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Investigations of the Mechanochromic Behavior of Poly(urethane-diacetylene) Segmented Copolymers

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ABSTRACT: The optical properties of a number of structurally and morphologically different segmented polyurethanes containing a small fraction of conjugated poly(diacetylene) chains in their hard domains were examined during tensile elongation by visible dichroism techniques. In all cases, the poly(diacetylene) chains were found to orient into the stretch direction during elongation, implying that the hard segments orient transverse to the stretch direction during this process. All of the elastomers were found to exhibit mechanochromic behavior, visually observed during stretching as color changes from blue to red or yellow. The unique color changes observed during stretching were attributed to either a mechanically induced disordering of the hard domains or a stress-induced phase transition within the hard domains. In the latter case, it was found that the reversibility of the phase transition was influenced by the soft-segment molecular weight. Completely reversible phase transitions were identified in segmented polyurethanes containing crystalline hard domains. Evidence for significant irreversible hard-domain disruption was only found at strain levels greater than ca. 250%. In some cases, it was found that suitable mechanical treatments can actually improve the local molecular order of the hard domains by relieving localized stress concentrations.

1. Introduction

The optical properties of poly(diacetylenes) are known to be very sensitive to the molecular environment of their conjugated polymer backbones. Variations in backbone planarity and/or the level of stress experienced by the backbone can result in significant changes in the energy, shape, and breadth of the absorption bands characteristic of these materials.[1,2] The electronic states are therefore strongly coupled to the conformation of the conjugated backbone. As a result of this strong coupling, the poly(diacetylenes) exhibit a wide variety of chromic transitions that can be induced by temperature, stress, or solvent changes.[1,3,4]

When the poly(diacetylene) backbone is contained within a highly ordered matrix, such as a single-crystal lattice, the absorption band is usually comprised of a narrow, well-defined excitonic peak followed by vibronic sidebands that are shifted to the higher energy side of the excitonic transition by an amount equivalent to the stretching frequencies of the carbon double- and triple-bond vibrations of the backbone.[5] As disorder is introduced into the system, the primary excitonic peak broadens and the higher energy vibronic sidebands become obscured by a very broad absorption band that, in some cases, can dominate the entire spectrum. This latter absorption band represents the wide distribution of excitation energies resulting from the various molecular environments created by a random disordering process. In the extreme case of a completely disordered system only a broad, featureless absorption band in the higher energy region of the visible spectrum is observed.

The position of the primary absorption band of a poly(diacetylene), on the other hand, depends on the kinds of static distortions imposed on its conjugated backbone by the molecular environment, mainly via the polymer's side groups. The exact nature of these backbone distortions is still highly debated, although it is generally accepted that they strongly influence the extent of electron delocalization possible along the backbone. Theoretical calculations have shown,[6] for example, that small variations in bond angles can result in large optical shifts of the absorption band. Thus, the lowest energy optical transition of a poly(diacetylene) can exist throughout the entire visible range due to variations in the packing and ordering of its side groups. It has also been found that the absorption band of a poly(diacetylene) will reversibly shift to lower energies when the chains are placed under a compressive load and to higher energies when they are under a tensile load.[7] This means that information about the level and type of stress experienced by the poly(diacetylene) chains in a given phase can also be obtained by visible spectroscopy.

The sensitivity of the electronic states of the poly(diacetylene) conjugated backbone to local molecular environment makes this polymer an ideal molecular probe for examining changes in the hard-domain structure of segmented polyurethanes. By observing changes in the position and shape of the polymer's absorption band during tensile elongation, it is possible to identify structural changes in the hard domains ranging from simple disordering processes to crystallographic phase transitions. The one-dimensional nature of the fully extended chains also results in highly anisotropic optical properties and hence an absorption band whose intensity is highly dependent on the direction of polarization light. This latter phenomenon can be used to ascertain the direction in which the poly(diacetylene) chains are orienting under an applied stress.

We have recently described the synthesis and properties of a new class of segmented polyurethanes containing diacetylene groups within their hard segments.[8,9] The diacetylene groups remain inactive during processing but can be subsequently reacted in the solid state to produce materials containing fully extended poly(diacetylene) chains. In such materials, the poly(diacetylene) chains reside exclusively in phase-separated hard domains dispersed throughout a soft elastomeric matrix. Thus, any changes in the electronic states of the conjugated backbone are a direct result of changes in the molecular organization of the hard domains. Previous work has demonstrated that these materials exhibit thermochromic behavior[1] and that their mechanical properties and swelling behavior can be systematically controlled by varying the level of diacetylene polymerization within the hard domains.[9] For example, in some cases it is possible to double the ultimate

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tensile strength of these materials by diacetylene polymerization. These new elastomers therefore exhibit an unusual collection of mechanical and optical properties that can be directly traced to their two-phase microstructures. This paper examines the influence of tensile elongation on the orientation and molecular organization of hard-segment domains containing a small fraction of poly(diacetylene) chains.

2. Experimental Procedures

Synthesis. The details of the synthesis of the poly(urethane–diacetylene) segmented copolymers can be found in our previous publications.[8,9] The soft segments are comprised of poly(tetramethylene oxide) (PTMO) having an average molecular weight of either 1000 or 2000. The hard segments are based on 4,4′-methylenebis(phenyl isocyanate) (MDI) or hexamethylene diisocyanate (HDI), while the chain extenders are either 2,4-hexadiyne-1,6-diol or 5,7-dodecadiyne-1,12-diol. The molar ratio of the diisocyanate, PTMO, and chain extender used in the polymerization reaction is approximately 2:1:1. The diacetylene groups are introduced into the hard segments via the chain extender and remain dormant until exposed to electron beam radiation, ultraviolet light, or heat. As a result of the reactant ratios used to prepare the elastomers, the hard segments contain on the average about one diacetylene group per hard segment. The elastomers are designated by the monomers used to synthesize them. For example, HDI-5,7-2000 refers to an elastomer synthesized from HDI, 5,7-dodecadiyne-1,12-diol, and PTMO of molecular weight 2000.

