Novel Optical Properties of Polyurethane–Diacetylene Segmented Copolymers

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Received February 4, 1986

ABSTRACT: The optical properties of polyurethane–diacetylene segmented copolymers were evaluated. Solid-state cross-polymerization of the diacetylene groups residing in the phase-separated hard domains of the copolymers resulted in materials that absorb strongly in the visible region of the spectrum. The spectral shapes, line widths, and excitation energies of the resultant absorption bands were found to be sensitive to the local environment of the newly formed conjugated backbones in the hard domains. The cross-polymerized copolymers exhibited both reversible and irreversible thermochromic transitions during temperature cycling. Partially cross-polymerized copolymers were used to examine the effects of tensile stress on the microphase structures of these new materials. The polyurethane–diacetylene segmented copolymers exhibit many of the optical properties characteristic of poly(diacetylenes) synthesized from conventional diacetylene monomers.

I. Introduction

In the preceding paper, the synthesis, characterization, and thermal properties of a new class of diacetylene–containing segmented polyurethanes were described with an emphasis on the polyurethane-like properties of these materials. These new polyurethane–diacetylene segmented copolymers are characterized by a two-phase domain morphology comprised of soft and hard segments in which reactive diacetylene groups reside in the hard-segment domains. As a result of this microstructural organization, it is possible to initiate the solid-state cross-polymerization of the diacetylene groups within the hard domains, thereby modifying the thermal, mechanical, and optical properties of the elastomers. This modification proceeds via the formation of a network of poly(diacetylene) chains within the hard domains. Once formed, the conjugated chains impart to the elastomers many of the optical properties exhibited by poly(diacetylenes) synthesized from conventional diacetylene monomers.

In this paper, the optical properties of the elastomers will be examined. In particular, the optical changes taking place during cross-polymerization of the diacetylene groups will be discussed. In addition, a discussion of the temperature- and stress-dependent optical properties of the cross-polymerized polyurethane–diacetylene segmented copolymers will be presented.

II. Experimental Section

The polyurethane–diacetylene segmented copolymers were synthesized with standard two-step solution polymerization techniques for the preparation of segmented polyurethanes. The resultant copolymers consist of soft segments of an elastomeric material (poly(tetramethylene oxide)) (PTMO) alternating with urethane-based hard segments containing the reactive diacetylene group. Phase separation of these incompatible segments results in a two-phase domain morphology as verified by thermal and spectroscopic analysis. The synthesis and structures of these new copolymers were described in the preceding paper. Materials are designated by the monomers used to prepare them. For example, HDI-5,7-1000 refers to an elastomer prepared from HDI (hexamethylene diisocyanate), 5,7-dodecadiyne-1,12-diol, and PTMO of molecular weight 1000.

Visible absorption spectra were recorded with a Cary 17 spectrophotometer. Temperature studies were conducted with a heated precision cell equipped with a Fenwal Model 550 temperature controller (temperature range, 25–200 °C). Absorption spectra were typically recorded after 5 min at a given temperature. To examine variations in the spectra induced by stress, partially cross-polymerized thin films of the elastomers about 0.05 mm thick were stretched uniformly and secured in the elongated state in the spectrophotometer sample window. The strain in the region of the material placed in the spectrophotometer window was measured with gage marks.

Cross-polymerization of the copolymers initiated by exposure to a ^{60}Co γ radiation source or by thermal annealing was carried out with the samples sealed under vacuum or under an inert atmosphere. Cross-polymerization of the copolymers by UV radiation was accomplished in air by exposing the materials to a collection of 15-W GTE Sylvania germicidal lamps (90% of the output energy is at 254 nm). Unless otherwise noted, all films were annealed at 90 °C for 2 h prior to cross-polymerization to develop a high degree of order within the hard domains.

III. Results and Discussion

A. Cross-Polymerization. The properties of the polyurethane–diacetylene segmented copolymers can be dramatically modified by initiating the solid-state cross-polymerization of the diacetylene groups present in their phase-separated hard domains. Cross-polymerization takes place via a 1,4 addition polymerization of the diacetylene groups, producing a network of fully extended conjugated polydiacetylene backbones within the hard domains. The formation of these unsaturated backbones can be readily observed by the dramatic color changes that occur during their creation. Since the electronic transitions of the π-electrons of the backbone occur in the wavelength region of visible light, the materials become highly colored as the conjugated backbone is formed. The electronic transitions of the molecules of the soft segments and the urethane moieties of the hard segments occur at much higher energies and are therefore not observed in the visible portion of the spectrum. Thus, visible spectroscopy can be used to directly probe the electronic states of the poly(diacetylene) backbones formed within the hard domains of the copolymers. It is to be expected that the basic spectral features of the poly(diacetylene) conjugated backbones within the hard domains will be similar to those observed in poly(diacetylenes) obtained from diacetylene monomers.

Figure 1 shows the visible absorption spectra of a thin film of the elastomer HDI-5,7-1000 recorded after different time exposures to 254-nm UV radiation of 3 mW/cm^2 intensity. As can be seen, the copolymer develops an intense absorption band with an absorption maximum at about 655 nm after a 30-min exposure to UV radiation. The copolymer changes from a colorless transparent material to an deep blue material as cross-polymerization initiated by the UV radiation occurs. Exposing the elastomer to UV radiation for more than 30 min resulted in a decrease in the intensity of its absorption band, indicative of UV-radiation-induced degradation of the newly formed conjugated backbones. This degradation process has also

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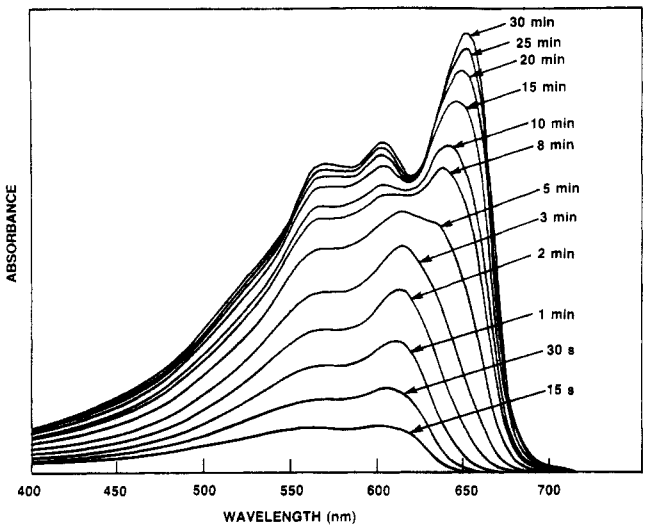

Figure 1. Visible absorption spectra of a thin film of HDI-5,7-1000 recorded after various exposure times to UV radiation.

been observed during the UV-initiated polymerization of diacetylene multilayers[1] and, in some cases,[2] has been used to obtain poly(diacetylenes) with varying molecular weights.

