phase separated soft segment which supports polydiacetylene chain formation. The photo-reactive diacetylene units in HDI-1,8/AA-10,12-1320 are present in a high melting phase mixed region. This region supports the formation of polydiacetylene chains which have a wide distribution of effective conjugation lengths. Were diacetylene units to be incorporated into the hard segment portion of this material as well, it is unlikely that the resulting polydiacetylene chains would exhibit two distinct thermochromic transitions.

In light of this data, subsequent segmented polyurethanes were synthesized using the higher molecular weight soft segments as a model.

As noted before, the choice of such large soft segments will produce segmented polyurethanes with a high volume fraction of soft segment material. For the design of segmented polyurethanes with diacetylene units in both the hard and soft segments, this poses a potential problem. The high volume fraction of soft segment material will produce a segmented polyurethane with a higher concentration of diacetylene units in the soft segments than the hard segments. It is a concern as to whether the absorption bands of the resulting polydiacetylene chains in the two segments will be of comparable magnitudes.

One way to avoid this potential problem would be to increase the volume fraction of diacetylene unit containing hard segment material by varying the stoichiometry of the diisocyanate and chain extender. However, this technique poses one major drawback: it would be necessary to synthesize numerous materials to obtain the correct relative ratios of hard and soft segment volume fractions. Additionally, this ratio will change depending upon the choice of hard and soft segment chemistries, as each has its own relative diacetylene unit reactivity. If one wanted to vary the relative absorbance intensities of the polydiacetylene chains in the two phases, a new segmented polyurethane would have to be synthesized.

A second method to this end would be to use a larger fraction of soft segment material, while being able to selectively cross-polymerize the diacetylene units in the hard segments only. In this way, one could first cross-polymerize only the diacetylene units in the hard segments, and then cross-polymerize primarily the soft segment diacetylene units until the desired ratio polydiacetylene chains is reached.

To determine if this technique was possible, three segmented polyurethanes were synthesized: one with diacetylene units in the hard segments only, HDI-5,7/commercial polyester-1050 (HD), one with diacetylene units in the soft segments only, HDI-1,8/AA-10,12-1710 (SD), and one with diacetylene units in both the hard and soft segments HDI-5,7/AA-10,12-1670 (DD, or "dual environment" diacetylene units). The structures of these polymers were presented in Table 4.3.

Each of these three segmented polyurethanes was exposed to uv light under two separate conditions: room temperature ($T = 25\ ^{o}C$), and a temperature above the melting point of the soft segments ($T_{m,s}$) but below that of the hard segments ($T_{m,h}$). The results of these cross-polymerization conditions are shown for the three materials in Figure 4.3.

Since the two conditions are both below the melting temperature of the hard segments, the diacetylene units in the hard segments are still in an ordered form, and are able to cross-polymerize, which results in the identical absorption spectra shown for HD in Figure 4.3. However, when the SD polymer is exposed to uv light above the melting temperature of the soft segment crystallites, the diacetylene units are no longer in the proper geometry for the cross-polymerization to take place. Similarly, in the DD polymer, at room temperature cross polymerization takes place in both the hard and soft segments. However, at the higher temperature, we only observe an absorption spectra characteristic of the resulting hard segment polydiacetylene chains. By combining the high temperature cross-polymerization with the room temperature cross-polymerization, it is possible to vary the relative concentrations and therefore absorption spectra of the polydiacetylene chains in the two phases.

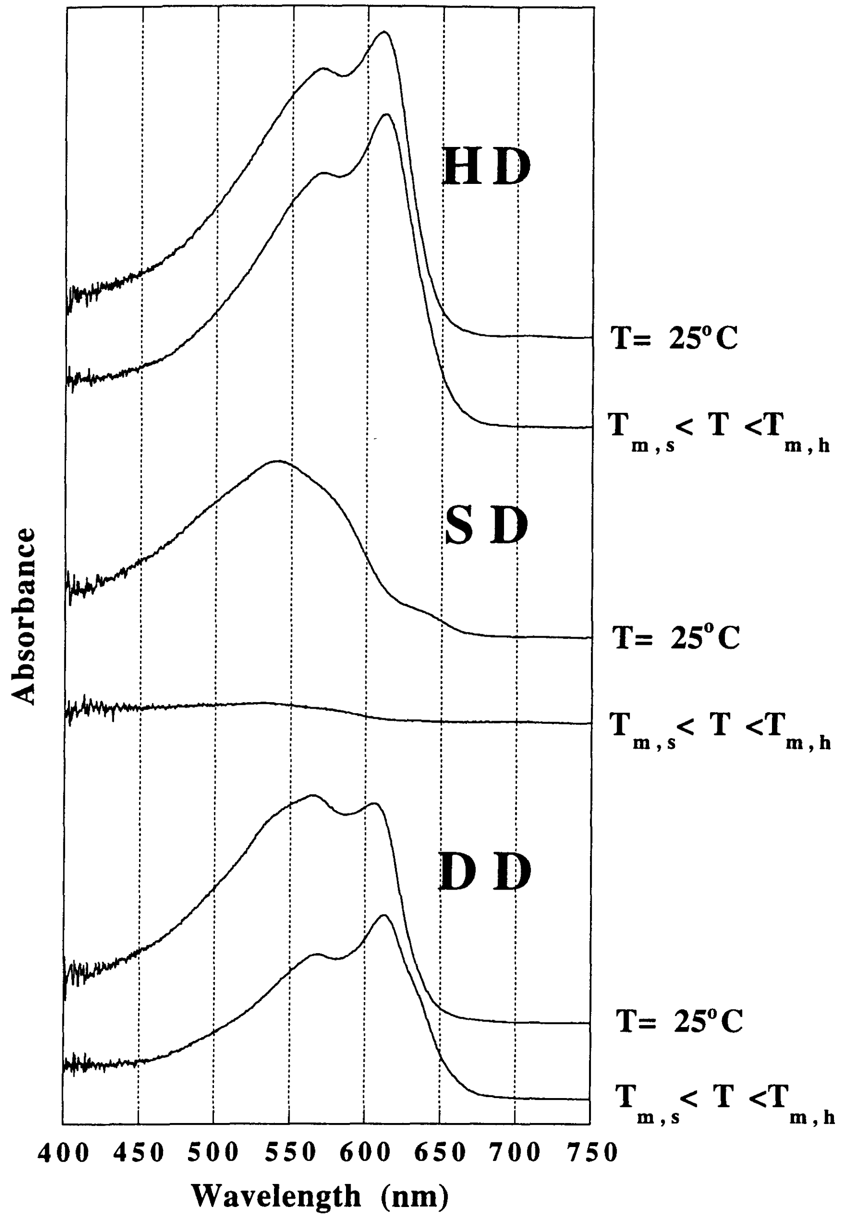


Figure 4.3 Demonstration of selective cross-polymerization of diacetylene units in segmented polyurethanes. Temperatures indicate the temperature at which cross-polymerization was initiated for each sample.

4.1.2 Dual Thermochromic Transition Materials

For the study of dual thermochromic systems, two different segmented polyurethanes with diacetylene units in both the hard and soft segments were synthesized; one with AA-10,12 (HDI-5,7/10,12-AA-4820) and one with MA-10,12 (HDI-5,7/10,12-MA-5550) as the soft segment material. The details of the molecular weights and structures are given in Tables 4.1 and 4.2.

DSC data for these two materials is shown in Figure 4.4. The endothermic portions of the two curves in region **A** are due to soft segment material which crystallized below room temperature, and therefore is not representative of the segmented polyurethanes under ambient conditions. Region **B** shows the melting regime of the soft segment material, while the smaller endotherm in region **C** is the melting of the hard segment material. As the soft and hard segment melting temperatures are well separated, it should be possible to pick a temperature in between, such as 70 °C, to use for the selective cross-polymerization of the hard segment diacetylene units.

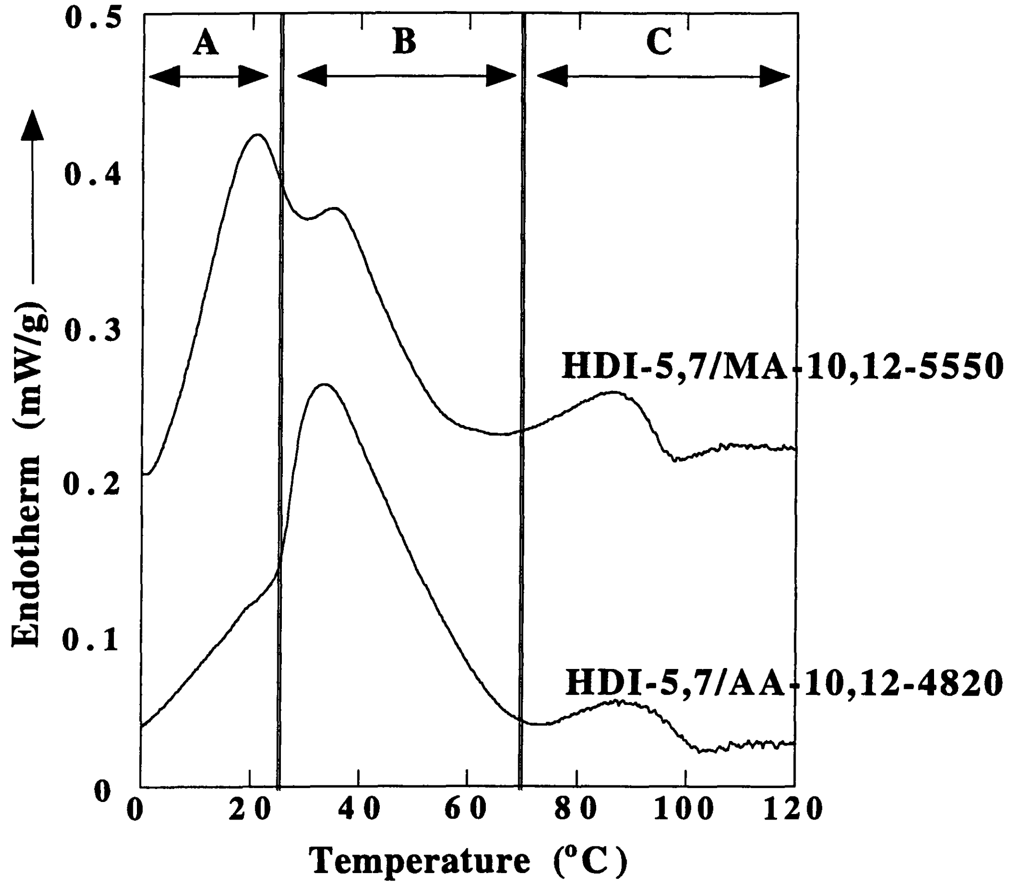


Figure 4.4 DSC thermograms of DD segmented polyurethanes. Thermograms are offset vertically for clarity.

In order to distinguish between the thermochromic transitions of the hard and soft segments, it is instructive to observe the transitions for one of these phases. This is most easily accomplished by selectively cross-polymerizing the hard segment diacetylene units with uv light at 70 °C. The thermochromic shifts for HDI-5,7/10,12-MA-5550 selectively cross-polymerized, both at the elevated temperatures and at room temperature after heating to the elevated temperatures (which demonstrates how "reversible" the transition is), are shown in Figure 4.5.

The absorbance spectra seen in Figure 4.5(a) indicate a spectral shift that begins at 40 °C and ends around 100 °C. This in itself seems odd, since the spectral shift should be coupled to the melting of the hard segment material, which DSC has shown to be from 70 to 95 °C. The reversibility data (Figure 4.5(b)) sheds some light on this mystery. These spectra indicate that the spectral shifts below 85 °C are not of a permanent nature. This means that the thermochromic shift below 85 °C is probably due to thermal expansion of the lattice and surrounding polymeric material. At 85 °C when the hard segments demonstrate large scale melting, the transition becomes irreversible.

The higher temperature of the irreversible transition (85-105 °C) relative to the melting peak (70-95 °C) is most likely caused by the increased thermal stability of the hard segment crystallites due to the presence of the polydiacetylene crosslinks. This is in agreement with the increased thermal stability demonstrated with the cross-polymerized homopolyester as shown in Figures 3.9 and 3.10.