Sample Preparation. Samples for mechanical and optical testing were prepared by a static solvent casting technique in which a solution containing the elastomer in a mixture comprised of tetrahydrofuran and toluene was allowed to slowly evaporate in a confined chamber (typically 2 days) under a flow of nitrogen. MDI-2,4-1000 was cast from a mixture consisting of 50% toluene and 50% THF. The HDI-based elastomers were cast from a mixture of 75% toluene and 25% THF. All samples were annealed at 90 °C for 45 min unless stated otherwise to improve ordering. Annealing was carried out under normal atmospheric conditions in an oven, and thereafter the samples were removed from the oven and allowed to air cool. They were then cut into strips 0.25 or 0.375 in. wide and 3–4 in. long for tensile testing.

Cross-Polymerization. Polymerization of the diacetylene groups contained within the hard domains was accomplished by exposure to high-energy electrons from a Van de Graaff electron accelerator operated at 2.6 MeV or by thermal annealing treatments. Low dosages were used to ensure that only a small fraction of the diacetylene groups were converted to poly(diacetylene)chains. It is estimated that <5% of the diacetylene groups in the hard segments were cross-polymerized. In other words, 95% of the diacetylene groups remained unreacted. This resulted in very lightly cross-polymerized samples with mechanical properties nearly identical with those of the starting material. Partial polymerization HDI-5,7-1000 and HDI-5,7-2000 was accomplished by exposure to 0.02 and 0.08 Mrads of electron beam radiation, respectively, while for MDI-2,4-1000 it was accomplished by annealing at 90 °C for 45 min. The low level of diacetylene polymerization initiated by these treatments ensures that the deformation response of the polymer will not be significantly altered by cross-polymerization. Since the poly(diacetylene) backbone is a very strong chromophore with a large absorption coefficient, it is readily detected even at these very low concentrations.

Tensile Testing. Tensile testing was done at room temperature on an Instron Model 1122 using elastomeric or pneumatic grips to prevent slippage of the samples. Strain was measured with an incremental extensometer that recorded strain automatically, thus eliminating less reliable manual pipping procedures. A constant cross-head speed of 50 mm/min was used. Values for stress were calculated based on the initial cross-sectional area. Hysteresis measurements were made by loading and unloading specimens at a constant cross-head speed of 50 mm/min to an increasing strain level for each successive cycle. The end of a cycle was taken as the point where the material displayed zero stress on the unloading curve.

Simultaneous Visible Spectroscopy and Tensile Testing. Visible absorption spectroscopy was performed with an Oriel Instaspec System 250 multichannel analyzer. Each spectrum was typically recorded in 41 ms, and the instrument was programmed to take spectra continuously at specified time intervals. A halogen lamp was used as the light source, while the light signal was detected with a diode array having 1024 detectors. Visible spectroscopy and tensile testing were performed simultaneously to study the changes in the absorption spectra as a function of strain. To accomplish this, a halogen lamp was placed behind the sample which was mounted in the Instron. A liquid light guide positioned in front of the sample was used to collect and transmit the signal to the multichannel analyzer. When polarized light was required, a polarizer was placed between the lamp and the sample. Hysteresis tests involved stretching the sample to a given strain level, measuring its absorption spectrum in both vertically and horizontally polarized light (both spectra were recorded within <0.5 min after reaching a given strain level), then relaxing the sample at the same rate (50 mm/min) to zero stress, and again recording the spectrum in polarized light. The cycle would then be repeated at successively higher strains until the sample finally broke. Hence for each strain level there are four spectra—two in the stretched state and two in the relaxed state. Spectra were also recorded with polarized and nonpolarized light while the sample was continually stretched. It should be borne in mind that when the absorption spectra of these elastomers are examined as a function of strain, a part of the observed decrease in intensity is a result of a decrease in the sample thickness that accompanies the elongation of the sample.

During simulataneous visible spectroscopy and tensile testing, it was possible to measure only the load and the absorption spectrum. Strain was therefore obtained indirectly as follows: a master stress–strain curve was generated for the material under consideration with the given radiation dosage by taking an average of a large number (5–6) of simple stress–strain runs. This master curve was then used to obtain strain levels at the given stress values.

Dichroic ratios were calculated by taking the ratio of the area under the absorption curve due to light polarized parallel to the stretch direction to the area under the absorption curve due to light polarized perpendicular to the stretch direction. The region of consideration in all cases was from 425 to 700 nm. A limitation of using this wavelength range is that at high strain levels a portion of the polymer spectrum shifts outside of the range of detection of the spectrophotometer, and thus its contribution to the area (both horizontal and vertical spectra) is not reflected in the data. Dichroic ratios were also calculated by taking the ratio of the heights of the most intense peaks in the respective absorption spectra. Although the latter dichroic ratios are not reported here, it should be noted that the trends of the dichroic ratios with respect to strain were similar in both cases. The integrated intensities represent the contributions from the poly(diacetylene) chains present in the hard domains. Although some hard segments are dissolved in the soft-segment phase, they are isolated and therefore do not cross-polymerize. Thus, it can be assumed that these isolated hard segments have no significant effect on the visible absorption of the cross-polymerized polymer.