The lowest energy optical transition of the π-electrons of the poly(diacetylene) conjugated backbone has been attributed to exciton creation,[3] which is an excitation believed to be localized over only a few backbone atoms. The expected transition between the valence band and the conduction band (interband transition), on the other hand, has been shown by photoconductivity experiments to occur at much higher energies.[4] The one-dimensional nature of the fully extended poly(diacetylene) backbone also gives rise to distinct vibrational sidebands due to a coupling of the valence electronic levels with the vibrations of the backbone double bond and triple bond.[5] Thus, the intense relatively sharp absorption occurring at about 655 nm in HDI-5,7-1000 can be assigned to exciton formation with the weaker higher energy absorptions at about 602 and 572 nm resulting from a coupling of the exciton with the vibrational modes of the backbone. The shifts of the higher energy absorptions from the excitonic peak of about 1344 and 2215 cm^{-1} are near the values expected for the carbon double and triple bond vibrations of the backbone. The breadth of these absorptions, however, precludes a more accurate determination of these excited-state values. These features are characteristic of the conjugated backbone and are found in most poly(diacetylenes) regardless of their side-group structures. The exact energies of these transitions and their spectral shapes and line widths, however, are determined by the local environment of the backbone, which is sensitive to the structure, organization, and molecular interactions of the side groups.[6] The numerous possible variations in these parameters are responsible for the wide range of excitation energies and profiles observed for different poly(diacetylenes).

Examination of the spectra in Figure 1 reveals that the initially formed absorption band centered at about 615 nm is suddenly overcome by the development of a red-shifted absorption band after about 5-min exposure to UV radiation. The absorption maximum in the initially formed band continuously shifts to lower energies as it develops, as does the maximum in the red-shifted absorption band. The final red-shifted absorption band, however, is not the result of a continuous shifting of the initially formed absorption band which eventually becomes buried under the final absorption band.

There are at least two possible explanations for this behavior. First, cross-polymerization may result in a reaction-induced phase transition within the hard domains whereby the environment of the conjugated backbone is modified as the transformation from diacetylene to poly(diacetylene) occurs. This modification of the chain environment may result from the spontaneous rearrangement of the side groups of the newly formed conjugated backbone as has been described by Enkelmann[7] for certain poly(diacetylenes). The second possibility is that cross-polymerization proceeds as a homogeneous single-phase reaction. In this case, the changes observed reflect the transition from a macromonomer-dominated solid solution in which isolated poly(diacetylene) chains are accommodated within the macromonomer matrix (within the hard domains) to a poly(diacetylene)-dominated solid solution in which the remaining macromonomer is now confined within the newly formed poly(diacetylene) matrix. The well-characterized poly(diacetylene) polyPTS obtained by the polymerization of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate) is an example of a material formed via a homogeneous single-phase polymerization.[8] The polymerization is characterized by an autocatalytic effect in which the polymerization rate increases dramatically after about 10% polymer conversion.[9] The lowest energy optical transition of polyPTS originally at about 572 nm is overcome by a red-shifted transition centered at about 615 nm during this sudden change in the polymerization rate.[8,10] In addition, it has been shown that the polymer chains are initially expanded by the lattice mismatch needed to maintain a single-phase homogeneous polymerization and that this backbone distortion is relieved as polymerization proceeds.[8] The polymer chain length is also affected by this transition from a monomer-dominated to a polymer-dominated solid solution due to the differences in lattice strain experienced by the growing polymer chains under each condition. The latter state has been shown to produce longer chains relative to the former state.[11]

The optical behavior of HDI-5,7-1000 during cross-polymerization by UV radiation is clearly very similar to that of PTS during polymerization. The difference in energy between the initially formed absorption band and the final absorption band are about the same for both materials. In addition, the continuous shifting of the absorption bands of HDI-5,7-1000 to lower energies as cross-polymerization proceeds is consistent with the concept of a single-phase polymerization proceeding with continuously changing lattice parameters. Preliminary results from resonance Raman spectroscopy (RRS) studies[12] show that, as in the case of PTS, the frequencies of the backbone vibrations shift to higher energies during cross-polymerization. Thus, it is reasonable to conclude that the spectral changes observed during the cross-polymerization of HDI-5,7-1000 are a manifestation of a homogeneous single-phase polymerization process. The autocatalytic effect observed during the thermal polymerization of PTS, however, was not detected during the UV-initiated cross-polymerization of HDI-5,7-1000. This is not surprising since it has been shown by Chance and Patel[9] that such effects are difficult to observe due to the inhomogeneity of UV-initiated polymerizations.

Figure 2 shows the visible absorption spectra of a thin film of the elastomer HDI-2,4-1000 recorded as a function of varying exposure times to UV radiation. In this case, a single absorption band develops with a absorption maximum centered at about 565 nm after 12 min of UV irradiation. Unlike HDI-5,7-1000, the maximum of the absorption band continuously shifts to higher energies as

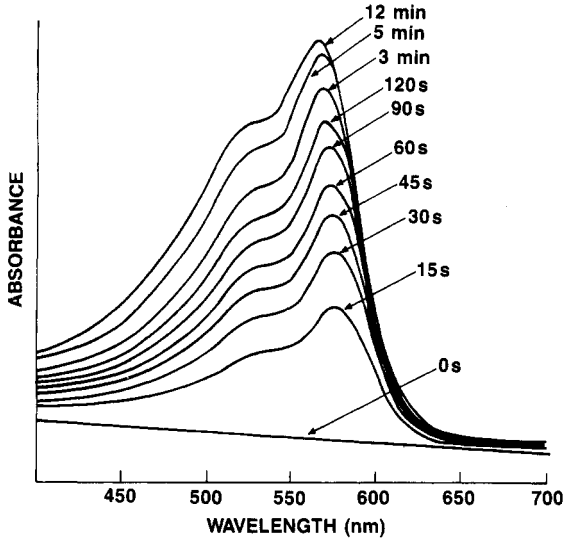

Figure 2. Visible absorption spectra of a thin film of HDI-2,4-1000 recorded after various exposure times to UV radiation.

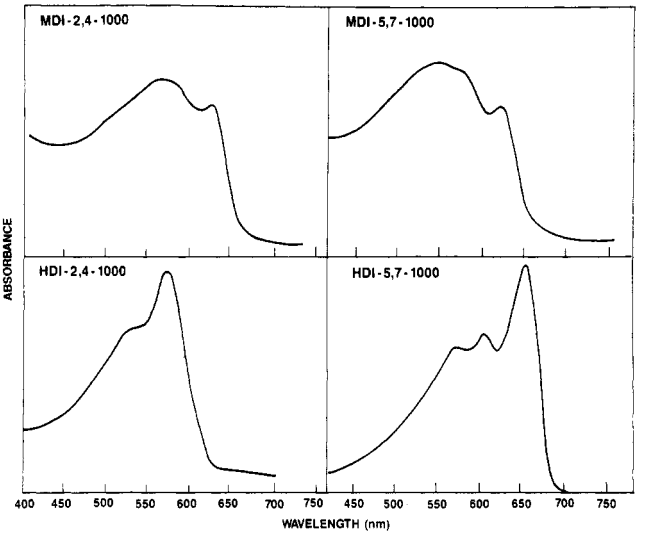

Figure 3. Visible absorption spectra of the polyurethane–diacetylene segmented copolymers recorded after cross-polymerization.