If this same segmented polyurethane is exposed to uv light at room temperature, it is expected that both the hard and soft segments will cross-polymerize, yielding two separate thermochromic transitions. The results at temperature and at room temperature are shown in Figure 4.6

Figure 4.6 (b) clearly shows the vast majority of the transition taking place from 40 to 55 °C, which is due to the soft segment polydiacetylene chains. However, by 55 °C, the absorption peak left over due to the hard segment polydiacetylene chains is barely visible. This is most likely due to the difference in quantity of soft segment and hard segment diacetylene units. However, modifying these relative ratios is quite simple. By selective cross-polymerizing the hard segment diacetylene units at 70 °C and then additionally cross-polymerizing the soft (and a small fraction of the hard) segment diacetylene units at room temperature, it is possible to adjust the

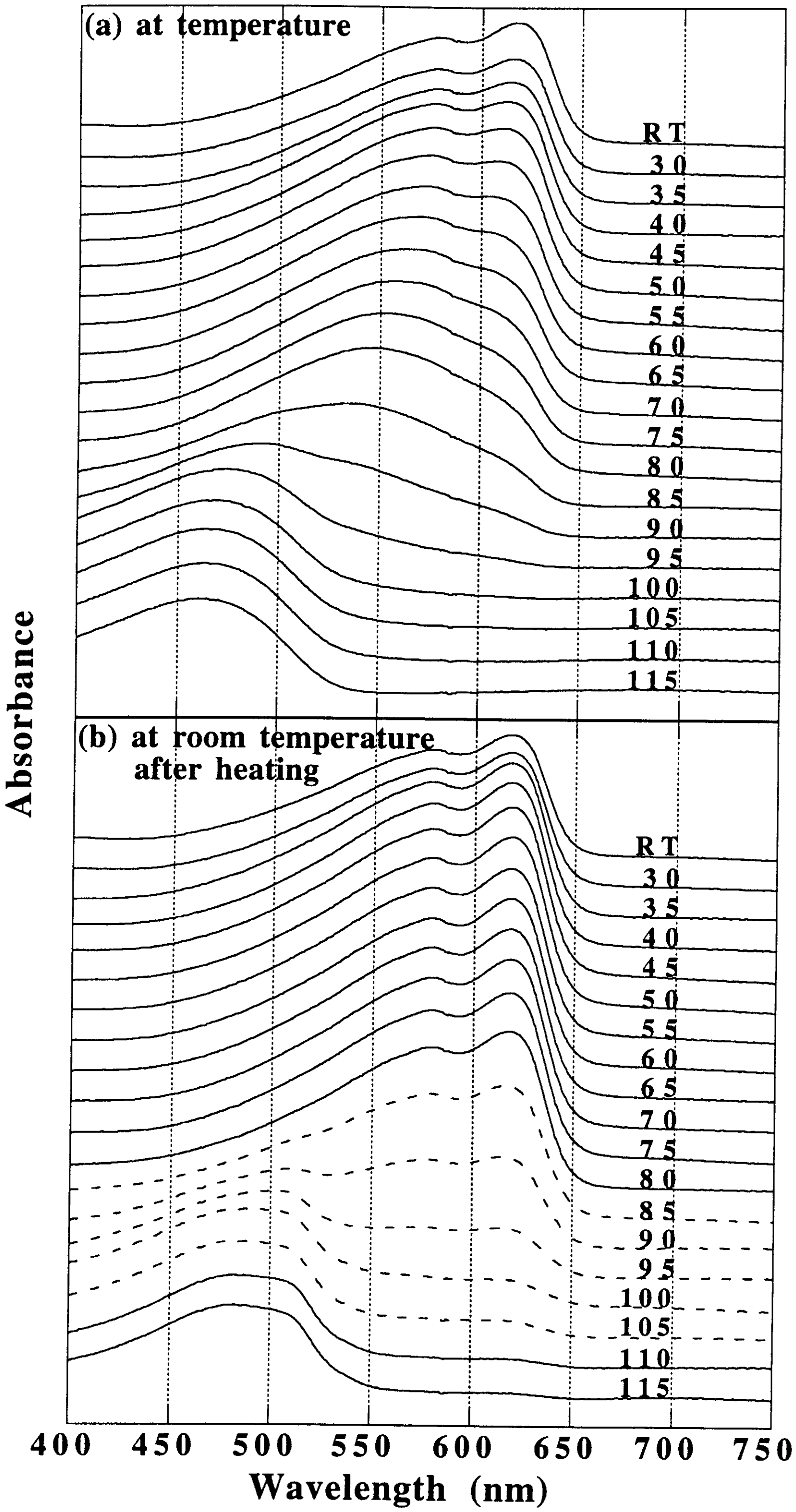


Figure 4.5 Thermochromic shifts at temperature and at room temperature after heating for HDI-5,7/10,12-MA-5550 selectively cross-polymerized for 2 minutes at 70 °C.

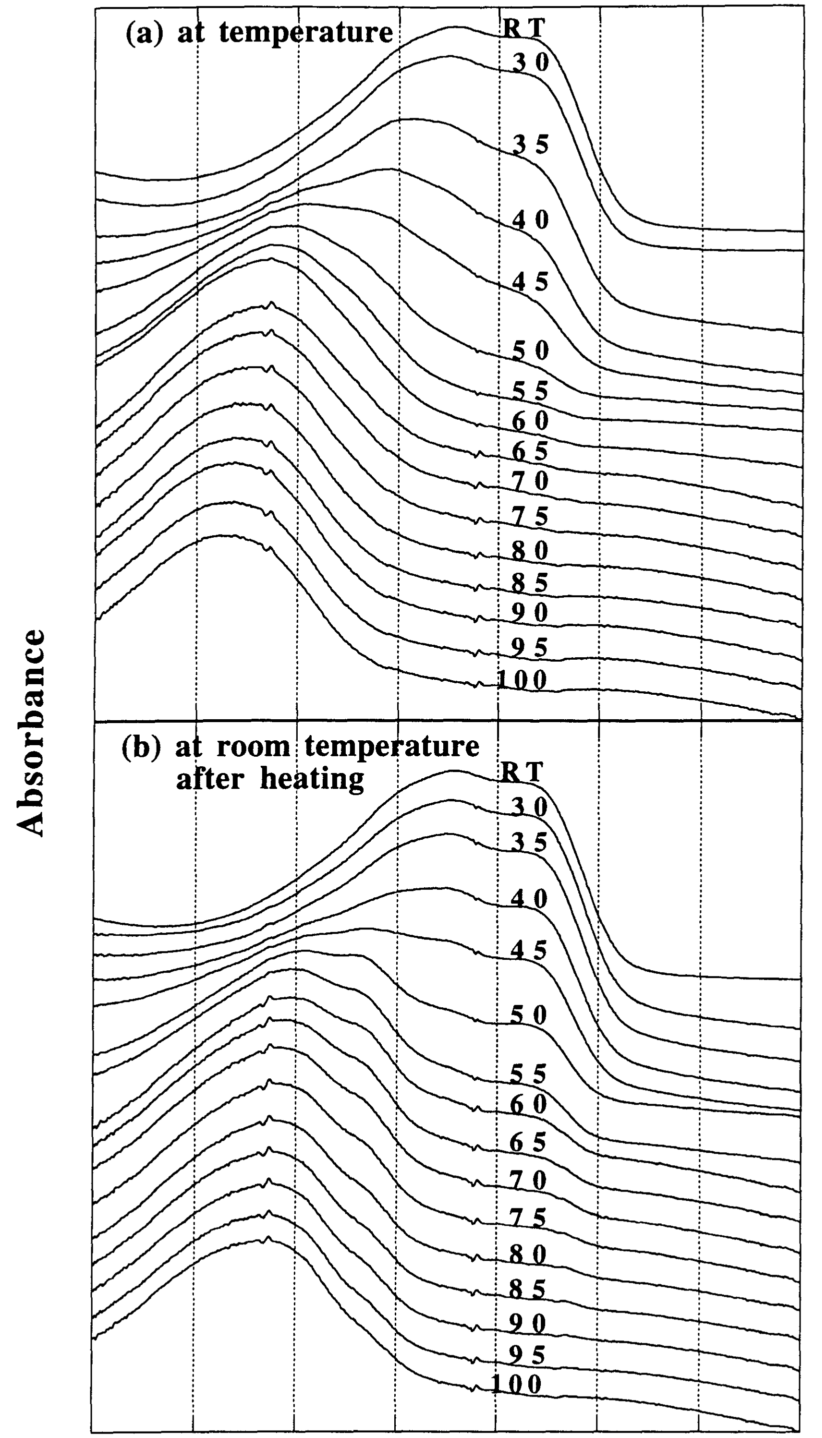


Figure 4.6 Thermochromic shifts at temperature and at room temperature after heating for HDI-5,7/10,12-MA-5550 which has been cross-polymerized for 2 minutes at room temperature.

relative quantities of hard and soft segment polydiacetylene chains. This in turn effects the magnitude of the two thermochromic shifts.

Figure 4.7 shows the thermochromic shifts during the heating process for this material. Two main thermochromic transitions appear to be taking place at low and high temperatures. However, the spectral shifts in the hard segment polydiacetylene chains due to thermal lattice expansion at lower temperatures obscures the definition of these two separate transitions.

The absorption spectra of the material at room temperature after heating to various temperatures removes the chromic effects of the hard segment lattice expansion. Figure 4.8 presents only the permanent nature of the color change at room temperature in an expanded form, as this most clearly details the separate contributions due to the two domains.

This same technique has been demonstrated with the other DD segmented polyurethane system, HDI-5,7/AA-10,12-4820 (results not shown). Since the AA-10,12 soft segments absorb in a different region than the MA-10,12 soft segments, the initial color of the segmented polyurethane is slightly different. As the proportions of the hard and soft segment polydiacetylene chains in these two systems are different, they have slightly different colors throughout the entire thermochromic process.

4.1.3 Concluding Remarks

We have utilized the multiphase structure of segmented polyurethanes to drive multiple thermochromic transitions in polydiacetylene chains present in these separate phases. By utilizing the selective cross-polymerization technique, it is possible to adjust the relative quantities of polydiacetylene chains present in the two phases, which in turn effects the color changes of the polymer over the entire temperature range. Additionally, by choosing different chemical constituents we have been able to further alter the absorption spectra of these dual diacetylene unit containing systems.

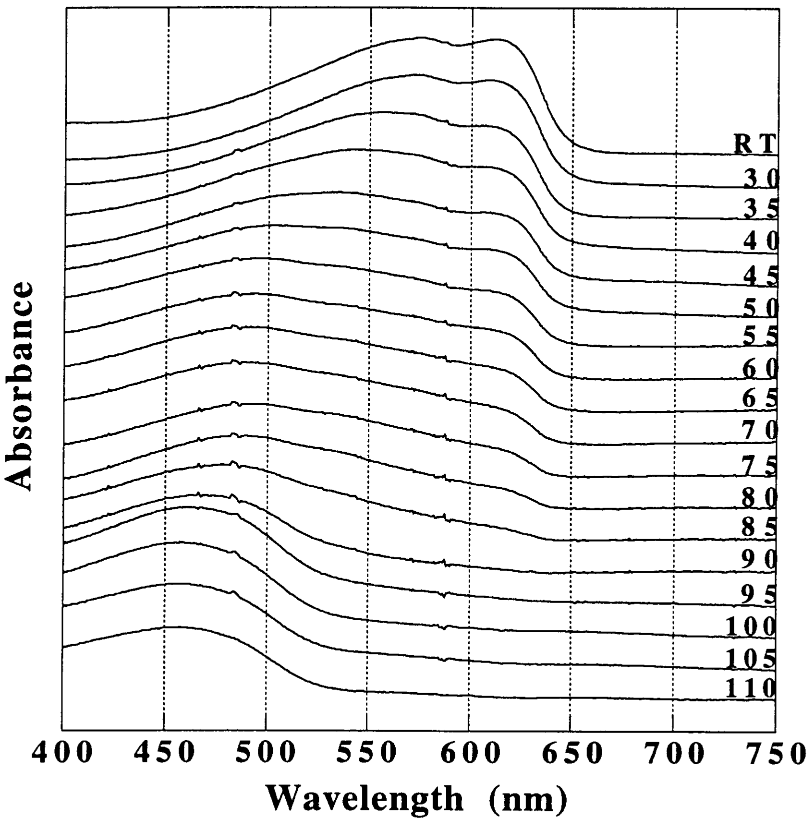


Figure 4.7 Thermochromic shifts at temperature for HDI-5,7/MA-10,12-5550 which has been cross-polymerized at 70 °C for 30 seconds, allowed to recrystallize, and then cross-polymerized at room temperature for 1.5 minutes.