3. Results

The stress–strain curves of the diacetylene elastomer samples used for optical studies are presented in Figure 1. The upturn observed in the curve of HDI-5,7-2000 and most dramatically in the curve of MDI-2,4-1000 is associated with strain-induced crystallization of the soft segments as confirmed[9] by X-ray and optical measurements. The more interconnected morphology of HDI-5,7-1000 inhibits soft-segment crystallization, thereby eliminating this important strengthening mechanism. We have previously identified[9] two basic modes of deformation active in the poly(urethane–diacetylene) segmented copolymers. In one case, tensile elongation takes place primarily by a reversible extension and alignment of the soft-segment phase. In this mode of deformation, the hard domains are usually isolated entities that remain struc-

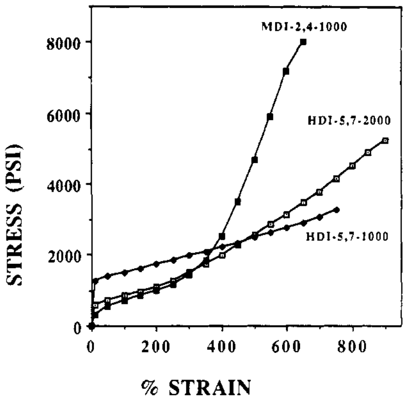

Figure 1. Stress–strain curves of the elastomers (with low levels of diacetylene cross-polymerization) used for optical studies.

turally intact during the early stages of deformation, possibly becoming oriented into the direction of the elongation. In the second mode of deformation, tensile elongation requires irreversible deformation and reorganization of both phases of the microstructure during nearly all stages of elongation. Such behavior is usually encountered in materials with well-phase-separated morphologies and highly crystalline and interconnected hard domains. These two distinct modes of deformation represent two extreme cases; hence, it would be expected that many materials would exhibit both modes of deformation.

In order to determine the effect of tensile elongation on the order and orientation of the hard segments in both the stretched and relaxed states, samples were subjected to a series of loading and unloading cycles. Spectra were therefore recorded with horizontally and vertically polarized light on samples in the stretched state and after they had been relaxed from a given strain to the unstretched state. Visible dichroism measurements of this type provide valuable insights into the mode of deformation dominant in each of these samples. The results of such studies are presented in the sections that follow.

3.1. Visible Dichroism Studies of MDI-2,4-1000. Figure 2a displays the absorption spectra of MDI-2,4-1000 measured with vertically polarized light (parallel to the stretch direction) as a function of increasing strain levels. Figure 2b, on the other hand, displays the spectra recorded with horizontally polarized light (normal to the stretch direction) at similar strain levels. Before any stress is applied, the material exhibits a well-defined absorption band typical of poly(diacetylenes) with an excitonic peak at ca. 625 nm that gives the film a light blue color in transmitted light. The broad absorption bands at higher energy are due to the presence of various levels of molecular order within the hard domains that give rise to a range of effective backbone conjugation lengths and, hence, a distribution of excitation energies. Also buried under these peaks are the vibronic sidebands of the primary excitation.

The spectra recorded with vertically polarized light reveal that the primary absorption band continuously shifts to higher energies, broadens, and becomes poorly defined as a function of increasing strain. The color of the film changes from blue to red during this process. At the highest strain levels, only a broad, featureless absorption band centered around 470 nm is observed. Note that even at strains as low as 40% there is a significant shift of the absorption band to higher energies. This clearly indicates that stress is transmitted to the hard domains even at low strains and consequently affects the molecular environment of the poly(diacetylene) backbone. The broad featureless absorption band observed at the highest strains suggests that the hard domains have become highly disordered, creating a broad distribution of poly(diacetylene) backbone distortions.

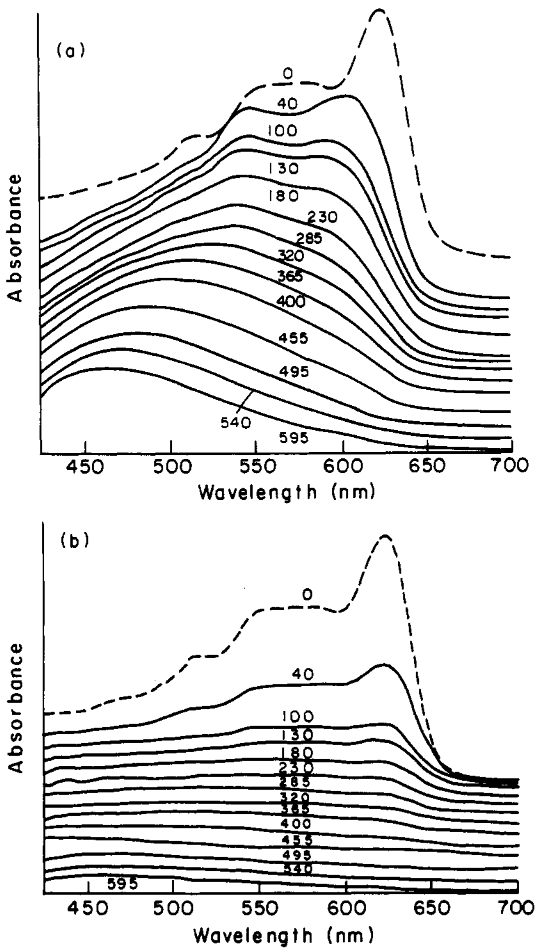

Figure 2. Visible absorption spectra of MDI-2,4-1000 recorded in the stretched state as a function of increasing strain with (a) vertically polarized light and (b) horizontally polarized light. Numbers indicate strain levels (spectra have been arbitrarily offset along the absorption axis for clarity).