it is formed. During this process, the copolymer changes from a transparent colorless material to a deep red material. If it is again assumed that cross-polymerization takes place in a single phase via the formation of a solid solution of the poly(diacetylene) chains in the macromonomer hard-domain matrix, then the slight shift to higher energy of the absorption maximum with increasing UV-irradiation times can be attributed to a small expansion of the poly(diacetylene) chains during polymerization. The shift to higher energies implies that the initially formed conjugated chains are slightly contracted in the solid solution due to a lattice mismatch between the macromonomer and the conjugated polymer and that this mismatch is reduced as more conjugated chains are formed and the appropriate lattice dimensions expand. This is contrast to HDI-5,7-1000, in which the conjugated chains must be initially expanded in the solid solution to account for the shifts to lower energies that occur during cross-polymerization. As can be seen in Figure 2, the initially formed absorption band of HDI-2,4-1000 is retained during polymerization. However, if a sample of partially cross-polymerized HDI-2,4-1000 is cooled to liquid nitrogen temperatures, the elastomer reversibly changes from red to blue, indicating a significant red shift in its absorption band. Fully cross-polymerized HDI-2,4-1000, on the other hand, remains red on cooling to liquid nitrogen temperatures. This can be explained again by using the concept of a solid solution. For the partially cross-polymerized material, the poly(diacetylene) chains are confined within the macromonomer matrix. Upon cooling, the matrix contracts and the fully extended conjugated chains are also forced to contract, producing a shift in the absorption band to lower energies and hence the change from red to blue. Once fully cross-polymerized, thermal contraction of the hard domains is controlled by the more rigid poly(diacetylene) network, rendering them less sensitive to temperature changes. This clearly demonstrates the strong influence that the molecular environment of the conjugated chains has on the optical properties of these materials.

The visible absorption spectra of the elastomers after cross-polymerization are shown in Figure 3. In the case of the HDI-based copolymers, cross-polymerization was initiated by UV radiation. For the MDI-based elastomers, however, cross-polymerization was accomplished either by γ irradiation (MDI-5,7-1000) or by thermal annealing at 90 °C in nitrogen (MDI-2,4-1000). This was necessary since solution-cast thin films or compression-molded thin films of the MDI-based copolymers were insensitive to UV radiation. In fact, UV-initiated cross-polymerization of the MDI-based copolymers could only be accomplished with the as-prepared powders, which were only slightly UV active. This appears to be due to a competitive absorption of the UV radiation by the MDI groups which inhibits polymerization of the diacetylene groups. Quenching of the diacetylene excited state by the MDI units is also a possible reason for the insensitivity to UV radiation. The HDI-based copolymers, on the other hand, were highly sensitive to both UV and γ radiation.

Unlike the HDI-based copolymers, which exhibit fairly well-defined absorption bands, the MDI-based copolymers exhibit broad absorptions extending into the UV region of the spectrum, characteristic of a highly disordered poly(diacetylene) with a broad distribution of backbone distortions. In the previous paper, it was shown that the HDI-based copolymers are characterized by crystalline hard domains, with HDI-5,7-1000 exhibiting the most extensive hard-segment crystallinity. The hard domains of the MDI-based copolymers, on the other hand, were found to be essentially amorphous. These variations in hard-segment ordering are clearly reflected in the optical spectra obtained for the different elastomers. Since cross-polymerization is best facilitated in a crystalline organization in which the diacetylene groups are stacked in the correct geometric arrangement to undergo the 1,4 addition polymerization,[7] the HDI-based copolymers are best suited for this reaction. Hard-segment crystallinity in HDI-5,7-1000 is, for the most part, retained during cross-polymerization (as would be expected for a topochemical polymerization process), resulting in the relatively sharper optical features observed for this material. In the case of the MDI-based copolymers, cross-polymerization can only occur in regions in which the diacetylene groups at least have sufficient short-range order to undergo reaction with neighboring diacetylenes. Cross-polymerization within this liquid-crystalline type arrangement produces a highly disordered final hard-domain structure and the resultant broad absorption features observed in the optical spectra.

B. Effects of Temperature. It is clear from the previous discussion that the molecular structure and organization of the pendant groups of the poly(diacetylene) conjugated backbone have a profound effect on the optical properties of these materials. This effect is illustrated by

a comparison of the optical spectra of the HDI-based copolymers. HDI-2,4-1000 has its lowest energy optical transition at about 565 nm and appears red whereas HDI-5,7-1000 exhibits this transition at about 655 nm and appears blue. The structures of these two materials vary simply by the number of methylene groups connecting the diacetylene functionality to the urethane linkage of the HDI residue. This small difference in structure modifies the packing of the macromonomer chains within the hard domains and also results in variations in the inter- and intramolecular interactions of these chains when they become the side groups of the poly(diacetylene) backbone after cross-polymerization. The conjugated backbone is sensitive to these variations in the side-group organization since it is forced to comply with the dimensional constraints imposed on it by the side groups. This presumably produces a distortion of the backbone resulting from the static deformation of its bond lengths and/or bond angles peculiar to the particular side-group organization. The exact structural changes of the backbone induced by these distortions are still highly debated; however, the wide variations in excitation energies of the backbone π-electrons that result from these distortions are well documented in the literature.[13]

Since the molecular environment of the poly(diacetylene) chains can be modified by thermal means, it is possible to further modify the optical properties of the poly(diacetylenes) by changes in temperature. At least two different situations can be identified that would be expected to produce changes in the optical spectrum of a poly(diacetylene). First, if the poly(diacetylene) chains are confined within a solid solution of its monomer, then dramatic changes in the energy of the lowest energy optical transition could be expected with temperature change if the monomer undergoes a thermally induced phase transition or has a high coefficient of thermal expansion. In this case, the conjugated chains are simply responding to the changing molecular environment of the monomer. An example of this type of behavior has already been given for partially cross-polymerized HDI-2,4-1000, which changes from red to blue on cooling to liquid nitrogen temperatures. It is also possible to destroy the solid solution by heating to the melting temperature of the monomer whereby phase separation ensues and the poly(diacetylene) chains are free to adopt their unperturbed equilibrium dimensions determined by their side-group organization. Many of the surface-active poly(diacetylenes) exhibit this type of irreversible phase separation on heating, which is accompanied by a blue to red change.[1,14] The second possibility is that a fully polymerized poly(diacetylene) undergoes a thermally induced phase transition. This can take the form of an order–disorder transition as would occur during the melting of a crystalline polymer or during the thermal disruption of liquid crystalline regions of a less ordered polymer. Alternatively, the conjugated polymer could undergo a crystallographic phase transition with the concomitant reorganization of its side groups, producing the expected optical changes. The thermochromic behavior of poly4BCMU films in which the side group is $-(CH_2)_4OC(O)NHCH_2C(O)OC_4H_9$ has been attributed to the former phenomenon.[15] An example of the latter phenomenon has not been unambiguously demonstrated due to the difficulty of obtaining acceptable X-ray structural information for both the high- and low-temperature phases of certain thermochromic poly(diacetylenes). It has been proposed[16] that polyETCD, in which the side-group structure is $-(CH_2)_4OC(O)NHC_2H_5$, may be an example of a poly(diacetylene)that exhibits a crystallographic phase transition at elevated temperatures. In the lower temperature regime, however, polyPTS has been shown to undergo a second-order phase transition that results in a splitting of its absorption bands due the presence of two inequivalent polymer chains in the low-temperature unit cell.[7]

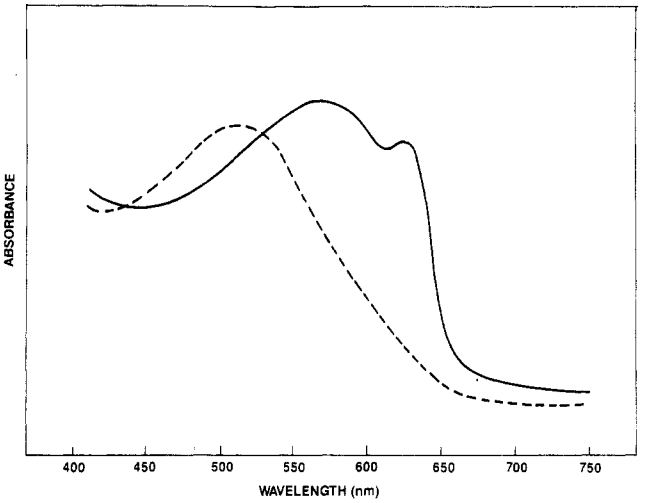

Figure 4. Visible absorption spectra of a thin film of cross-polymerized MDI-2,4-1000 recorded as prepared (solid line) and after heating to 120 °C and cooling to room temperature (dashed line).