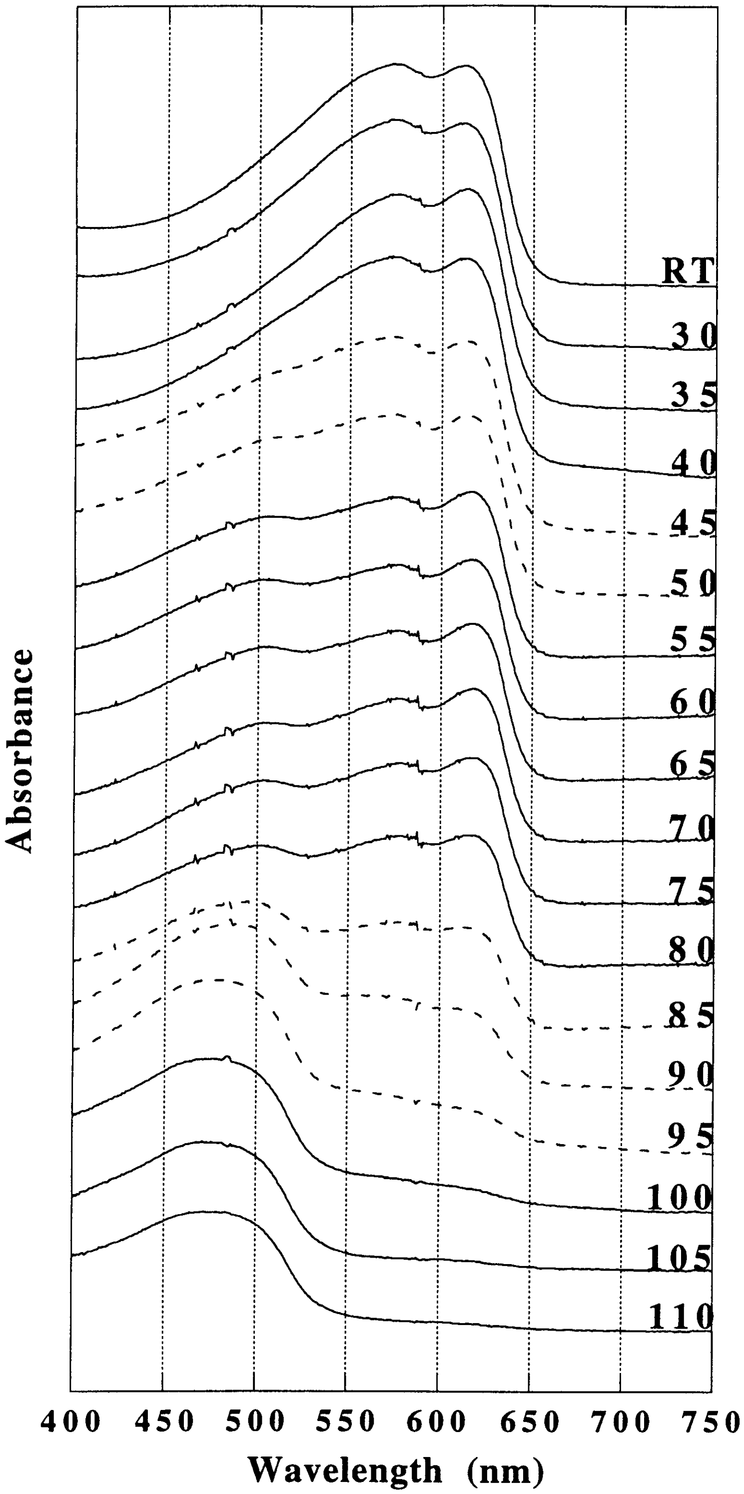


Figure 4.8 Thermochromic shifts at room temperature after heating for HDI-5,7/MA-10,12-5550 which has been cross-polymerized at 70 °C for 30 seconds, allowed to recrystallize, and then cross-polymerized at room temperature for 1.5 minutes.

4.2 Mechanochromic Properties

4.2.1 Deformation Characteristics of HD Segmented Polyurethanes based on Polytetramethylene Oxide (PTMO) Soft Segments

Previous studies of segmented polyurethanes with diacetylene unit containing diols as the chain extenders in the hard segments have shown several mechanochromic effects [29]. These effects vary greatly depending upon the length of soft segment and the thermal treatment prior to stretching. In general, during the first stages of deformation, the polydiacetylene chains orient parallel to the stretch direction, implying that the hard segment chains are orienting perpendicular to the stretch direction. The model proposed to explain this phenomenon is that of hard segment lamellae, possibly ordered in a spherulitic fashion, as shown in Figure 4.9. These orientation results are in agreement with other segmented polyurethanes exhibiting isolated hard segments in a continuous matrix of soft segments studied by such means as IR dichroism [62-65] and X-ray studies [66].

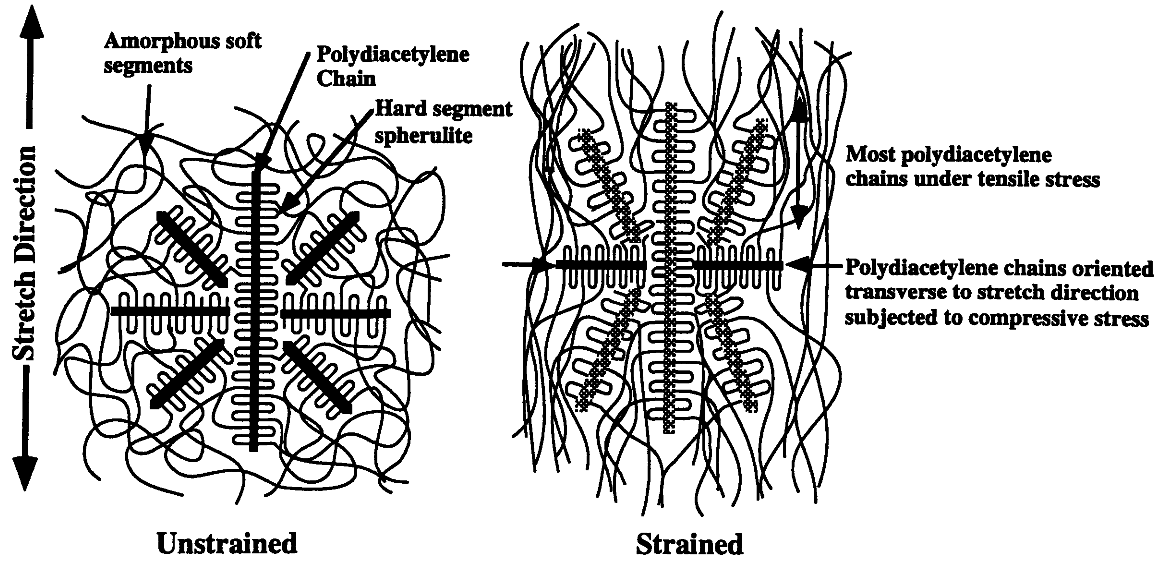


Figure 4.9 Proposed model of orientation of spherulites containing diacetylene chains during deformation.

Next, as stress is applied to these lamellae and transferred to the polydiacetylene chains, there is a shift in the absorption band parallel to the stretch direction to higher energies due to the torque placed upon the conjugated chains. Since the majority of polydiacetylene chains have oriented parallel to the stretch direction, there is only a small component in the perpendicular direction. However, the absorption bands of these perpendicular polydiacetylene chains do not shift to higher energies. It is theorized that this is because they are in lamellae whose chain axes were parallel to the stretch direction before deformation, so that they merely undergo some compression, as can be seen in Figure 4.9.

The last "stage" which the material undergoes is the breakdown of the hard segment material. This is indicated by a decrease in the dichroic ratio of the polydiacetylene chains, which is a ratio of the areas under the absorption curves of the parallel polarization to the perpendicular polarization. Additionally, it has been noted that although there is a mechanochromic shift during deformation, after relaxation the material recovers most of its original color at smaller strains. At relatively higher strains, upon recovery the material will display optical hysteresis, which indicates that the hard segments have undergone some form of permanent deformation.

IR orientation studies [67] of hard segments have shown similar deformation phenomenon. In segmented polyurethanes which show transverse orientation during the initial stages of deformation, the orientation is reversible. However, at higher strains when the hard segment chains begin to orient parallel to the stretch direction, the orientation becomes irreversible. Additionally, this permanent orientation, which the authors attribute to plastic deformation of the hard segments due to shearing forces, is associated with high levels of mechanical hysteresis.

Because the optical hysteresis of the polydiacetylene chains appears to be associated with the permanent deformation of the host crystalline lattice, it is possible to use the polydiacetylene chains as molecular probes for the investigation of both the orientation and deformation mechanics of the polydiacetylene chain containing domains during the macroscopic deformation process.

By observing the mechanochromic effects, both during stretching and in the relaxed state for the hard and soft segments, it should be possible to make relative comparisons of not only their deformation properties, but also make qualitative statements about the relative strengths of the different domains and their role in the mechanical hysteresis of the material.

4.2.2 Segmented Polyurethanes with Polydiacetylene Chains Present in the Hard Segments Only

Before attempting to decipher which mechanochromic shifts are due to which phase in a dual environment polydiacetylene chain containing polymer, it is necessary to observe the individual contributions of each domain, similar to the method used to determine the thermochromic shifts discussed in section 4.1.2.

Using selective cross-polymerization, the hard segments in a film of HDI-5,7/AA-10,12-4820 were cross-polymerized for 2 minutes at 70 °C. The absorption as a function of strain with light polarized parallel (PP) and normal (NP) to the stretch direction is shown in Figure 4.10.

In the parallel polarized direction, beginning at 10% strain, the peak at 575 nm grows at the expense of the excitonic peak originally at 625 nm due to the stress transferred to the polydiacetylene chains. At 120% strain, a third high energy peak at 490 nm begins to grow due to a population of disordered polydiacetylene chains. This disordered population continues to grow as well and shift to 460 nm up to 350% strain, where it represents the state of almost all of the polydiacetylene chains oriented in this direction. Additionally, the peaks centered originally at 625 and 575 nm shift to higher energies of 610 and 560 nm respectively up to 250% strain, where they become difficult to determine.

In the normal direction, it is apparent that the intensity of the absorption is greatly decreasing with strain, indicating that the polydiacetylene chains are orienting in the parallel direction, similar to the previous studies. Since considerable baseline manipulation is needed in these spectra (see Appendix A), no quantitative analysis of peak areas is possible. Therefore it is not possible to obtain accurate dichroic ratios to determine the strain at which the polydiacetylene chains are maximally oriented. The absorption spectra in this direction remains essentially unchanged until around 50% strain, where the peak at 575 begins to increase in relation to the peak at 625. Additionally at this strain it appears that a very small population of slightly disordered polydiacetylene chains begins to grow, possibly centered around 540 nm. This

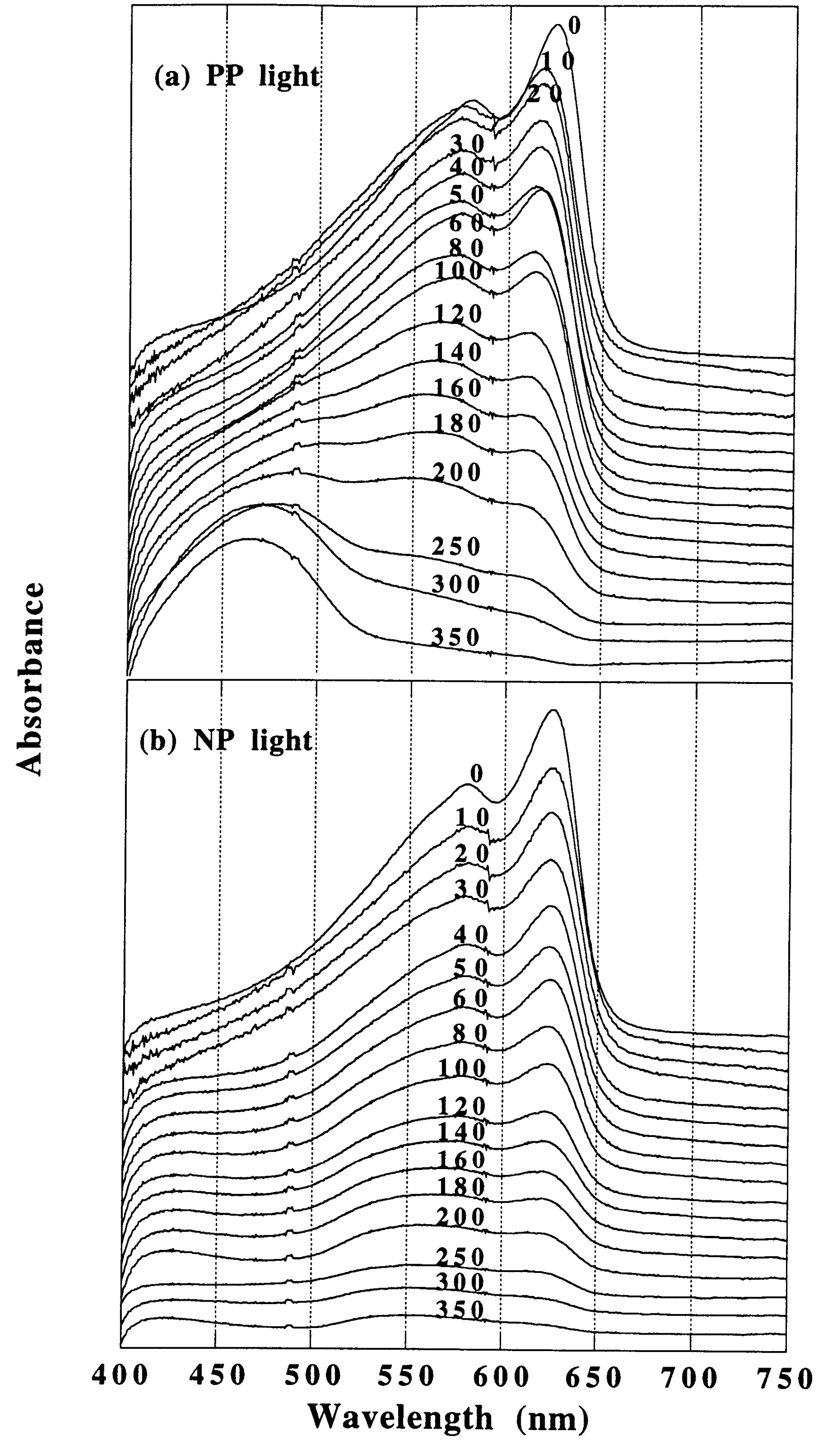


Figure 4.10 Absorption spectra (a) parallel and (b) normal to the stretch direction of HDI-5,7/AA-10,12-4820 as a function of strain. Hard segment diacetylene units selectively cross-polymerized at 70°C for 2 min.

process continues gradually until 350% strain, where the 540 nm peak is the largest and the overall number of polydiacetylene chains oriented in this direction is quite small.