In sharp contrast to the spectra obtained with light polarized along the stretch direction, the excitonic peak observed in the spectra recorded with horizontally polarized light (Figure 2b) shifts much less dramatically to higher energy with increasing strain level. The intensity of the overall absorption band, however, decreases significantly (relative to that observed with vertically polarized light) with increasing strain level, eventually becoming barely detectable above 400% strain. The dramatic decrease in intensity of the absorption bands observed with horizontally polarized light clearly indicates that the fully extended poly(diacetylene) chains are orienting into the stretch direction during tensile elongation. The fact that the excitonic peak shifts less dramatically to higher energies and retains its shape to higher strains indicates that the poly(diacetylene) chains lying perpendicular to the stretch direction are not subjected to the high levels of stress experienced by the chains forced to align into the stretch direction.

Figure 3 contains the spectra of MDI-2,4-1000 recorded in the relaxed, unstrained state after stretching the polymer to the indicated strain levels. These spectra provide information about residual hard-domain orientation and the reversiblity of the deformation process. As can be seen in Figure 3a, the shape and position of the original absorption band of the poly(diacetylene) chains are

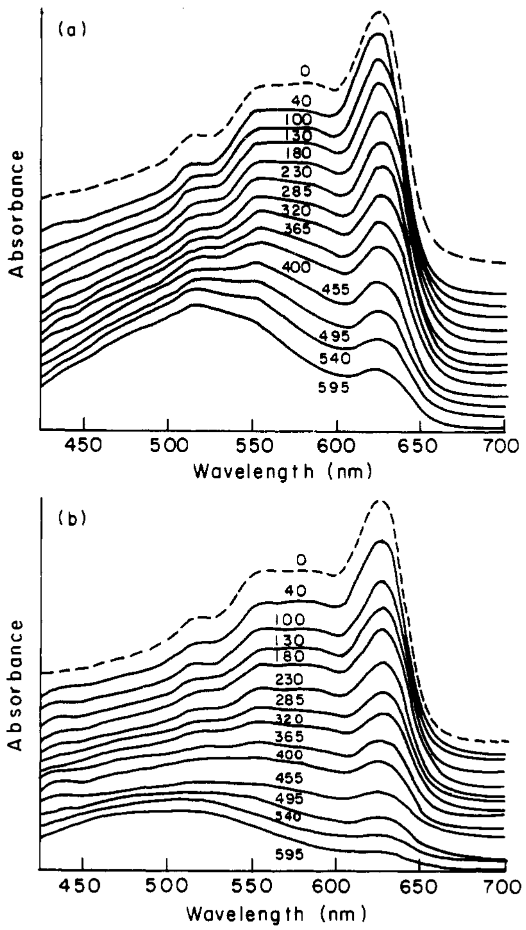

Figure 3. Visible absorption spectra of MDI-2,4-1000 recorded after relaxation from the indicated strain levels with (a) vertically polarized light and (b) horizontally polarized light. Spectra have been arbitrarily offset along the absorption axis for clarity.

completely recovered after relaxing from strains up to 100%. As the material is stretched to higher strain levels, however, there is a gradual reduction in the intensity of the excitonic peak relative to the broader higher energy absorption bands. At strains higher than 400%, the higher energy absorption bands become more intense than the excitonic peak. Thus, it appears that the hard domains remain structurally intact at strain levels up to at least 100% and gradually deform and disorder at increasingly higher strain levels. Similar changes were observed in the spectra generated with horizontally polarized light.

It should be noted that optical measurements made on MDI-2,4-1000 samples during continuous-stretching experiments revealed a dramatic increase in total absorbance at strain levels greater than 500%. This increase in absorbance, which eventually completely obscures the absorption band of the poly(diacetylene) chains, is due to strain-induced crystallization of the soft segments and the concomitant increase in scattering associated with the presence of soft-segment crystallites. As might be expected, the material visually changes from transparent to translucent at these same strain levels. Even though strain-induced crytallization sets in much before 500%, it is not manifested in the optical data since the crystallites formed are either too small or too few to scatter sufficient light. It is interesting to note that no strain-induced crystallization was detected during hysteresis type experiments. It should also be noted that complementary studies[10] performed on MDI-2,4-1000 samples that were more highly cross-linked show that the hard domains remain structurally intact to higher strain levels and become more oriented during elongation than the less cross-linked samples reported in this paper. Clearly, the level of hard-domain cross-linking influences the deformation response of the polymer.

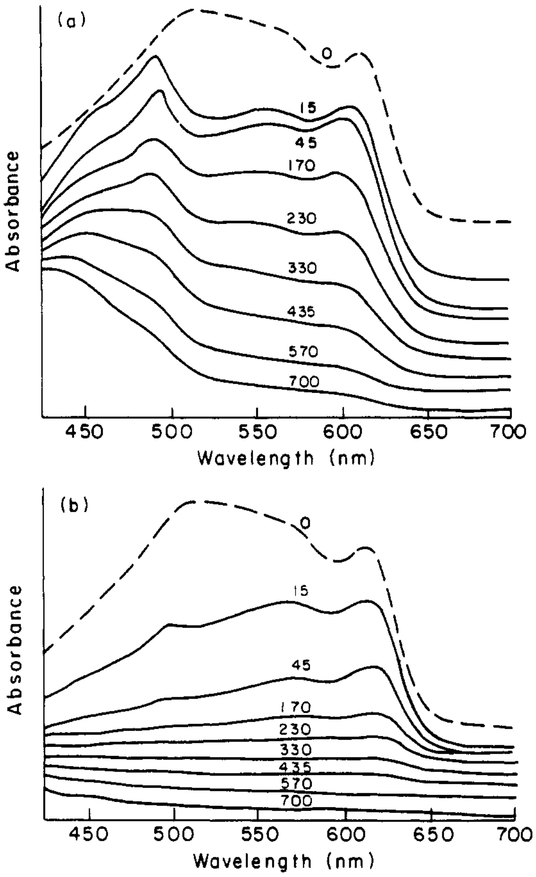

Figure 4. Visible absorption spectra of HDI-5,7-1000 recorded in the stretched state as a function of increasing strain with (a) vertically polarized light and (b) horizontally polarized light. Numbers indicate strain levels (spectra have been arbitrarily offset along the absorption axis for clarity).