The absorption spectra of the elastomer MDI-2,4-1000 at room temperature and after heating to 120 °C and cooling to room temperature are shown in Figure 4. In this case, an irreversible shift of the absorption band to higher energies has occurred during temperature cycling. The resultant broad featureless absorption band is similar to that exhibited by a soluble poly(diacetylene) when it is dissolved in a thermodynamically "good" solvent.[17] The small amount of structure present in the original absorption band is completely lost during this irreversible transition. Thus, this is an example of a thermally induced disordering process in which the poly(diacetylene) chains originally organized in regions of limited long-range order are completely disordered upon heating. The final state of disorder is the same as in the solution state in which the chains adopt a broad distribution of backbone distortions with limited interchain interactions occurring due to the inherent disorder of the system.[17]

In contrast to the behavior of MDI-2,4-1000, in which the color changes observed during heating are the result of a disordering process, the spectral changes that occur during the heating of HDI-5,7-1000 appear to take place without incurring a significant amount of disorder in the system. The changes observed can be seen in Figure 5 which shows the visible absorption spectra of a thin film of cross-polymerized (30-min exposure to 254-nm UV radiation of 3 mW/cm^2 intensity) HDI-5,7-1000 recorded as a function of temperature (film cast from a toluene solution). These spectra show that HDI-5,7-1000 exhibits a thermochromic transition with an onset at about 100 °C. The elastomer changes from blue to red to yellow during this transition. The initial absorption band at 655 nm continuously shifts to higher energies with increasing temperature due to the effects of thermal expansion of the polymer matrix on the conjugated backbone until about 90 °C at which temperature a new absorption band at about 510 nm begins to evolve, eventually replacing the original absorption band at higher temperatures. Also note that the high-temperature absorption band retains the sharp features characteristic of a highly ordered poly(di-

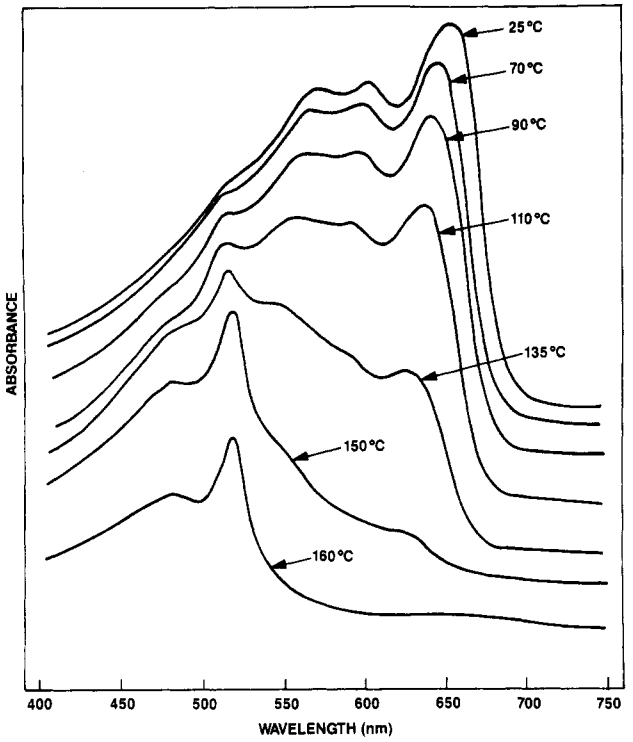

Figure 5. Visible absorption spectra of a thin film of cross-polymerized HDI-5,7-1000 (prepared by casting from a toluene solution) recorded as a function of temperature (spectra have been arbitrarily offset along the absorbance axis for clarity).

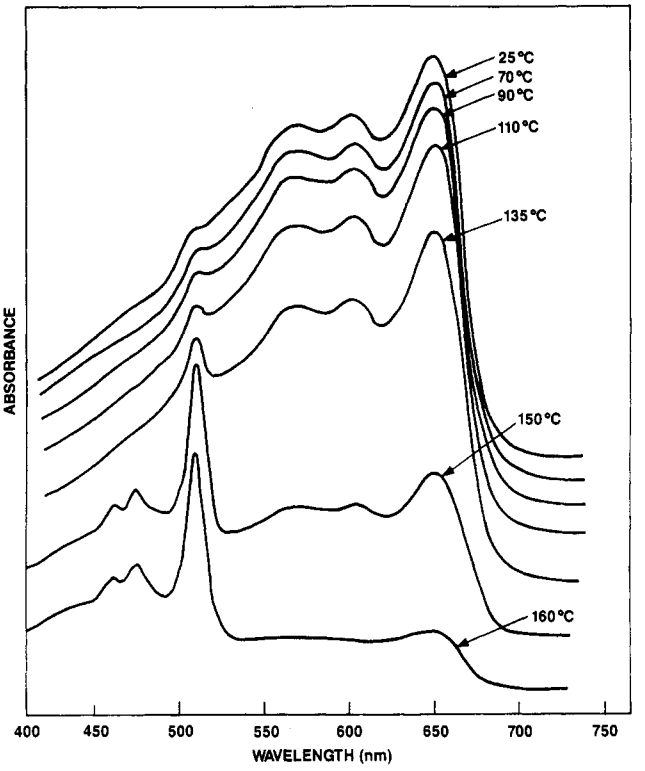

Figure 6. Visible absorption spectra of a thin film of cross-polymerized HDI-5,7-1000 recorded at room temperature after heating to the indicated temperatures (spectra have been arbitrarily offset along the absorption axis for clarity).

acetylene) matrix although it does exhibit less detail due to the effects of line broadening at high temperatures.

To determine the reversibility of this transition, room temperature spectra were recorded after heating a sample to each temperature evaluated during the heating experiment. These spectra are presented in Figure 6. As can be seen, the transition is nearly reversible up to about 130 °C but becomes permantely irreversible after this point. However, even after heating to 160 °C, at which temperature there is no indication of the original blue phase, cooling to room temperature regenerates a small but discernible absorption in the blue-phase region of the spectrum. Heating to temperatures between 130 and 160 °C results in a greater recovery of the 655-nm absorption band, as can be seen for the sample heated to 150 °C and cooled to room temperature. In the cases where the yellow phase reversed to the blue phase, no significant hysteresis effects were observed during the cooling runs. The blue phase must therefore be a metastable state that has a slightly higher energy than the more thermodynamically stable yellow phase. Hence, sufficient energy is available at room temperature to overcome the small energy barrier between these two states and reform a small amount of the initial blue phase. It is also possible that the reverse transition from the higher temperature phase to the blue phase is kinetically controlled, being possible only when some of the blue phase is still present to act as nucleation centers during the reverse phase transition. The thermochromic transition of HDI-5,7-1000, however, is clearly irreversible.