There are some important distinctions to be made between the parallel and perpendicular stretch directions. The first is that although the intensities of the 625 and 575 nm peaks decrease under stress in the perpendicular direction, they remain centered at 625 and 575 nm during the entire deformation process. This indicates that a significant percentage of these polydiacetylene chains are not subjected to any tensile stress which is to be expected when they are oriented perpendicular to the stretch direction (as was discussed for previous studies; see model in Figure 4.8). Secondly, the percentage of polydiacetylene chains that shift to form a higher energy peak in the perpendicular direction is significantly less than in the parallel direction. This once again is due to polydiacetylene chains oriented in the perpendicular direction not experiencing as much of the tensile stress. Lastly, the third peak that begins to form is at a much higher energy in the parallel direction (490-460 nm) than it is in the perpendicular direction (540 nm). This is probably because the disordering stresses that are applied to the polydiacetylene chains in the perpendicular direction are not as great and are not able to cause as much disruption as the stresses applied to the chains in the parallel direction.

Figure 4.11 shows the spectra for the two stretch directions in the unstressed state after stretching to a particular strain. This reversibility, or optical hysteresis, is a good indicator of permanent deformation in the hard segments.

In the parallel direction, the absorption spectrum fully recovers to its original form up until around 180% strain. At 200% strain, the population of higher energy disordered polydiacetylene chains begins to appear and becomes the dominant population by 350% strain. These results would *seem* to indicate that although the polydiacetylene chains experience a significant amount of stress at lower strains, the hard segments do not undergo any significant deformation until 200% strain.

In the perpendicular direction, there appears to be a change in the 540 nm range starting at around 100% strain, although the contribution is not significant until a strain of 160%. Taking these results into account, it appears that although the majority of hard segment material does not undergo permanent deformation until 200%, small amounts which contain the

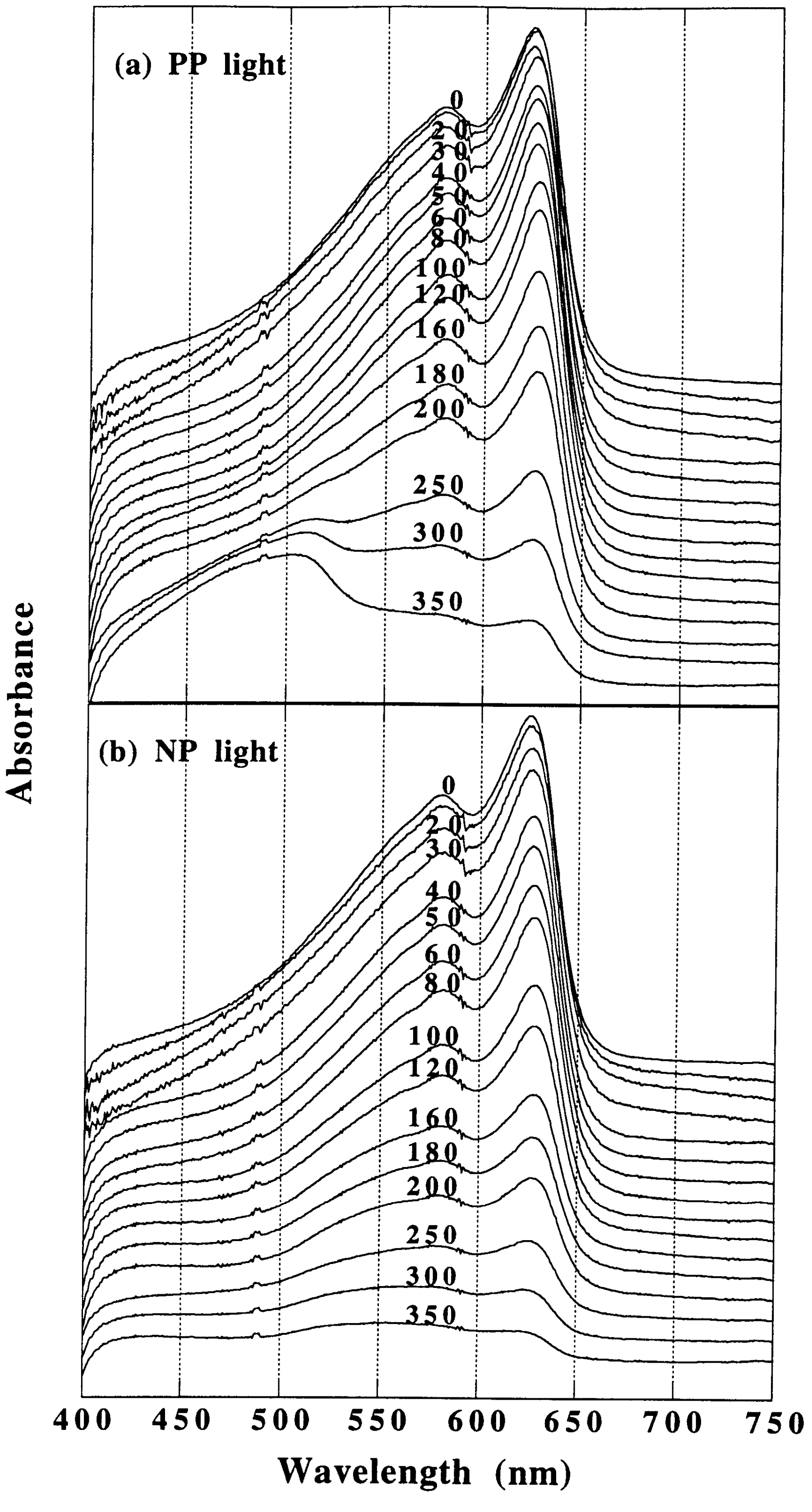


Figure 4.11 Absorption spectra (a) parallel and (b) normal to the stretch direction of HDI-5,7/AA-10,12-4820 in unstressed state after stretching. Hard segment diacetylene units selectively cross-polymerized at 70 °C for 2 min.

perpendicularly oriented polydiacetylene chains experience some permanent deformation at lower strains.

4.2.3 Segmented Polyurethanes with Polydiacetylene Chains Present in the Soft Segments Only

As no method has been found for these materials to selectively cross-polymerize only the soft segments, it was necessary to use HDI-1,8/AA-10,12-5850 to study soft segments exclusively containing polydiacetylene chains. Since the hard segment of this segmented polyurethane and the previous polymer are chemically different, it is suspect that deformation characteristics of the soft segments in these two materials are the same. However, as the soft segments are the dominant phase by a considerable amount, the stoichiometric ratio of the hard and soft segments are the same, and the hard segments are of comparable size, it is assumed here that any effects of the hard segments upon the mechanical properties of these soft segments will be modest.

The parallel and perpendicularly polarized spectra for the stretched material are shown in Figure 4.12. Significant absorption changes do not take place until 30% strain, where the high energy peak centered at 490 begins to grow. By 100% strain, it has quickly become representative of the majority of the polydiacetylene chain population in this direction. It continues to grow until 250% strain, where all of the lower energy conformations have been disordered. Additionally, the absorption maximum of this high energy peak shifts to 460 nm by a strain of 350%.

In the perpendicular direction, there is a significant decrease in absorption relative to the parallel direction, once again indicating that the crystallites are of a lamellar form. Increase in the high energy peak at 490 nm begins at 30% strain, and this grows steadily, although more slowly than in the parallel direction. By roughly 250%, it represents the entire polydiacetylene chain population, and by 350% is has shifted to 465 nm.

Comparing these results to those of the polydiacetylene chains contained within hard segment material, there appear to be two distinct differences. The first is that creation of a higher energy population occurs at a lower strain (30%) in the SD material than in the HD material (120%). Furthermore, the growth of this disordered peak is far more rapid in the SD material. This

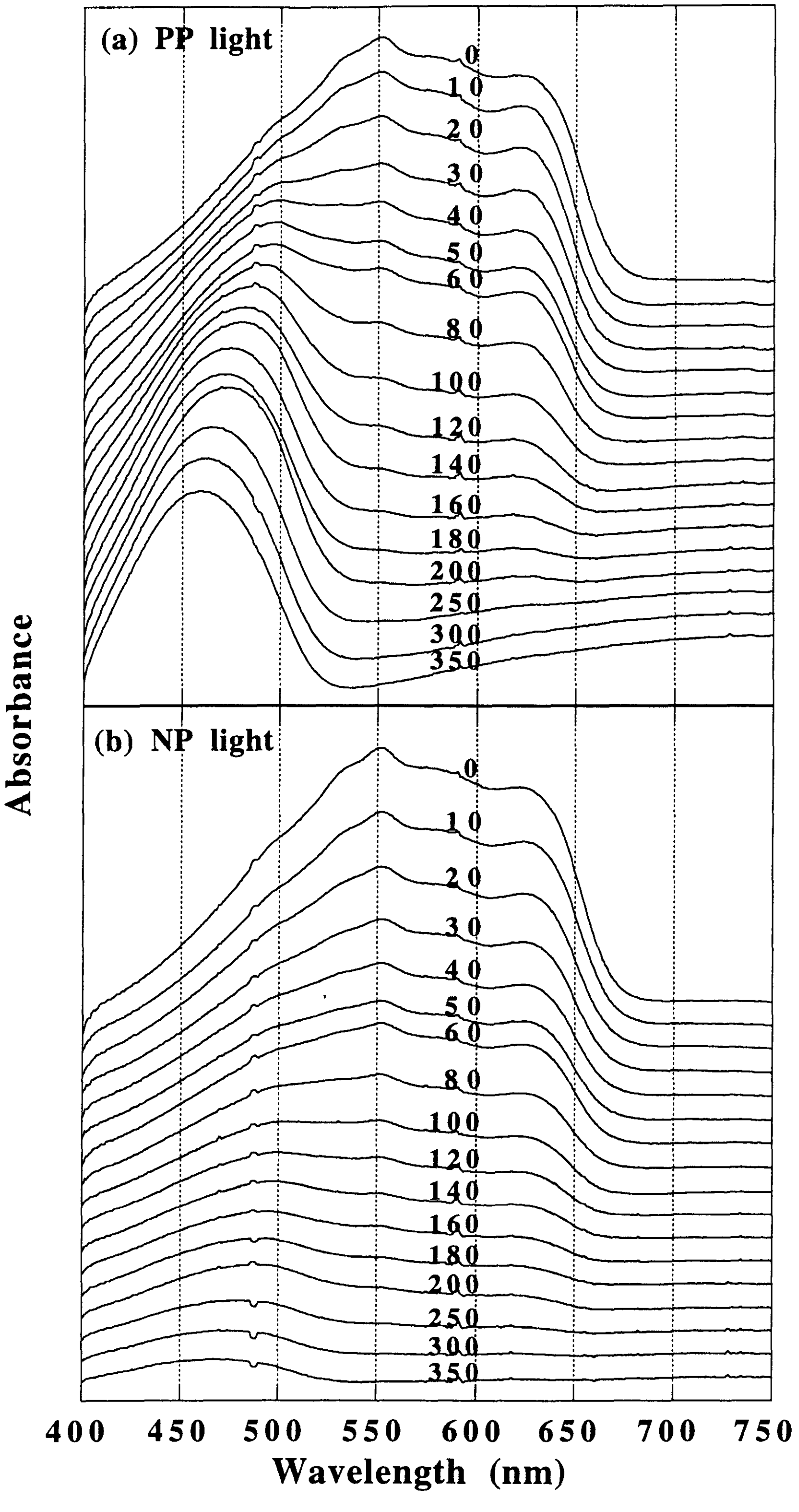


Figure 4.12 Absorption spectra (a) parallel and (b) normal to the stretch direction of HDI-1,8/10,12-AA-5850 as a function of strain. The soft segment diacetylene chains were cross-polymerized at room temperature for 2 minutes.

certainly seems to indicate that hard segment crystallites have a larger cohesive energy density than the soft segment crystallites, which allows them to stay coherent to higher stresses, and thus larger strains. The rigid and ionic nature of the hard segments are responsible for this, just as they are primarily responsible for the higher melting temperatures of the hard segments.