3.2. Visible Dichroism Studies of HDI-5,7-1000. The absorption spectra of HDI-5,7-1000 measured with vertically and horizontally polarized light in the stretched state as a function of increasing strain level are displayed in Figure 4. Prior to stretching, the absorption spectrum of this material exhibits an excitonic peak at 615 nm (designated as the blue phase) followed by a more intense, significantly broader absorption band with a peak maximum at ca. 520 nm. The intensity and breadth of this latter band indicate that there initially exists a wide range of molecular environments in the hard domains within which the poly(diacetylene) chains are contained. These different molecular environments are most likely present in less ordered regions of the hard domains and are brought about by the local stresses created during diacetylene polymerization that would be expected to cause slight backbone distortions of the resultant conjugated chains. As the elastomer is stretched, the excitonic peak observed in vertically polarized light (Figure 4a) shifts to higher energies and broadens as was the case for MDI-2,4-1000. In sharp contrast, however, a completely new absorption band centered initially at ca. 495 nm appears (designated as the yellow phase) and grows in intensity at the expense of the original absorption band with increasing strain. This new absorption band is also seen to shift to higher energies and broaden with increasing strain level.

The emergence of a new, well-defined absorption band during tensile elongation indicates that a mechanically

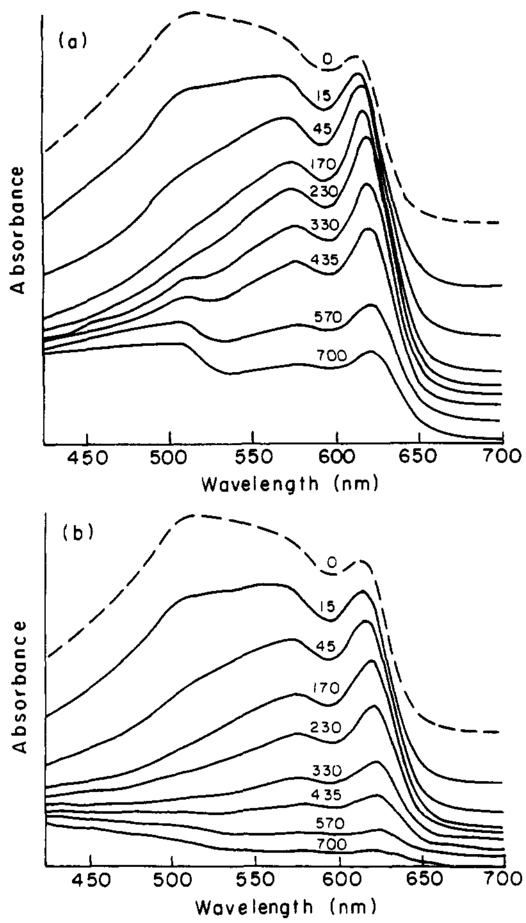

Figure 5. Visible absorption spectra of HDI-5,7-1000 recorded after relaxation from the indicated strain levels with (a) vertically polarized light and (b) horizontally polarized light. Spectra have been arbitrarily offset along the absorption axis for clarity.

induced phase transition is taking place within the hard domains. Thus, two distinctly different molecular environments exist for the poly(diacetylene) chains during stretching, each of which is populated with a relatively narrow distribution of effective conjugation lengths. This entire process is visually observed as a color change from blue to yellow during tensile elongation.

Again it can be seen that the intensities of the absorption bands observed with light polarized orthogonal to the stretch direction (Figure 4b) decrease dramatically with increasing strain level, becoming barely detectable at strains above 450 nm. As was the case for MDI-2,4-1000, these results indicate that the poly(diacetylene) chains are continuously orienting into the stretch direction. Horizontally polarized light also reveals that the peak of the lowest energy optical transition actually shifts to slightly lower energies with increasing strain level and that the mechanically induced phase transition is much less evident with this polarization mode. The poly(diacetylene) chains lying normal to the stretch direction are therefore not subjected to the same level or type of stress as those forced to orient into the stretch direction.

The spectra recorded in the relaxed state (Figure 5) show that the mechanically induced phase transition observed with vertically polarized light is completely reversible up to strains of ca. 300%. In fact, the primary absorption band present in the spectra recorded in the relaxed state actually becomes better defined and more narrow with increasing levels of strain. The higher energy shoulder of this band is also significantly reduced in intensity after relaxation from successively increasing strain levels. Only after strains greater than 300% does the higher energy band start to reappear and develop into a much broader and higher energy form. Note, however, that even after stretching to strains as high as 700%, at which point the original absorption band is essentially nonexistent, relaxation to the unstretched state reestablishes a spectrum still strongly influenced by the original absorption band. Figure 5 also shows that the wavelength of the excitonic peak continuously shifts to lower energies after relaxation from increasing higher strain levels. Similar effects were observed with horizontally polarized light.

The following explanation is suggested by these results. Before stretching, the conjugated backbones of the poly(diacetylene) chains exhibit a wide dispersion of effective conjugation lengths as evidenced by the broad, high-energy absorption band following the primary excitonic peak. During stretching, the mechanical energy supplied to the hard domains induces a reversible phase transition that creates a new molecular environment for the poly(diacetylene) chains. At high strain levels, the majority of the poly(diacetylene) chains are converted into this new hard-domain phase. Relaxation from this new high-strain phase allows the poly(diacetylene) chains to return almost exclusively to the more ordered molecular organization of the blue-phase state as opposed to the initial state of hard-domain order which was characterized by a wider distribution of local molecular environments. Thus, many of the poly(diacetylene) backbone distortions created by the stresses introduced during diacetylene polymerization are eliminated by stretching. Only when the samples are subjected to very high strain levels (>300%) is there an indication that substantial hard-domain disordering is taking place, and this most likely represents the point at which hard-domain breakup begins to occur. These results provide direct evidence that suitable mechanical treatments can actually improve the local molecular order of the hard domains by relieving localized stress concentrations.