The thermochromic behavior of HDI-5,7-100 was found to be influenced by the degree of hard-segment order of the sample under investigation. By varying the solvent system used to dissolve the elastomer and the film casting and annealing conditions, it was possible to obtain materials with varying degrees of hard-segment crystallinity and/or crystallite size as indicated by the intensity and breadth of the hard-segment crystalline diffraction peak in the wide-angle X-ray diffraction pattern of the films. Films cast from toluene at about 50 °C and subsequently annealed at 90 °C for 2 h were found to exhibit the most intense diffraction peaks, whereas films cast at room temperature from DMF solutions or from toluene/THF solutions exhibited much less intense diffraction peaks. The resultant spectral features and temperature-dependent optical properties of these latter materials were quite different than those of the samples cast from the toluene solutions. For example, Figure 7 displays the optical spectra of a thin film of HDI-5,7-1000 cast from a 50/50 vol % THF/toluene solution recorded as a function of temperature. It is immediately apparent that the room temperature spectrum of this material exhibits broader features and a stronger absorbance in the shorter wavelength region (around 570 nm) than the same material cast from a toluene solution (representative sample in Figures 5 and 6). In addition, the onset of the thermochromic transition and the obtainment of the final high-temperature phase occur about 20 °C lower than in the same material cast from the toluene solution. Thus, the greater degree of disorder present in the hard domains of this material produces the broader absorption bands and results in a depression of the thermochromic transition temperature.

Note that the room temperature spectrum of the newly formed yellow phase (see spectrum in Figure 6 recorded after heating to 160 °C) exhibits a very narrow well-defined absorption band at about 511 nm with equally sharp higher energy vibrational sidebands at 475 and 462 nm. The shifts of these latter bands of 1502 and 2095 cm^{-1} correspond to the stretching frequencies of the carbon double bond and triple bond vibrations of the backbone. It is worth noting that, to the authors knowledge, this is the first example of a fully polymerized poly(diacetylene) that exhibits such well-defined narrow absorption bands in the wavelength region below 550 nm, which is usually domi-

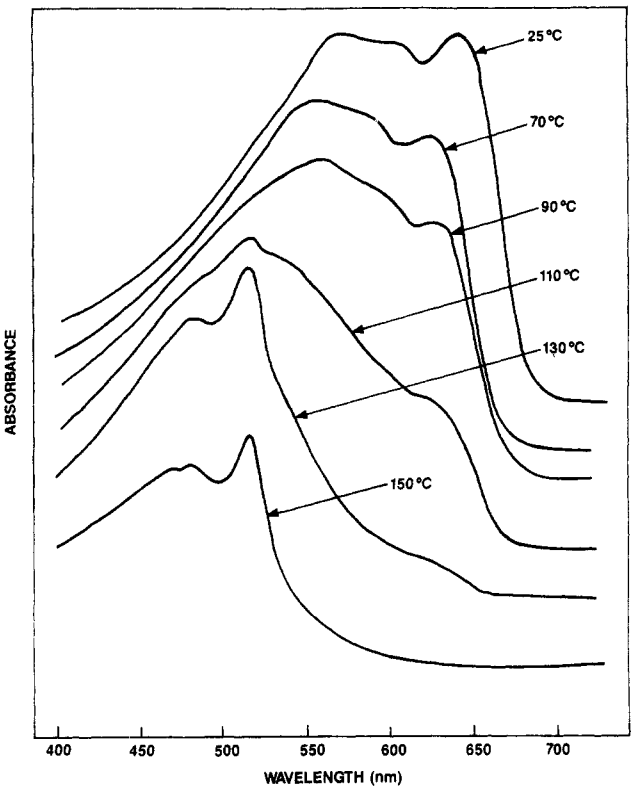

Figure 7. Visible absorption spectra of a thin film of cross-polymerized HDI-5,7-1000 (prepared by casting from a THF/toluene solution) recorded as a function of temperature (spectra have been arbitrarily offset along the absorbance axis for clarity).

nated by broad absorptions due to disorder. It has been proposed by some researchers[16] that the thermochromic transitions exhibited by some of the urethane-substituted poly(diacetylenes) result from a change in the conjugated backbone structure from acetylene-like (=RCC≡CCR=) to butatriene-like (RC=C=C=CR). This transition is believed to be a consequence of the change in backbone distortion resulting from the reorganization of the side-group structures taking place during the transition from the low-temperature phase to the high-temperature phase.[18] The acetylenic form is said to be characterized by highly structured absorption bands with excitation energies in the wavelength region of about 645 nm. The butatrienic form, on the other hand, is said to exhibit less structured absorption bands with excitation energies in the wavelength region of about 550 nm.[19] The narrow well-structured absorption bands exhibited by the yellow phase of HDI-5,7-1000 are similar in band shape and line width to the absorption bands exhibited by poly(diacetylenes) such as polyPTS and polyDCH, which have been designated as the prototype model systems for a poly(diacetylene) with an acetylenic-type backbone structure. The excitation energy of its lowest energy optical transition, however, is in the wavelength region proposed to be characteristic of the butatrienic form of the backbone. The absence of structure in the high-temperature phase of HDI-5,7-1000 (at 160 °C) can be seen here as a simple consequence of thermally induced line broadening which is reduced as the newly formed high-temperature phase is cooled to room temperature. The spectral characteristics of this new phase indicate that the acetylene-like backbone structure is retained during the thermochromic phase transition.

The original assignment of these spectral characteristics to the different forms of the backbone was based on X-ray crystallography data obtained on poly(diacetylenes) that were believed to be representative of the two extreme backbones. The prime example given of a poly(diacetylene) with a butatriene-like backbone was polyTCDU.[20] However, the interpretation of the X-ray data taken for polyTCDU is still highly debated.[7] In addition, recent results obtained from solid-state ^{13}C NMR experiments[21] indicate that the backbone structure of polyTCDU is not butatrienic but is best represented by the acetylene-like structure. Thus, it appears that a transition between these two backbone forms is an unlikely explanation for the dramatic spectral changes that take place during the thermochromic transitions of urethane-substituted poly(diacetylenes). Therefore, the dramatic color changes that occur are most likely the result of varying distortions of the acetylene-like backbone.