The difference between the HD and SD materials is even more profound in terms of the optical hysteresis. Figure 4.13 shows the recovery of the SD polydiacetylene chains after stretching to the various strains indicated. Unlike the hard segments, there is far less recovery of the original conjugated forms after stretching in both directions. In the case of the hard segments, up to strains as high as 200%, there is a considerable shift in absorption with negligible optical hysteresis upon recovery. Even though the polydiacetylene chains are experiencing large stresses, the hard segment material is still coherent. In the case of the soft segments, the creation of the higher energy peak in the diacetylene chains accompanies the breakdown of the host crystallites themselves. Therefore very little recovery is possible once the unifying matrix has been destroyed.

This also helps to explain the rapid growth of the SD high energy peak during stretching. For the HD material, increased strain merely transfers increased stress to the polydiacetylene chain population. In the SD material, increased strain is quickly breaking down all of the soft segment host crystallites, quickly driving the high energy conformational shift.

4.2.4 Segmented Polyurethanes with Polydiacetylene Chains in Both Phases

Finally, a DD polymer was produced from HDI-5,7/AA-10,12-5550 by exposure to uv light for 2 minutes at room temperature. The parallel and normal optical hysteresis data, which most strongly exposes the differences between the two polydiacetylene chain environments, is presented in Figure 4.14. As the spectra corresponding to 0% strain shows, this irradiation regimen yielded significant fraction of both soft and hard segment polydiacetylene chains.

It is possible to tell that these results are a combination of those obtained for HD and SD systems. In the parallel direction, at strains below 200%, the formation of the high energy peak is due to deformation of polydiacetylene chains contained in soft segment crystallites. Above 200%, the only ordered

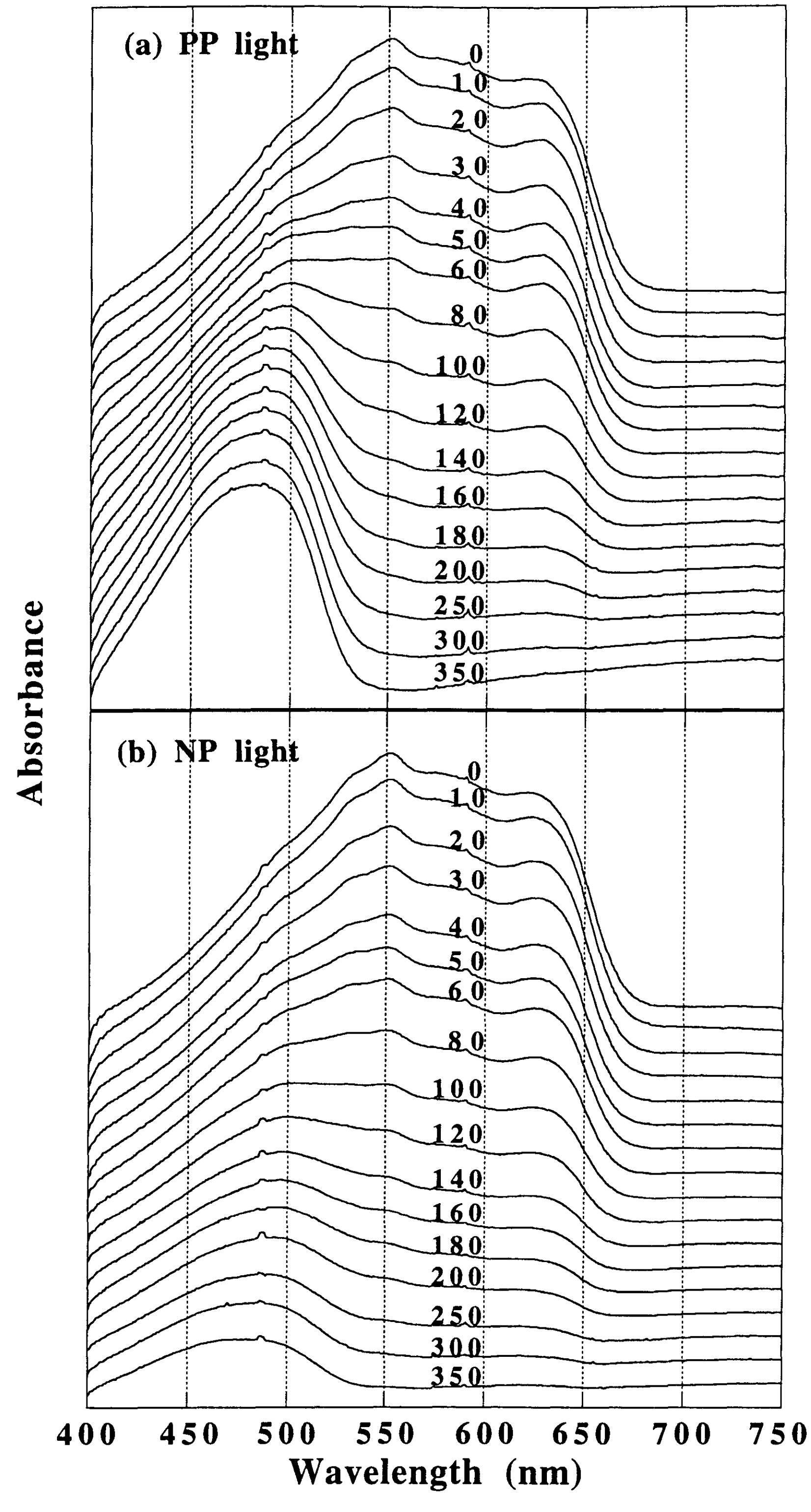


Figure 4.13 Absorption spectra (a) parallel and (b) normal to the stretch direction of HDI-1,8/AA-10,12-5850 in unstressed state after stretching. Soft segment diacetylene chains were cross-polymerized at room temperature for 2 minutes.

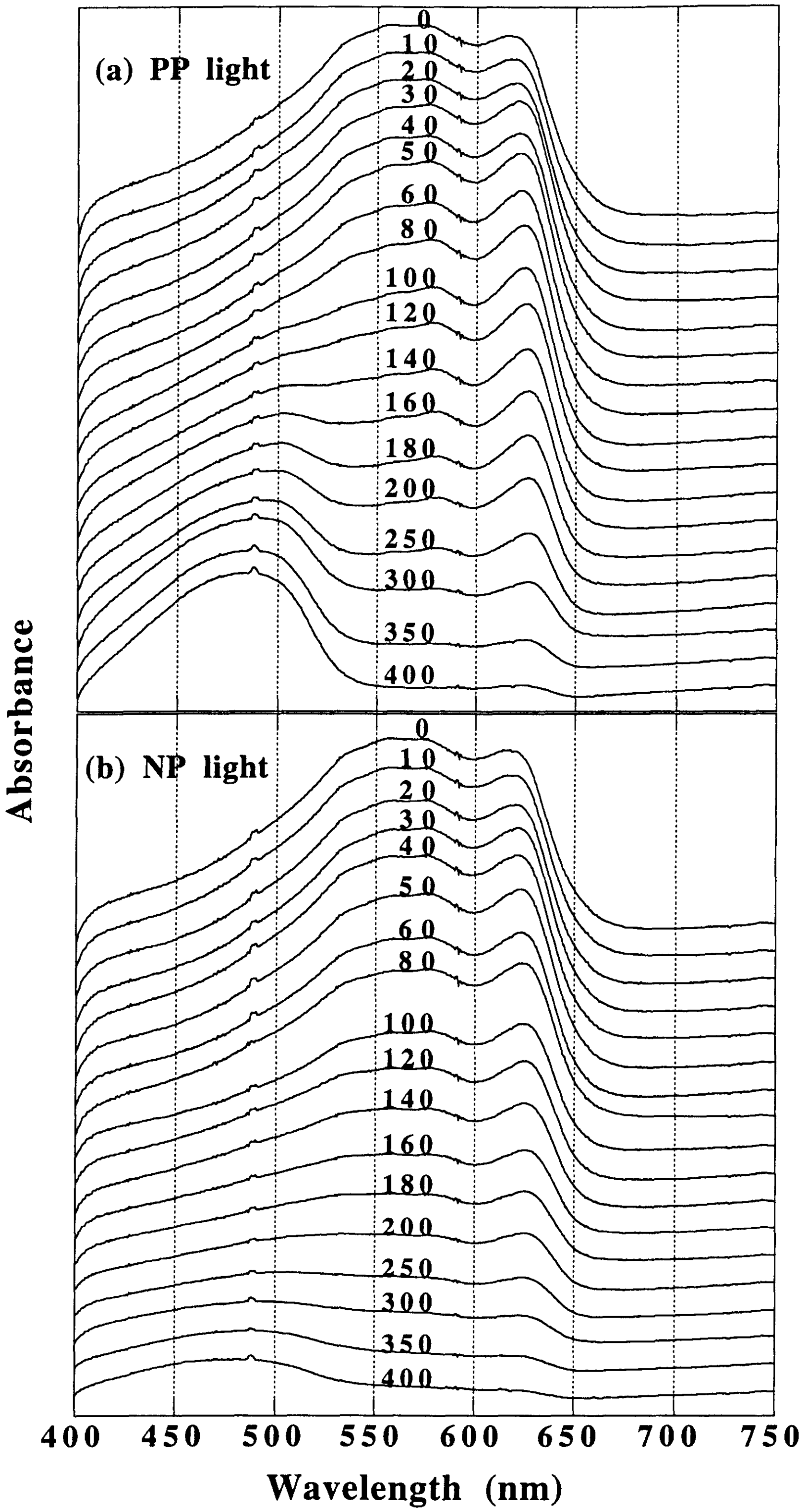


Figure 4.14 Absorption spectra (a) parallel and (b) normal to the stretch direction of HDI-5,7/AA-10,12-5550 in unstressed state after stretching. Both soft and hard segment diacetylene units were cross-polymerized at room temperature for 2 min.

absorption peaks are due to polydiacetylene chains present in the hard segments, which begin to disorder up to 400% strain. In this way we are able to simultaneously observe the deformation and orientation characteristics after stretching of the hard and soft segments. During the deformation process (not shown), there is considerable overlap of the chromic shifts due to the hard and soft segment polydiacetylene chains, and the contributions of each to the higher energy peak are not distinctly discernible.

4.2.5 Dual Absorption Band Selective Polarizers

The polydiacetylene chains in the hard and soft segment crystallites yield important information about the morphological changes which take place in these phases during deformation. However, to greatly simplify the morphology of these polymers, there is a third major phase to be considered: the amorphous soft segment material. Polydiacetylene chains cannot be used to track the orientation and deformation of the amorphous phase for the simple reason that they do not form unless present in an ordered crystalline or paracrystalline phase (refer to Chapter 1.1).

However, there are still diacetylene units present in the amorphous soft segment material. During deformation it is common for amorphous fractions of the soft segment material to undergo strain induced crystallization [33,34,66] which results in soft segment crystallites with their chain axes oriented parallel to the stretch direction. If the molecular parameters of the strain induced crystallites are sufficient, it is then possible to cross-polymerize the polydiacetylene chains in this previously amorphous third phase.

To avoid the effects of the hard segment polydiacetylene chains, an SD (HDI-1,8/AA-10,12-5850) was cross polymerized while being held at a strain of 200%. This strain was chosen because, as Figure 4.13 shows, almost all previously existing soft segment crystallites have been destroyed at this point, so that they will not effect the results. After cross polymerization, absorption parallel and perpendicular to the stretch direction was taken first at 200% strain, then at reduced strains while the material was allowed to relax (1), and then at strains higher than 200% as the material was restretched (2). The data is shown in Figure 4.15.