3.3. Visible Dichroism Studies of HDI-5,7-2000.

Since the hard-domain structure of HDI-5,7-2000 is the same as that in HDI-5,7-1000, one would expect similar mechanooptical behavior. This, in general, turned out to be the case, although the difference in molecular weight of the soft-segment phase was found to play an important role in the reversibility of the mechanically induced phase transition of the hard domains.

Figure 6 shows the visible spectra of HDI-5,7-2000 recorded with vertically and horizontally polarized light as a function of increasing strain levels. The absorption spectrum in the unstretched state exhibits an excitonic peak at 620 nm followed by a relatively broad absorption band centered at ca. 570 nm. As the elastomer is stretched, the original excitonic peak moves to higher energies and is gradually eliminated, while a new higher energy absorption band centered initially at ca. 500 nm (at 55% strain) begins to grow in intensity, broaden, and also shift to higher energies. During this process, the material changes dramatically from a blue to a yellow color. As was the case for HDI-5,7-1000, the emergence of a new absorption band suggests that the color change is the result of a strain-induced phase transition within the hard domains. The shifting of the absorption bands characteristic of each phase to higher energies with increasing strain level and the peak broadening that accompanies this process are a direct manifestation of the stress that is transmitted to the hard domains during tensile elongation.

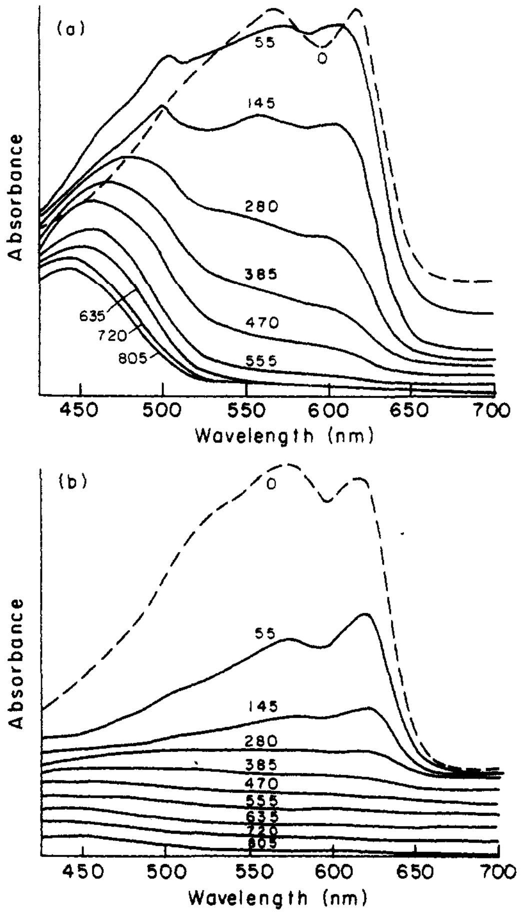

Figure 6. Visible absorption spectra of HDI-5,7-2000 recorded in the stretched state as a function of increasing strain with (a) vertically polarized light and (b) horizontally polarized light. Numbers indicate strain levels (spectra have been arbitrarily offset along the absorption axis for clarity).

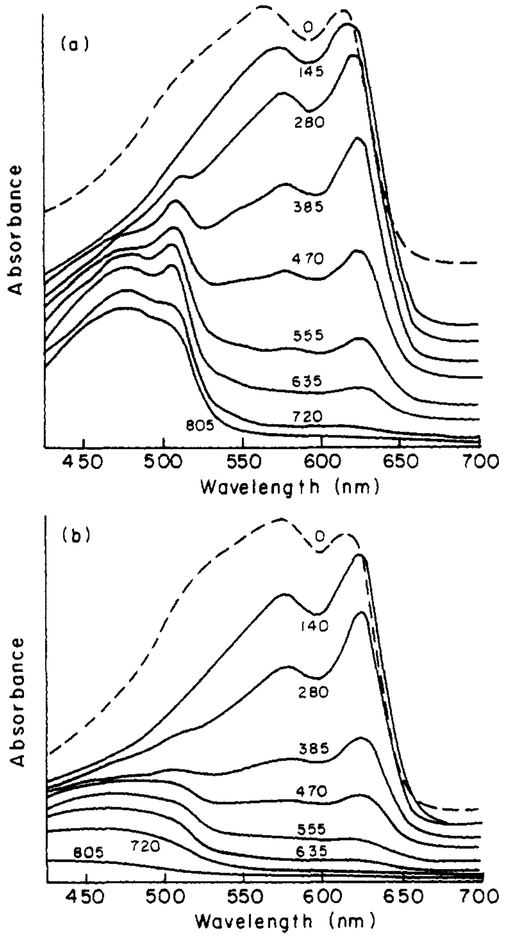

Figure 7. Visible absorption spectra of HDI-5,7-2000 recorded after relaxation from the indicated strain levels with (a) vertically polarized light and (b) horizontally polarized light. Spectra have been arbitrarily offset along the absorption axis for clarity.