In the preceding paper it was shown by FTIR temperature studies that the thermochromic transition of HDI-5,7-1000 was not the result of an order–disorder transition involving thermal disruption of the interurethane hydrogen bonded network of the hard domains. In fact, the level of hard-domain crystallinity was, for the most part, retained after conversion of the blue phase to the yellow phase. Although no major change in the extent of hydrogen bonding was detected during the transition, a distinct slope discontinuity in the temperature–absorbance curves was found to occur at the temperature of the thermochromic transition. The change in slope was attributed to an abrupt change in the thermal expansion coefficient of HDI-5,7-1000 occurring during the thermochromic phase transition. This implies that either a crystallographic phase transition has taken place or that the local environment of the urethane groups has undergone a sudden change. Similar temperature-dependent FTIR experiments performed on the thermochromic poly(diacetylene) polyETCD also revealed[12] that the thermochromic transition occurs with retention of hydrogen bonds and is characterized by a slope change in the temperature–absorbance curves. Thus, the origin of thermochromism in HDI-5,7-1000 and polyETCD appears to be the same. The exact organizational changes that take place during the thermochromic transition of either of these materials are still unknown. However, it is clear from this work that both their high-temperature and room temperature phases are fully hydrogen bonded organizations. It is possible that to maintain this complete association of the urethane groups in the lattice during the thermochromic transition, the hydrocarbon segments of the side groups nearest the backbone must undergo a certain amount of twisting out of their room temperature conformations. This conformational rearrangement of the methylene groups could occur without disturbing the hydrogen bonds and would result in a distortion of the bond angles of the conjugated backbone and hence the color changes. A complete crystallographic phase transition need not be the cause of these conformational changes, as it is possible that a local reorganization or disordering of the hydrocarbon segments could occur without major changes in the packing of the side groups. It is interesting to note that the thermochromic transitions of some of the urethane-substituted poly(diacetylenes) occur at the same temperatures as the melting of their monomers. This suggests a possible role of residual unreacted monomer in the thermochromic activity of these materials. Clearly, more work is needed in this area to establish the exact mechanisms and structural changes responsible for these interesting transitions.

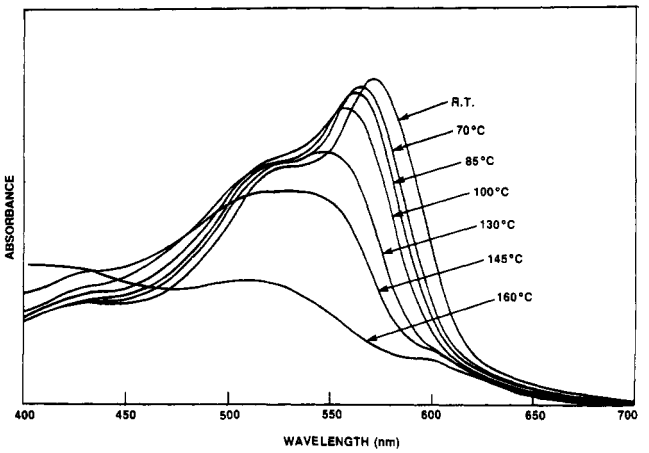

Figure 8. Visible absorption spectra of a thin film of cross-polymerized HDI-2,4-1000 recorded as a function of temperature.

Evidence that the slope discontinuity observed in the temperature–absorbance data of HDI-5,7-1000 and polyETCD is related to the thermochromic transition of these materials is provided by results obtained on cross-polymerized HDI-2,4-1000. As discussed in the previous paper, this material does not exhibit any changes in slope in its temperature–absorbance curves. Therefore, HDI-2,4-1000 should not display the spectral changes characteristic of a thermochromic transition. This is the case as can be seen in Figure 8, which shows the visible absorption spectra of cross-polymerized HDI-2,4-1000 recorded as a function of temperature. The absorption band shifts to higher energies with increasing temperature due to the effects of thermal expansion but never develops a new absorption band as was the case for HDI-5,7-1000. Instead, as the material is heated to higher temperatures, the excitonic structure of the absorption band is lost, and at very high temperatures, only a broad absorption extending into the UV portion of the spectrum remains. The room temperature spectra of cross-polymerized HDI-2,4-1000 recorded after heating to various temperatures show that these changes are essentially reversible up to about 100 °C but after heating to higher temperatures become irreversible as thermally induced disorder of the hard domains takes place.

C. Effects of Applied Stress. The ability of the diacetylene elastomers to undergo large tensile elongations allows one the opportunity to readily examine the influence of stress on the electronic states of the poly(diacetylene) conjugated backbones present in the hard domains. Also, since the electronic states of the conjugated backbone are sensitive to the molecular environment of the hard domains, changes in the organization of the hard domains induced by tensile elongation will result in changes in the optical spectrum of the elastomer. For partially cross-polymerized elastomers in which a few conjugated chains are randomly dispersed and isolated within the hard-domain matrix (characteristic of the solid-solution state), these changes will reflect the effects of strain on the structural integrity of the as-formed hard-segment domains. In this case, a low concentration of matrix-isolated poly(diacetylene) chains ensures that the modulus and rigidity of the hard domains are not significantly modified upon cross-polymerization, and hence their presence can be used as an internal probe to monitor such phenomena as stress-induced hard-domain disruption. This section will describe the influence of stress on the optical properties of partially cross-polymerized HDI-based polyurethane–diacetylene copolymers. The large absorption coefficient of the poly(diacetylene) backbone makes it possible to optically detect this chromophore at the low concentrations found in partially cross-polymerized materials.

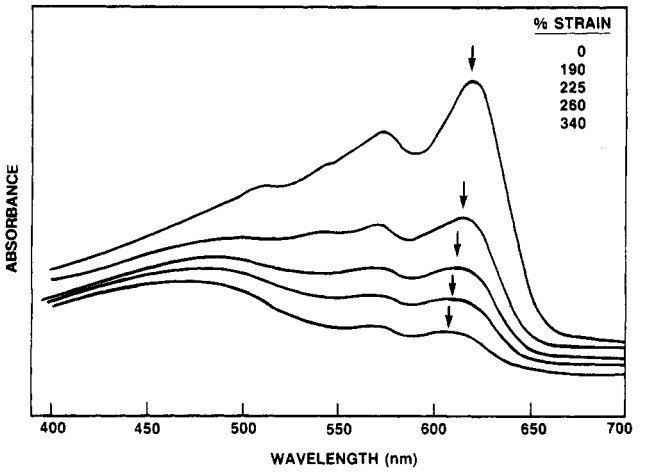

Figure 9. Visible absorption spectra of a thin film of partially cross-polymerized HDI-5,7-1000 recorded at the indicated levels of strain (top spectrum was recorded in the unstrained state).

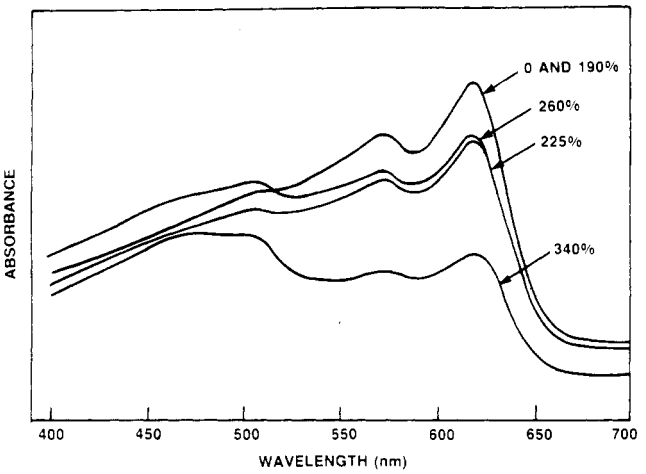

Figure 10. Visible absorption spectra of a thin film of partially cross-polymerized HDI-5,7-1000 recorded after stretching to the indicated levels of strain and relaxing to the unstrained state.