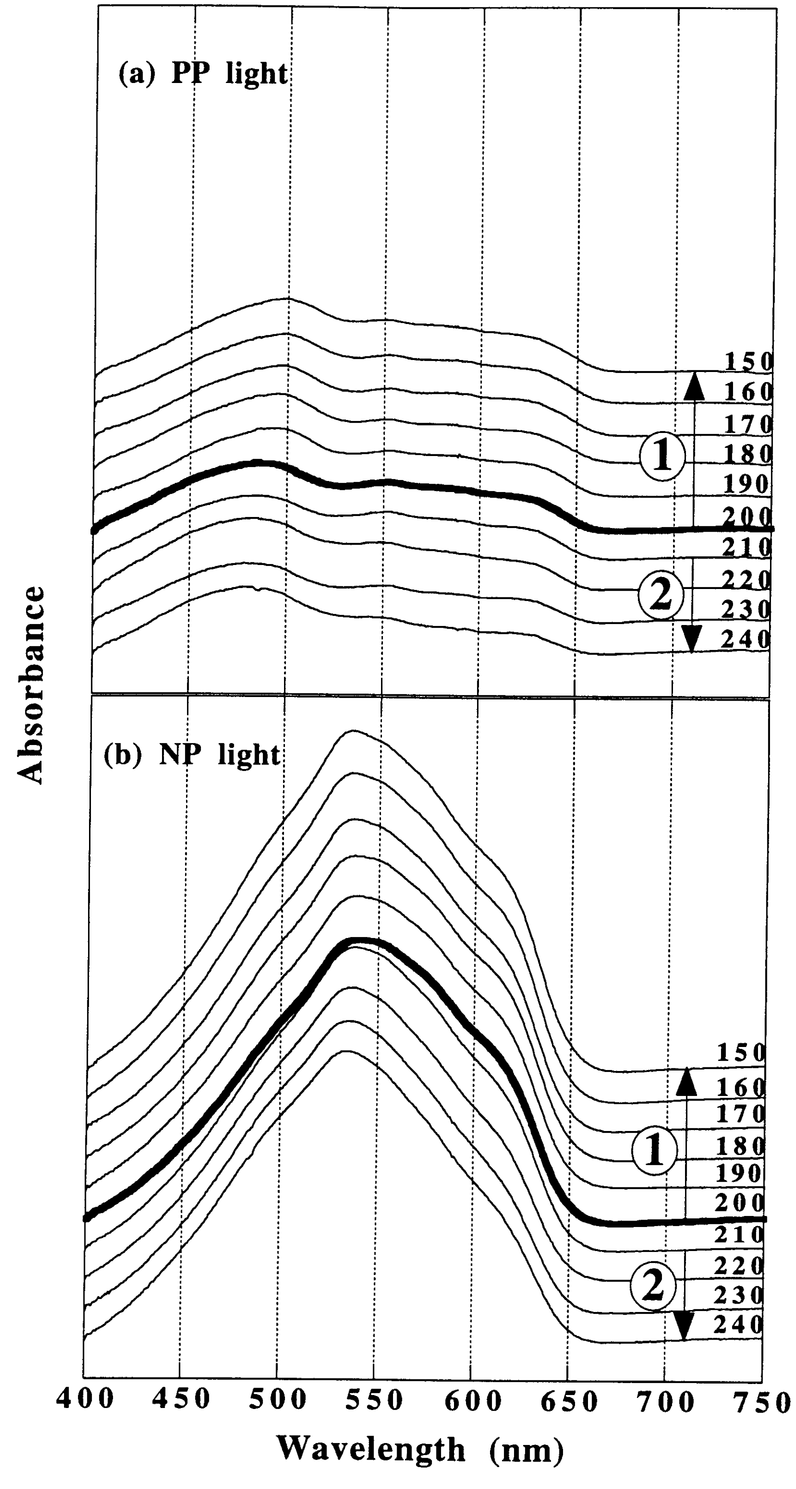


Figure 4.15 Absorption spectra of HDI-1,8/AA-10,12-5850 cross-polymerized after creating strain induced crystallites. Sample is stretched to 200% strain (thick line), then: (1) relaxed to 150% strain (full stress relaxation), then (2) restrained from 210% to 240% (point of failure) strain. Absorbance scales for the parallel and normal directions are identical.

Contrary to the results of the polymers which were cross-polymerized and then stretched, in this case the polydiacetylene chains almost exclusively absorb in the perpendicular direction. This means that the chain axes of the host crystalline material must be oriented into the stretch direction.

There are two possible explanations for this phenomenon. The first does not account for strain induced crystallization at all, but relies on preexisting lamellar crystallites oriented with their chain axes parallel to the stretch direction before stretching. It assumes these crystallites would not be deformed in tension, similar to the side arms in the hard segment spherulitic model proposed in Figure 4.9. After deformation, these lamellae would support polydiacetylene chains oriented transverse to the stretch direction. Lamellae oriented otherwise would be deformed under tension and would not support diacetylene unit cross-polymerization.

The second model supposes that during deformation, all pre-existing crystallites are destroyed, and the only soft segment crystallites present at 200% strain are those due to strain induced crystallization. Upon exposure to uv radiation, polydiacetylene chains would form transverse to the stretch direction.

The data available is overwhelmingly in support of the second hypothesis. Data shown in Figure 4.13 clearly indicates that almost all crystallites that supported polydiacetylene chains had been destroyed by 200% strain. Additionally, the magnitude of the absorption in the perpendicular direction of Figure 4.15 is far greater than would be possible due to only a small fraction of the original lamellae. DSC data (not shown) for the strained material has given a value of 42.34 J/g for the soft segment melting area, which is far larger than that of the unstretched material (22.02 J/g), supporting the assumption of strain induced crystallization. Lastly, as Figure 4.15 shows, upon relaxation or further stretching, there is no significant change in either the orientation or absorption characteristics. This also supports the model of strain induced crystallites, whose orientation would remain fairly constant, and whose chains would already be in extended form so that further extension could do nothing to disrupt the crystalline lattice.

Further conformation of this mechanism is achieved by revisiting the HD polymers based upon PTMO soft segments studied in previous work [29]. If the strong absorption in the transverse direction in the deformed SD polymer is due to soft segment strain induced crystallization, it should be exclusive to SD systems, and not be possible with HD polymers, as hard segments are not known to undergo any type of strain induced crystallization. This means that if we *are* able to achieve intense transverse absorption at a high strain for an HD polymer, the mechanism involved would have to be due to preexisting lamellar crystallites.

Two separate types of tests were performed. In the first, samples of HDI-5,7-1000 and HDI-5,7-2000 were stretched to a strain of 350% and irradiated. The polymers absorbed approximately three times as strongly in the parallel direction as compared to the perpendicular direction. The strong absorption was due to the preexisting crystallites which were still ordered at this strain, so that cross-polymerization was still possible. The absorption in the perpendicular direction was also rather weak , indicating that the intense transverse absorption in the stretched SD polymer cannot be due to entirely to preexisting crystallites.

In a second test, an unirradiated sample of HDI-5,7-2000 was stretched until the hard segment crystallites were completely disordered (700%) as determined by reversibility data in previous work [29]. This strain is analogous to a strain of 200% in the SD polymer, in which the soft segment crystallites have been shown to be completely disordered (Figure 4.13) When irradiated at this strain, the HDI-5,7-2000 polymer showed no significant absorption in either direction, since the disrupted hard segments could not support the cross-polymerization of the diacetylene units. As the hard segments do not undergo any form of strain induced crystallization, polydiacetylene chain formation was not supported.

The phenomenon of ordered polydiacetylene chain formation transverse to the stretch direction is therefore limited to diacetylene units present in strain induced crystallites, which in the case of segmented polyurethanes, must be formed in the soft segments.

As discussed earlier, deformation of polydiacetylene chains, especially those present in the soft segments, eventually results in a high energy absorption band oriented parallel to the stretch direction. Further cross-polymerization in the stretched state, as was demonstrated in Figure 4.15, will result in ordered polydiacetylene chains oriented transverse to the stretch direction. By combining these two effects, it is possible to produce a polarizer that blocks out two specific regions of light, each in a separate direction.

The first stage in the production of such a device is to cross-polymerize diacetylene units in the unstretched state, and then stretch them until they are both oriented in the stretch direction and disordered. For the segmented polyurethanes examined in this thesis, the polydiacetylene chains present in the soft segment crystallites are best suited for this purpose as they completely disorder by 200% strain. As the hard segments are more cohesive, they need to be stretched to higher strains, and in most cases the polymer fails before the final disordered form is reached.

The last step is to create ordered polydiacetylene chains oriented perpendicular to the stretch direction while the polymer is in the stretched state. The proposed molecular schematic of this phenomenon is shown in Figure 4.16.

A question which arises is whether it is possible to simply use the homopolyesters to produce these devices instead of going through the extra synthetic steps of producing a segmented polyurethane. The use of homopolyesters was examined, and although it was found to be possible using the homopolyester SA-10,12, there were several drawbacks as well. Since the homopolyester does not have the second hard segment phase dispersed throughout, the crystallites which form are far larger, and produce a highly scattering, opaque material. Secondly, upon extension, the material necks, and the strain induced crystallites which form scatter intensely. Because of the opaque nature of the polymer, it is not nearly as useful in terms of a polarizing device. Lastly, the tensile properties are not as good as the segmented polyurethanes, as they tend to tear and break at much lower strains, making it difficult to fully disorder and orient the original polydiacetylene chain containing lamellae.

Figure 4.17 shows the parallel and perpendicular polarized absorption spectra for the dual polarizers made form HDI-1,8/AA-10,12-5850 and SA-10,12.

Due to the adipic acid component in HDI-1,8/AA-10,12-5850, the polymer appears deep purple normal to the stretch direction and bright yellow in the parallel direction. The SA-10,12 homopolyester, due to the succinic component, appears blue and yellow in the normal and parallel directions respectively. Were an SD segmented polyurethane with either an SA-10,12 or MA-10,12 soft segment synthesized, it is most likely that this would produce a blue/yellow device similar to the SA-10,12 material, but with much less scattering.

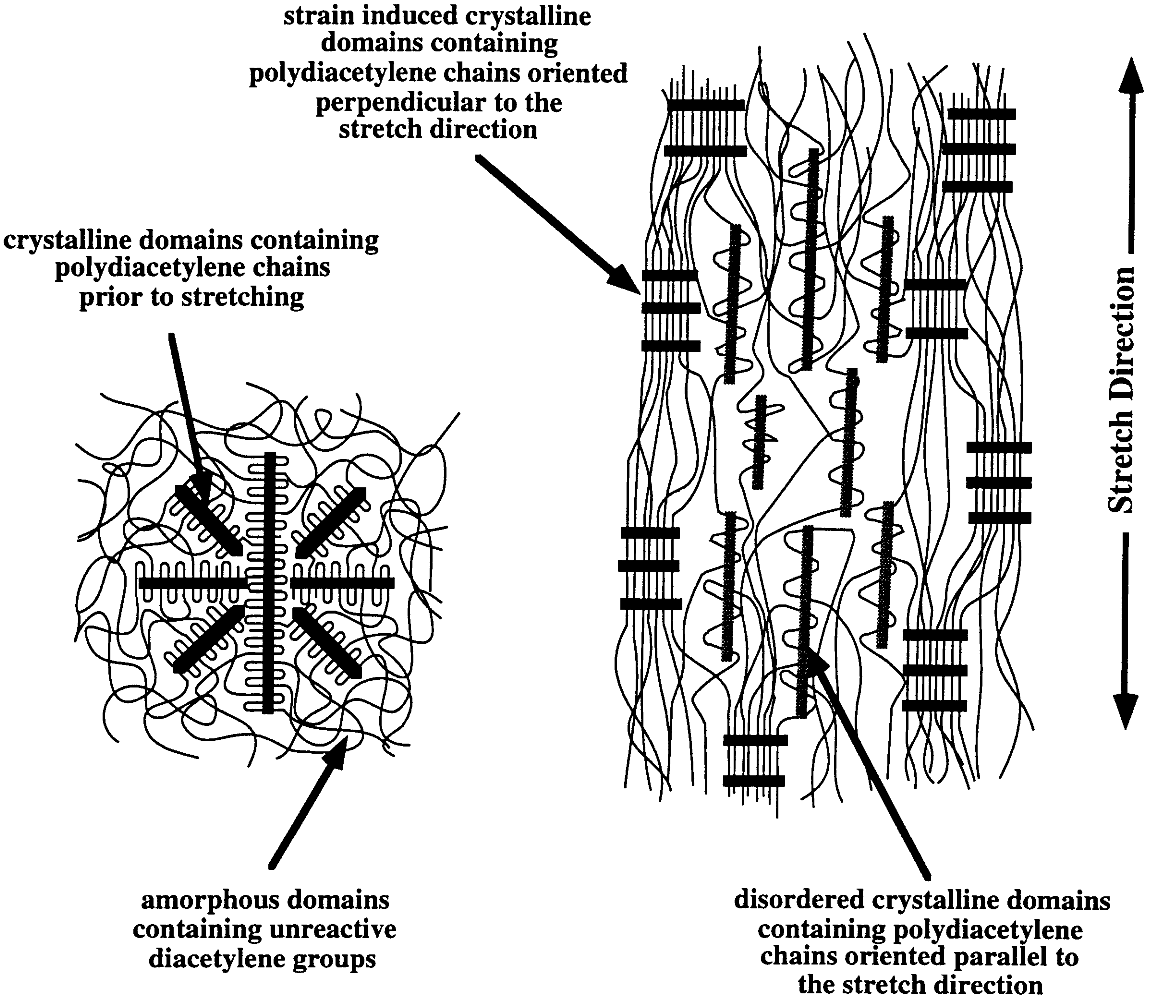


Figure 4.16 Proposed molecular model for the creation of ordered and disordered polydiacetylene chain absorption bands oriented parallel and perpendicular respectively to the stretch direction