In sharp contrast, the absorption band revealed by horizontally polarized light rapidly decreases in intensity with increasing strain and only shifts to higher energies at very large strains. The very weak intensity of this latter band at high strains relative to the intensity of the absorption band observed with vertically polarized light at similar strains indicates that the fully extended poly(diacetylene) chains are again preferentially orienting into the stretch direction. Thus, during stretching, the hard domains containing the poly(diacetylene) chains undergo a mechanically induced phase transition and become oriented with the poly(diacetylene) chains pointing into the stretch direction. The poly(diacetylene) chains that do not initially orient into the stretch direction apparently do not experience high stress levels as indicated by the initial insensitivity of the energy of the excitonic peak observed with horizontally polarized light to strain level.

Figure 7 contains the spectra recorded in the relaxed, unstrained state after stretching the polymer to the indicated strain levels. Focusing on the spectra generated with vertically polarized light, we can see that the strain-induced optical transition is essentially reversible up to strains of ca. 250%. As with HDI-5,7-1000, the original absorption band recovered after relaxation from the stretched state has shifted to slightly lower energies and exhibits a less intense higher energy peak. This would suggest that stretching to low strains (<300%) also relieves local stresses acting on the poly(diacetylene) chains within the hard domains of HDI-5,7-2000. Relaxation from higher strains, on the other hand, reveals the coexistence of two well-defined phases: a blue phase centered at 624 nm and a yellow phase centered around 510 nm. As the strain level increases, the yellow phase grows at the expense of the blue phase. Note, however, that even after stretching to strains as high as 635%, where the blue phase is essentially nonexistent, relaxation to the unstrained state leads to the reestablishment of a small but significant amount of this phase. Similar trends were observed with horizontally polarized light as indicated in Figure 7.

It is interesting to note that with HDI-5,7-2000 it is possible to produce an elastomer in the relaxed state in which both phases coexist in a fairly ordered form (as evidenced by the presence of absorption bands with definable excitonic peaks). This phenomenon was clearly not observed in HDI-5,7-1000, where the yellow phase was only isolated in the relaxed state in a very disordered form after stretching to high strain levels. The more flexible soft-segment matrix established by the higher molecular weight soft segments of HDI-5,7-2000 apparently influences the reversibility of the hard-domain phase transition and the state of order of the resultant yellow phase. It is reasonable to conclude that the more interconnected hard-domain morphology of HDI-5,7-1000 precludes the obtainment of a well-ordered yellow phase since at high strains the hard domains are forced to undergo irreversible molecular reorganizations during tensile elongation.

3.4. Dichroic Ratios. Figure 8 displays the strain dependence of the dichroic ratios of each of the elastomers evaluated. As mentioned earlier, the dichroic ratios were calculated from values obtained by integrating the area under the entire absorption curve and thus take into account all poly(diacetylene) chains excited by the po-

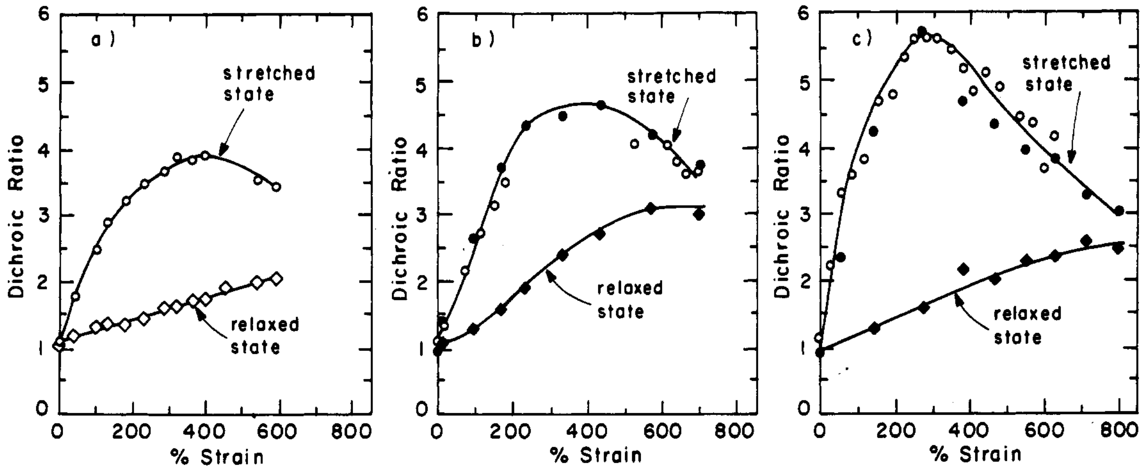

Figure 8. Dichroic ratios of (a) MDI-2,4-1000, (b) HDI-5,7-1000, and (c) HDI-5,7-2000 in the stretched and relaxed states as a function of increasing strain level. For the HDI-based elastomers, the closed data points represent hysteresis runs, whereas the open points represent continual stretching runs (see text for explanation).

larized light irrespective of their conjugation length or their state of stress. In all three cases, the dichroic ratio generated in the stretched state is seen to increase dramatically with increasing strain level up to strains of ca. 300%, beyond which point it levels off and decreases. Thus, the maximum level of poly(diacetylene) chain orientation in each of these elastomers occurs at ca. 300% strain. In addition, the HDI-based elastomers achieve a higher state of poly(diacetylene) chain alignment than the MDI-based elastomer, with HDI-5,7-2000 reaching the highest dichroic ratio in the stretched state of ca. 5.6.