The visible absorption spectra of a thin film of partially cross-polymerized (30-s exposure to 254-nm UV light of 1 mW/cm^2 intensity) HDI-5,7-1000 recorded as a function of strain are found in Figure 9. The application of a macroscopic tensile stress to this material results in a change in the position and shape of its absorption band. As the elastomer is stretched, the peak of the lowest energy optical transition shifts to higher energies and decreases in intensity relative to the higher energy absorptions. In addition, a broad absorption centered at about 475 nm develops when the strain exceeds about 200%. Also note that the absorbance of the film throughout the entire visible range decreases as the film becomes thinner on stretching. The occurrence of the broad ill-defined absorption at high strains indicates that disordering has taken place within the hard domains during mechanical deformation of the copolymer. Figure 10 shows the spectra of the same film after it has been stretched to the indicated levels and relaxed to an unstrained state. Here it can be seen that below 200% strain, the process is completely reversible. Above this level, however, the disorder introduced on stretching is retained, as evidenced by the persistence of the broad absorbance centered at about 475 nm. However, a significant portion of the original absorption band is recovered even after a strain of 340%.

It has been proposed[22,23] by a number of researchers that the initial response of a segmented polyurethane to a tensile strain is a preferred orientation of the microphase structure occurring as the soft segments become extended under the applied load and exert a stress on the hard-segment domains. During this process, the structural integrity of the hard domains is essentially unchanged. Stretching to higher levels of strain, on the other hand, is believed to result in a disruption of the hard domains, eventually leading to their irreversible breakup into smaller entities. This latter effect is believed to be responsible for the stress softening and mechanical hysteresis effects frequently observed in these materials. The lack of reversibility of this deformation process is to be expected since, unlike the soft segments, in which recovery from elongation is driven by entropy, there are no strong restoring forces operating within the hard domains.

Given the above scenario, the results of the visible spectroscopy experiments can be interpreted as follows. During the initial elongation of the elastomer, up to about 200% strain, the hard domains experience a wide range of local stresses resulting from the random extension and orientation of soft-segment chains in the direction of the applied stress. This results in a repositioning of the hard domains as has been proposed by Bonart[22] which occurs without significant permanent disruption of the hard-domain organization. The optical manifestation of this process is a slight shift of the absorption band to higher energies, which is completely recovered when the elastomer is relaxed to an unstrained state. In this case, the varying tensile and shear forces acting on the hard domains are transmitted to the conjugated backbone via its side-group atoms (which in this case include the soft-segment atoms), producing a strain-induced deviation of the backbone bond angles and bond lengths from their equilibrium positions. Similar shifts to higher energies of the absorption edge of the poly(diacetylene) polyPTS have been reported by Batchelder and Bloor[24] for single-crystal samples subjected to a tensile strain. Due to the single-crystal nature of their samples and a knowledge of the chain axis direction relative to the applied stress, they were able to relate these shifts to changes in the separation between carbon atoms of the conjugated backbone. When stretched beyond 200%, the hard domains begin to disorganize, as evidenced by the development of a increased absorbance at higher energies, indicative of the presence of highly disordered poly(diacetylene) chains. Since this is an irreversible process, the disorder is retained on relaxation of the copolymer. At levels of strain above 300%, some of the hard domains begin to break apart, giving rise to the large permanently created absorption band centered at about 475 nm. These irreversible processes are responsible for the permanent set of the elastomer that occurs above 200% strain and can be seen in the absorption data as a reduction in the overall absorbance of the material after relaxation to the unstrained state.

To summarize, the changes in the absorption spectrum of partially cross-polymerized HDI-5,7-1000 taking place during tensile elongation can be attributed to two separate processes. The first process is reversible and involves a temporary distortion of the poly(diacetylene) backbone in response to the varying tensile and shear forces transmitted to it through the soft segments. This process takes place without any significant disruption of the organization within the hard domains. The changes observed as a result of this process are a shifting of the lowest energy optical transition to higher energies and a pronounced reduction of the intensity of this excitonic feature relative to the other higher energy absorptions of the backbone. The fact that a significant portion of the original absorption band is recovered upon relaxation from strains in excess of 300% indicates that the structural integrity of many of the hard domains is retained even at these high strain levels. This is not surprising since many of the hard domains will not experience the levels of stress needed for their disruption due to the complex morphological arrangement of the two phases within the copolymer, resulting in varying levels of microscopic stress throughout the material. The second process, which can only be detected above a strain of 200%, involves the plastic deformation of the hard-segment domains and their concomitant disorganization. This process is irreversible, resulting in the occurrence of a blue-shifted broad absorption band in the visible portion of the spectrum and a macroscopic plastic deformation of the film.

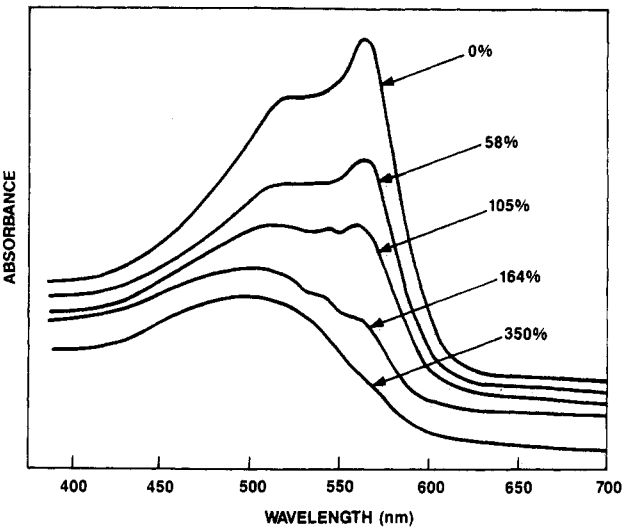

Figure 11. Visible absorption spectra of a thin film of partially cross-polymerized HDI-2,4-1000 recorded at the indicated levels of strain.

Similar changes were observed when a partially cross-polymerized film of HDI-2,4-1000 was stretched, as displayed in Figure 11. Again it can be seen that as the material is subjected to a tensile elongation, the lowest energy optical transition shifts to higher energies and decreases in intensity at a faster rate relative to the higher energy shoulder of the original absorption band. For this sample, the process was found to be nearly reversible up to about 110% strain. Beyond this level, permanent disruption of the hard-domain organization takes place and the material develops a featureless absorption band that continuously moves to higher energies as the film is stretched to higher levels and relaxed.

In order to examine the influence of the extent of partial cross-polymerization on these changes, a similarly prepared film of the same thickness was cross-polymerized to roughly twice the absorbance of the previously discussed film, i.e., to a greater extent of partial cross-polymerization. The spectra recorded of this film in the elongated state and after relaxation from this state are found in Figures 12 and 13, respectively. In this case, it can be seen that higher levels of strain are required to disorder the hard domains and produce the same spectral changes found at lower strains in the material with a lesser extent of cross-polymerization. For example, compare the spectrum of Figure 11 at 105% strain with the spectrum of Figure 12 at 223% strain. In addition, the material cross-polymerized to a greater extent retains a portion of the excitonic feature of its absorption band even after relax-

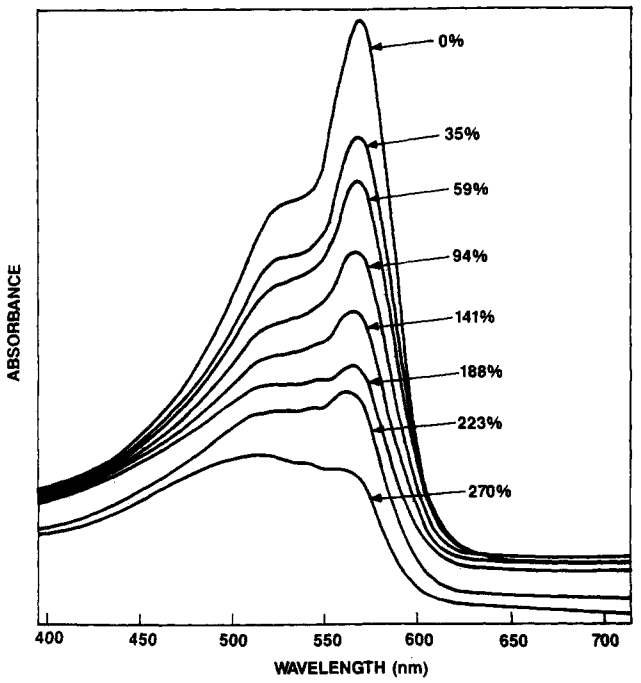

Figure 12. Visible absorption spectra of a thin film of partially cross-polymerized (increased extent of cross-polymerization) HDI-2,4-1000 recorded at the indicated levels of strain.