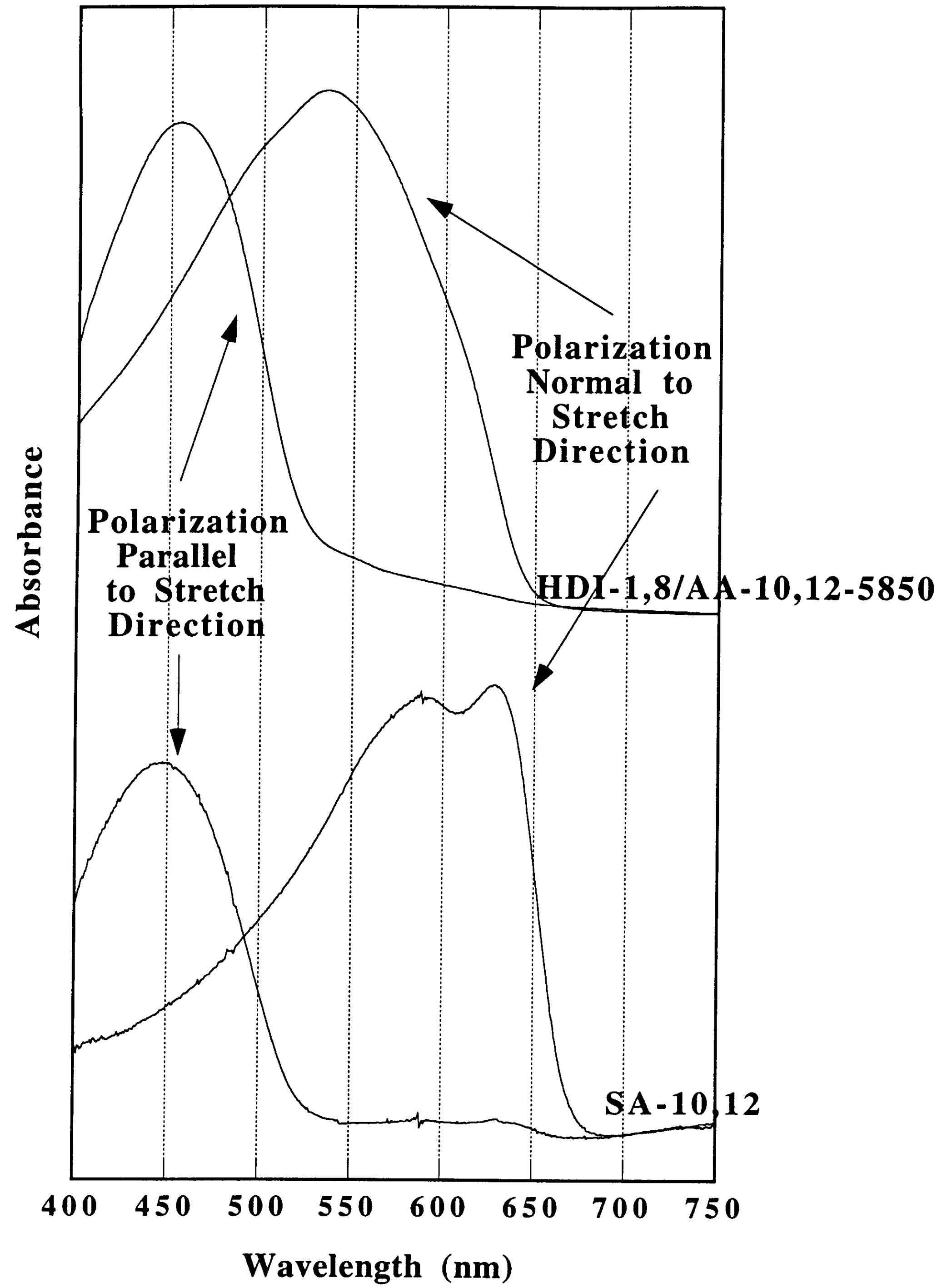


Figure 4.17 Absorption spectra of HDI-1,8/AA-10,12-5850 and SA-10,12 with disordered polydiacetylene chains oriented parallel to the stretch direction and ordered polydiacetylene chains oriented normal to the stretch direction.

4.3 Mechanical Enhancement

During the cross-polymerization process, the polydiacetylene chains which form are crosslinking the host polymer chains. The crosslinking, however, can also be utilized to enhance the mechanical and thermal properties, similar to the results seen for the homopolyesters shown in Chapter 3.3.3. When used as a molecular probe, it was necessary to produce a minimum of crosslinking so that the information which was gained about the deformation mechanics would be valid for segmented polyurethanes in general. Similar to the mechanical enhancement studies of the homopolyesters, electron beam irradiation was used for the mechanical cross-polymerization as it creates a high crosslink density and penetrates the full thickness of the sample.

The effects of crosslinking upon the storage modulus for an HD polymer, HDI-5,7/commercial polyester-1050 are demonstrated in Figure 4.18.

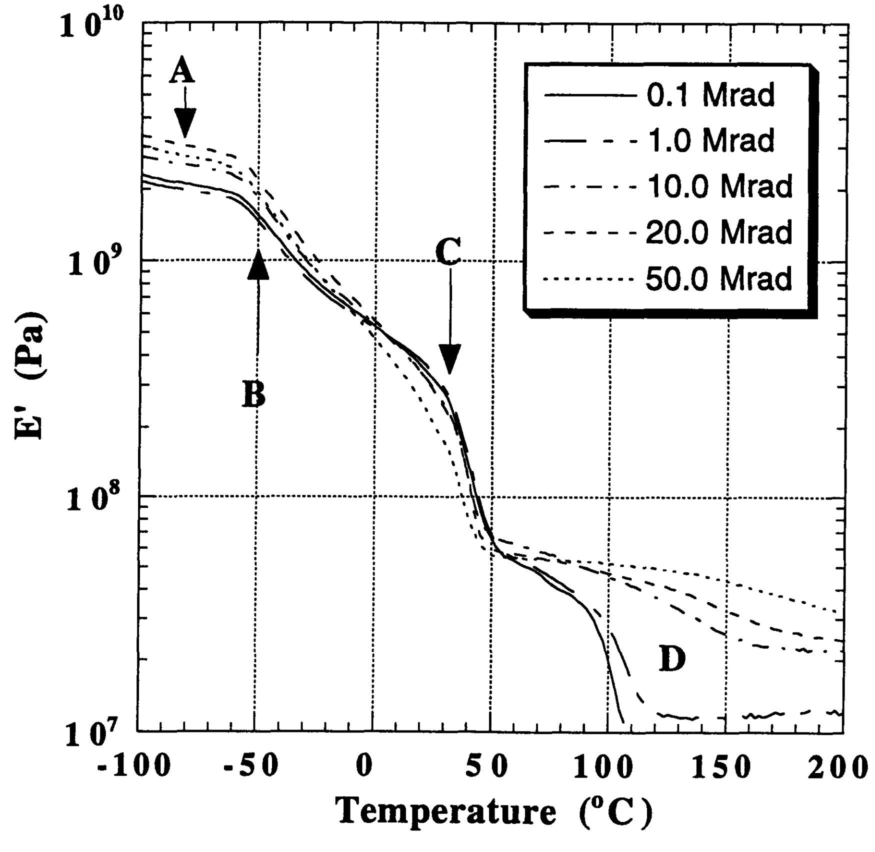


Figure 4.18 Effect of crosslinking upon the storage modulus for HDI-5,7/commercial polyester-1050. Radiation dosages are given in Mrads.

Region A denotes the glassy region, and, like the homopolyesters, there appears to be variation in the modulus which cannot be correlated with the amount of incident radiation. For these polymers, it was found by performing various experiments, that the variation in this region is due to difficulties in obtaining an accurate cross sectional area.

Point B denotes the glass transition temperature, which, as one might expect, does not vary with irradiation, as the soft segments are responsible for the glass transition temperature and are unaffected by crosslinking in the hard segments.

C is the melting point of the polyester soft segments. This rather large drop in modulus is due to the highly crystalline nature of the commercial polyester macrodiol. Only in the case of 50 Mrads does there appear to be a change in this melting behavior. It is believed possible, and will show up more prominently in the SD and DD materials, that the heat generated during the irradiation, not the irradiation itself, served to melt the soft segment crystallites. Once cooled, the soft segment recrystallization would take place very quickly, producing fewer and smaller crystallites which would account for the decreased modulus and melting temperature in this region.

Region D demonstrates the true effects of the cross-polymerization on the mechanical properties of this material. Two significant effects can be seen. The first is an extension of the plateau modulus to higher temperatures. The crosslinks increase the cohesive strength of the hard segments, and therefore reinforce them at high temperatures. The second effect is the trend towards the cessation of the melting phenomenon altogether. By 50 Mrads, the melting temperature has not only been greatly increased, but there is only a very small drop in the storage modulus at this transition point. The hard segments in this case are now bound by covalent bonds, so that they can only be dissociated by the breakdown of the chemical bonds themselves.

The effect of crosslinking on the mechanical properties of an SD polymer are somewhat different, as Figure 4.19 shows.

Similar to the effect seen for homopolyesters in Chapter 3.3.3, region A once again demonstrates the drop in modulus due either to the melting of the soft segment crystallites from the heat generated during irradiation, the disruption of the crystalline lattice from the cross-polymerization of the diacetylene units, or both.

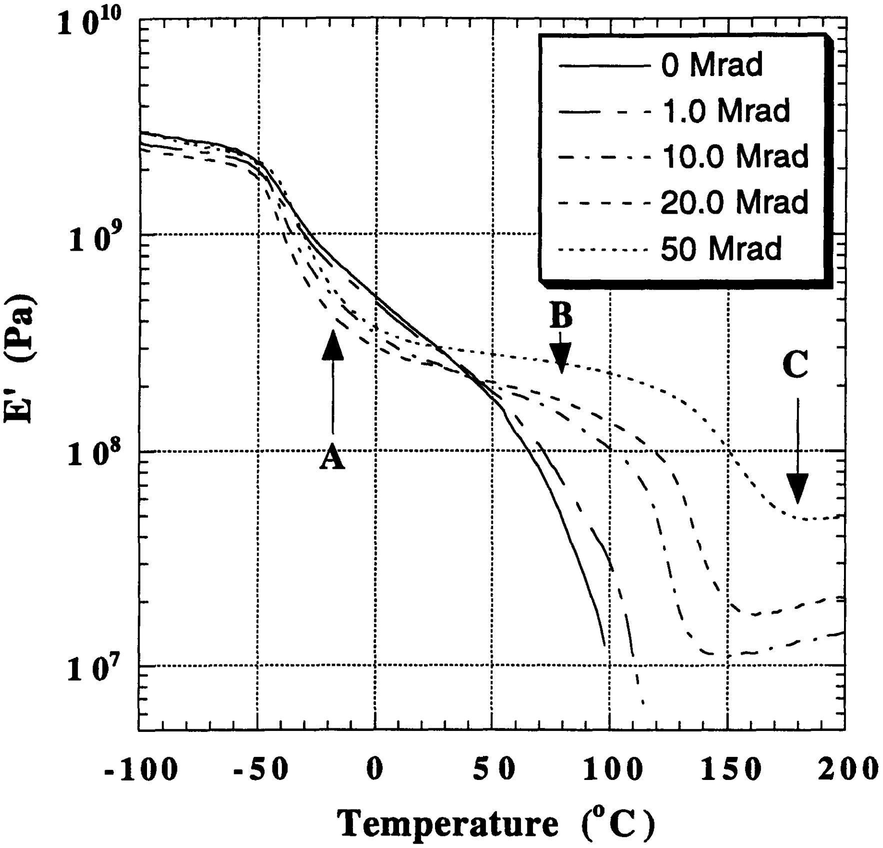


Figure 4.19 Effect of crosslinking upon the storage modulus for HDI-1,8/AA-10,12-1710. Radiation dosages are given in Mrads.

Region B shows an effect that appears to be unique to the crosslinking of soft segments. The modulus of the rubbery plateau appears to increase with increasing irradiation. A possible explanation is as follows. Even though a large quantity of soft segment crystallites appear to have been destroyed, which results in the decreased modulus directly after T_g, there is still an increase in crosslinking in the soft segments due to the cross-polymerization of the diacetylene units. When the host polyester crystalline material is disordered, the polydiacetylene chains still tie the soft segments together, which in turn reinforces the rubbery phase, and results in a higher storage modulus throughout the rubbery plateau.

This mechanical enhancement in the soft segments is analogous to the effects seen either by the addition of filler material [60] or an increase in hard segment content [44,62,68,69] which both serve to increase the modulus in the rubbery plateau region.

As the physical crosslinks created in the soft segments can tie numerous chain together, they can act like cohesive hard segments in terms of increasing high temperature stability, which is demonstrated in region C. Not only is the apparent melting temperature of the hard segments increased, but after melting the polymer is still held together by the soft segment crosslinks. Since the hard segments are not experiencing any crosslinking, the apparent extension of the plateau modulus is entirely due to the stabilizing effects of the soft segment polydiacetylene chains. This increased high temperature stability was also demonstrated with the homopolyesters (see Figure 3.4).