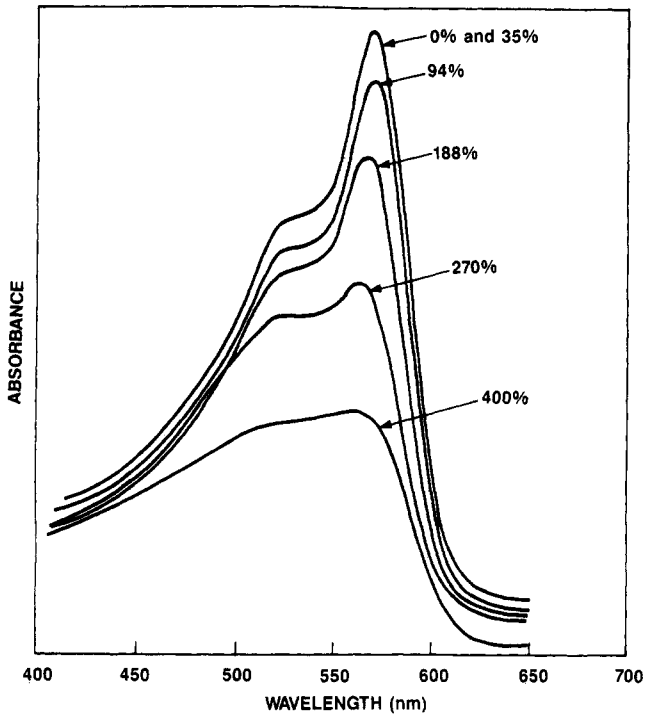

Figure 13. Visible absorption spectra of a thin film of partially cross-polymerized (increased extent of cross-polymerization) HDI-2,4-1000 recorded after stretching to the indicated levels of strain and relaxing to the unstrained state.

ation from a strain of 270%, at which point this feature is barely detectable. It is interesting to note, however, that the position of this peak has slightly blue-shifted as a result of stretching, which is in contrast to HDI-5,7-1000, in which the energy of the excitonic peak is the same after relaxation from the higher strains. For the film cross-polymerized to a lesser extent, this feature is completely lost after relaxation from a strain of 164%. Thus, the optical changes observed during the stretching of the more cross-polymerized film are reversible to higher strain levels. The different strain–optical behaviors of the HDI-2,4-1000 samples can be attributed to a change in hard-domain rigidity brought about by an increase in the extent of partial cross-polymerization of the diacetylene groups present in the hard segments. It is to be expected that as the extent of cross-polymerization increases, the modulus and rigidity of the hard domains will increase as the poly(diacetylene) network structure begins to dominate these properties. The formation of poly(diacetylene) chains and hence covalent cross-links between the segments within the hard domains inhibits chain slippage, thereby increasing the structural integrity of the hard domains. Thus, the hard domains of the more cross-polymerized elastomer are less deformable, and higher levels of stress are required to induce their disruption. This becomes very apparent if thin films of the HDI-based elastomers are completely cross-polymerized, rendering the hard domains highly rigid and thermally infusible, thereby significantly lowering the strain-to-failure of the elastomers and their degree of residual deformation after stretching.

IV. Conclusions and Summary

The optical properties of polyurethane–diacetylene segmented copolymers can be dramatically modified by initiating the solid-state cross-polymerization of the diacetylene groups present in their phase-separated hard domains. During cross-polymerization, the elastomers develop intense absorption bands in the visible portion of the spectrum, changing their appearance from transparent colorless materials to deep blue or red materials as poly(diacetylene) chains are formed within the hard domains. The spectral shapes, line widths, and excitation energies of the resultant absorption bands are highly sensitive to the local environment of the newly formed conjugated backbones. The HDI-based copolymers that are characterized by crystalline hard domains exhibited relatively narrow well-defined absorption bands whereas the MDI-based copolymers with essentially amorphous hard-domain organization exhibited broad ill-defined absorptions. The frequency shifts of the absorption bands observed during cross-polymerization of the HDI-based elastomers were attributed to the effects of solid-solution formation within the hard domains.

The cross-polymerized copolymers exhibited both reversible and irreversible thermochromic transitions during temperature cycling. An irreversible thermochromic transition exhibited by the elastomer MDI-2,4-1000 was attributed to a order–disorder process involving extensive disordering of the poly(diacetylene) chains present in the hard domains. Cross-polymerized HDI-5,7-1000, on the other hand, displayed a thermochromic transition that is partially reversible up to about 130 °C but becomes irreversible when heated beyond this temperature. This transition takes place without disruption of the hydrogen bonded network of the hard domains and results in a new narrow line width absorption band with well-defined vibronic sidebands. The features of the newly formed absorption band are characteristic of an acetylene-like backbone, indicating that an acetylenic-to-butatrienic backbone transformation does not take place during the thermochromic transition. The temperature-dependent optical behavior of HDI-2,4-1000 verified that the discontinuity in slope observed in the temperature–absorbance data of urethane-substituted thermochromic poly(diacetylenes) such as HDI-5,7-1000 and polyETCD was related to organization changes taking place during the thermochromic transitions of these materials.

Partially cross-polymerized HDI-based copolymers were used to examine the effects of tensile stress on the microphase structures of these materials. Changes in the

absorption spectra of partially cross-polymerized elastomers subjected to a macroscopic tensile elongation were ascribed to two separate processes. The first process is reversible and involves the transfer of stress from the soft segments to the conjugated backbones of the hard domains. The second process is irreversible and is due to the stress-induced disruption of the hard-domain organization.

In conclusion, the polyurethane–diacetylene segmented copolymers described in this paper exhibit many of the novel optical properties characteristic of poly(diacetylenes) derived from micromolecular diacetylene monomers. The combination of the optical properties of the poly(diacetylenes) and the mechanical properties of phase-separated segmented polyurethanes results in a new set of properties heretofore not found in either class of materials. Preliminary investigations of these new materials have already provided additional insights into the behavior of conventional poly(diacetylenes).

Acknowledgment. I gratefully acknowledge Professor Gary Wnek of MIT and Dr. Sukant Tripathy of GTE Laboratories for their guidance and encouragement of this work. In addition, I am grateful to Dr. Daniel Sandman of GTE Laboratories for very useful discussions. The assistance of Bert Smith and Steven Hoang of GTE Laboratories is also acknowledged.

Registry No. HDI-5,7-1000, 98973-20-7; HDI-2,4-1000, 98973-18-3; MDI-2,4-1000, 98973-17-2.

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