Petrovic et al [70] investigated a series of segmented polyurethanes where the soft segments were based upon varying compositions of diols and triols. The dynamic mechanical results indicated a slight extension in plateau modulus when the soft segment composition was varied from 0% to 100% triol content. No increase in plateau modulus was observed. The small extension of the plateau modulus and lack of plateau modulus enhancement is due to the relatively small amount of crosslinks in the overall structure. Although a quantitative comparison cannot be made due to the numerous structural differences, it is apparent that the polydiacetylene chains in the soft segments are extensively crosslinking the polymer chains.

Figure 4.20 demonstrates how these combined effects enhance the high temperature properties of a DD polymer. An increase in the plateau modulus is seen due to the reinforcing effects of the soft segment polydiacetylene chains. The extension of the plateau modulus to higher temperatures can be attributed to both the soft segment crosslinks and the increased cohesion of the hard segments from the hard segment polydiacetylene chains. Lastly, the final drop in modulus after the melting of the hard segments is greatly decreased due both to the reinforcing soft segment crosslinks and the hard segment crystallites which are tightly bound by crosslinks.

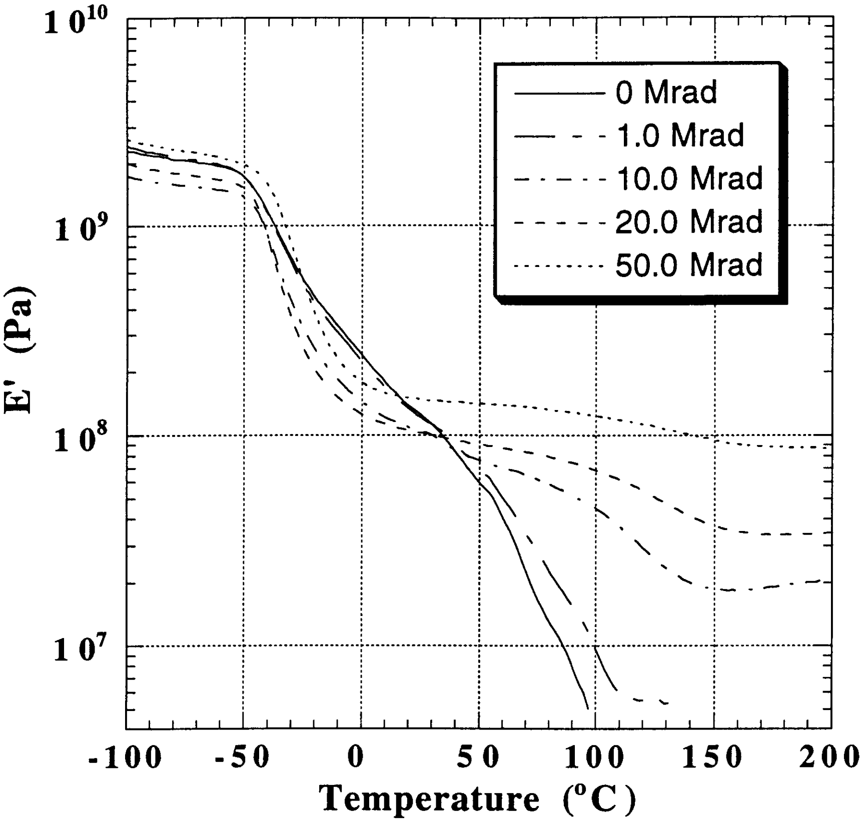


Figure 4.20 Effect of crosslinking upon the storage modulus for HDI-5,7/AA-10,12-1670. Radiation dosages are given in Mrads.

5. Conclusions

In this thesis, a synthetic technique for producing both high molecular weight and functionalized diacetylene unit containing polyesters was developed. The majority of the polyesters were found to cross-polymerize upon exposure to uv light. The absorption of the resulting polydiacetylene chains was found to vary depending upon the chemical structure of the polyester. The polyesters exhibited thermochromic transitions which were driven by the melting temperature of the host crystalline lattice. This melting temperature can be varied not only by structural changes, but by processing and the effects of cross-polymerization as well. The thermochromic transitions were found to occur at temperatures from 21 to 65 °C, well below those expected for polydiacetylene chains present in hard segments of segmented polyurethanes.

The most promising of these polyesters were incorporated into segmented polyurethanes, some of which additionally contained diacetylene groups in the hard segments. It was found that by heating the polymers above the melting temperature of the soft segments but below that of the hard segments, the hard segment diacetylene units could be selectively cross-polymerized upon exposure to uv light. By using this technique, coupled with cross-polymerization of both phases at room temperature, it was possible to vary the extent of the cross-polymerization in the two phases.

The polydiacetylene chains in the two phases contributed to two separate thermochromic transitions driven by the vastly different melting temperatures of the two molecular environments. The color changes which took place could be modified by changing the soft segment chemical structure.

The two polydiacetylene chain populations were also found to produce separate mechanochromic transitions upon stretching. The nature of these absorption shifts was indicative of the molecular changes taking place in the host environment. Upon stretching, both the hard and soft segment absorption bands were modified at strains as low as 20%, which is indicative of stress transfer to the conjugated backbone. The shift in absorption bands continued in the hard segment polydiacetylene chains to well over 350% strain, and in the soft segment polydiacetylene chains up to 200%. In both regions, the polydiacetylene chains were found to orient preferentially parallel to the stretch direction, indicating that the host crystalline chain axes are orienting perpendicular to the stretch direction. This orientation behavior is indicative of lamellar crystalline domains.

Upon relaxation, the hard segment polydiacetylene chains recovered the majority of their original absorption characteristics up to 200% strain, after which permanent optical hysteresis began. In stark contrast, the polydiacetylene chains present in soft segment crystallites exhibit virtually no optical hysteresis. By 200% strain, where the hard segment polydiacetylene chains begin to permanently deform, the soft segment polydiacetylene chains are completely disordered. Therefore, in polymers which contain diacetylene units in both environments, two separate shifts in the absorption band seen in the optical hysteresis data can be attributed to the deformation of the two phases.

The differences in the mechanochromic shifts provides an insight into the deformation mechanics of the superstructure. Since under tension, the polydiacetylene chains in both environments show changes in their absorption bands at low strains, it appears that stress is being transferred evenly throughout the polymer. Even though the hard segments are considered fairly rigid, they are not able to shield the polydiacetylene chains within from a modest amount of stress transfer.

However, the optical hysteresis data shows that this stress transfer does not destroy the cohesion of the hard segments, as they appear to resist any permanent deformation up to strains of 200%.

The soft segment crystallites which are composed largely of methylene groups, and do not enjoy the benefit of hydrogen bonds, are not able to withstand the applied stress. In comparison to the hard segments, they deform rather easily, which in turn drives the irreversible mechanochromic transition in the resident polydiacetylene chains.

At a strain of 200%, the soft segments were found to undergo not only complete disruption of the preexisting crystallites, but formation of strain induced crystallites as well. Polydiacetylene chains which were present in the preexisting soft segment crystallites become disordered and oriented with their chain axes parallel to the stretch direction. Further cross-polymerization of soft segment diacetylene units results in ordered polydiacetylene chains residing in the strain induced crystallites. The anisotropic orientation of these crystallites results in the ordered polydiacetylene chains having their chain axes perpendicular to the stretch direction.

The resulting material contains two separate absorption bands oriented perpendicular to each other. Although no specific application has been investigated, this unique set of optical properties is sure to prove valuable in numerous devices.

Lastly, heavy cross-polymerization of the diacetylene units in the two environments was investigated to study the effects upon the dynamic mechanical response and high temperature properties. This crosslinking in the hard segments was found to extend the rubbery plateau to higher temperatures and reinforce the hard segments against disruption at the melting temperature.

Cross-polymerization of the soft segment polydiacetylene chains modified the network structure in this phase. The crosslinks served to tie the soft segment chains together, effectively acting as additional hard segment domains. The characteristics this imparted on the material were an increased rubbery plateau modulus, extension of the rubbery plateau to higher temperatures, and reinforcement of the segmented polyurethanes matrix after melting of the hard segments.

In summary, the incorporation of diacetylene units in the segmented polyurethanes has proved to have potential in many areas. As devices, they have shown promise as indicators of temperature and stress. Additionally, they have been shown to produce dual wavelength polarizers which block different wavelength regions of light under different polarizations. They have shown potential to mechanically enhance segmented polyurethanes at high temperatures, and the differences in soft and hard segment crosslinking upon the high temperature properties gives some insight into the roles played by these regions at high temperatures. Lastly, their utility as molecular probes has been demonstrated, most strongly in the investigation of the deformation and orientation characteristics of soft segment crystallites during the deformation of the segmented polyurethane system.

6. Appendix A. Baseline Correction for Mechanochromic Samples

Because of the nature of the materials and their relative thickness, the mechanochromic films tend to scatter dramatically throughout the visible region. As noted previously, when attempting to use the polydiacetylene chains as a molecular probe, it is necessary to use relatively low levels of cross-polymerization, so that the mechanical properties of the host domain are not significantly modified. When the polydiacetylene chain densities are this small (uv exposures of 2 minutes), it is virtually impossible to observe small changes in the absorption bands since they are overshadowed by the scattering in the host polymer.

To adjust for this, the following procedure was used. Before irradiation, a spectra of the polymer film was taken to record the background scattering. The sample was then cross-polymerized, stretched, and scanned as described in the procedural section. When all of the scans were completed, the scattering was removed as follows:

1) The uncross-polymerized spectra, curve **i** in Figure 5.1, was plotted and fitted to a second order polynomial equation. This equation, curve **ii**, and the spectra to be modified, curve **iii**, were adjusted so that at 770 nm both curves intersect the x axis (point **A**).

2) Since the relative amount of scattering in the samples will change depending upon both the polarization and the thickness of the sample, which is thinning throughout the experiment, it is necessary to scale this "scattering removal" separately for each sample. This was done by selecting a point on each curve at 404 nm, points **B** and **C**, and using the following equation to obtain the adjusted data, curve **iv**:

$$\mathbf{iv = iii - ii(C/B)} \qquad \textbf{Equation 6.1}$$

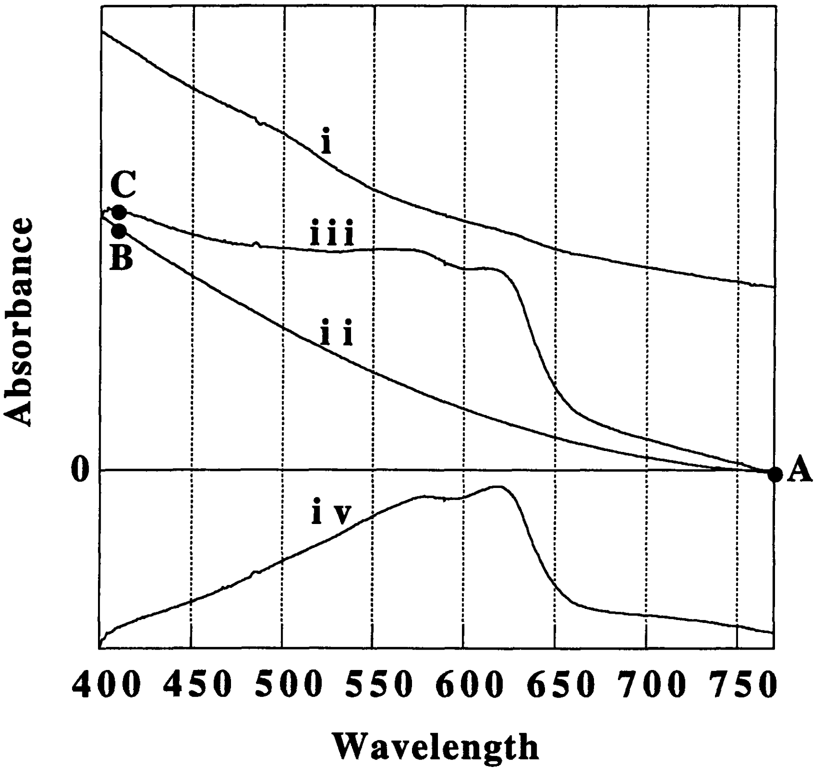


Figure 5.1 Baseline adjustment technique.

In theory, this should give fairly accurate results. However, quantitative problems arise when the polydiacetylene chains become highly disordered. When this happens, the high energy absorption peak trails into the 400 nm range. This means that the absorbance value C which is being used to adjust the relative amount of scattering is artificially high due to the absorption of the polydiacetylene chains. Larger high energy peaks will result in proportionally greater scattering subtraction, resulting in artificially small peak areas. For this reason the data should be considered qualitative, and quantitative peak area measurements cannot be made.

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