The decrease in dichroic ratio observed at high strains in each of the elastomers suggests that a significant amount of hard-domain breakup and restructuring is starting to occur at these strain levels. A significant breakup of the hard domains of these elastomers is possible since they are only lightly cross-polymerized. Because the detection limitations of the spectrophotometer are most problematic at high strain levels (a larger percentage of the absorption bands observed with both vertically and horizontally polarized light shifts out of the detection range), it is not possible to unambiguously conclude from these data that the drop in dichroic ratio is due to irreversible hard-domain disruption. A closer examination of the actual spectra, however, does seem to support this hypothesis. For example, in the case of HDI-5,7-1000, the spectra generated in the relaxed state (see Figure 5) clearly show evidence of irreversible hard-domain disordering starting at ca. 300% strain. The development of a very broad, high-energy absorption band after stretching the elastomer to strain levels greater than 300% is direct evidence that irreversible hard-domain reorganization begins to occur at these strain levels and becomes more prevalent after stretching to higher strains. A similar high-energy absorption band develops in the relaxed spectra of MDI-2,4-1000 (see Figure 3), although the gradual nature of the disordering process in this case makes it difficult to ascertain the exact point at which significant irreversible hard-domain restructuring actually begins. The spectrum, however, is clearly dominated by the higher energy band after stretching the material to strain levels greater than 400%. For HDI-5,7-2000, irreversible hard-domain disruption is also evident in the relaxed spectra recorded with horizontally polarized light (Figure 7), in this case starting at ca. 300% strain. The spectra recorded with vertically polarized light also show evidence for an irreversible change in the hard-domain organization. The presence of a clearly defined excitonic peak on the developing higher energy absorption band, however, suggests that this is actually a crystallographic phase transition accompanied by disordering at high strain levels.

The dichroic ratio in the stretched state was also determined in a separate set of experiments wherein the absorption spectra were measured during continuous stretching with both vertically and horizontally polarized light. The area under these absorption curves was again used to calculate the dichroic ratio. As indicated by the open circles found on the curves of the HDI-based elastomers, the dichroic ratios obtained from the different methods, i.e., hysteresis and continuous-stretching experiments, produce very similar results. In the case of HDI-5,7-2000, the dichroic ratios measured during hysteresis type experiments are slightly less than those measured by the continuous-stretching method, indicating that a small amount of relaxation does occur while recording the absorption spectra during the hysteresis experiments. This observation is consistent with the greater chain mobility exhibited by the soft segments of HDI-5,7-2000.

A comparison of the dichroic ratios generated from spectra recorded in the relaxed state as a function of increasing strain level reveals that both MDI-2,4-1000 and HDI-5,7-2000 exhibit dichroic ratios that increase gradually after relaxation from increasing higher strain levels but remain relatively small (compared to the corresponding stretched-state values) over the entire strain range. This would indicate that the level of residual orientation of the poly(diacetylene) chains after relaxation from the stretched state is rather small. Thus, once released from the stretched state, the poly(diacetylene) chains, or more specifically the hard domains that they are contained in, quickly relax to a near-isotropic state. This is not unexpected since the mobility of the soft segments of both materials is not severely restricted by their microstructures. This, in turn, ensures that entropically driven relaxations in the soft-segment phase will tend to randomize the orientation of the hard domains during relaxation from the stretched state. The dichroic ratio of HDI-5,7-1000 in the relaxed state, on the other hand, shows a more significant increase with increasing strain level, indicating that a higher level of orientation persists after the material has been relaxed from the stretched state. This latter observation is a consequence of the more interconnected hard-domain morphology of this material and the irreversible morphological changes that are characteristic of such a microstructure.

4. Discussion

Two major modes of hard-segment orientation have been previously observed in segmented polyurethanes during tensile deformation.[11-14] For materials with poorly ordered or paracrystalline hard domains, it has been found that the hard segments orient parallel to the stretch direction throughout the entire deformation process. However, for materials comprised of crystalline hard domains, the orientation of the hard segments at low strains was found to be initially transverse to the direction of stress.[11] Only at higher strain levels, where the hard domains were mechanically disrupted, did the hard segments realign into the direction of the applied stress. Transverse orientation of the hard segments has also been observed in polyether based poly(urea–urethanes)[14] and has been attributed to the orientation of lamellar-like hard domains along the stretch direction. Thus, depending on the structure, size, and molecular organization of the hard domains, it is possible to observe both transverse and parallel orientation of the hard domains during tensile elongation.

In the poly(urethane–diacetylene) elastomers, the fully extended poly(diacetylene) chains contained within the hard domains are aligned essentially perpendicular to the hard segments. An observation that the poly(diacetylene) chains are orienting into the stretch direction would therefore indicate that the hard segments are orienting transverse to the stretch direction. To date, all of the diacetylene-containing segmented polyurethanes that have been evaluated exhibit this particular mode of hard-segment orientation during elongation. This is an interesting observation considering the fact that the three elastomers evaluated in this work represent materials with distinctly different levels of hard-domain ordering and phase separation and different hard-domain structures (MDI versus HDI materials) and supermolecular structures. HDI-5,7-1000 and HDI-5,7-2000, for example, are both more phase separated than MDI-2,4-1000 and also exhibit highly crystalline hard domains as compared to the amorphous hard-domain structure identified in MDI-2,4-1000. Both MDI-2,4-1000 and HDI-5,7-2000, on the other hand, are representative of materials with isolated or semicontinuous hard domains, while the hard domains of HDI-5,7-1000 are more interconnected, forming a nearly continuous phase throughout the elastomer. Despite these structural and morphological differences, all of the elastomers show clear evidence of transverse hard-segment orientation during tensile elongation.

These results would suggest that the hard segments aggregate together to form lamellar- or ribbon-like hard domains in which the hard segments are aligned in the direction of the domain that defines its thickness, whereas the poly(diacetylene) chains are aligned parallel to the long axis of the domain. The exact supermolecular organization of these domains has yet to be determined, although given previous work on segmented polyurethanes and the general behavior of other semicrystalline polymers, it is reasonable to conclude that they are organized into spherulites as illustrated in Figure 9. In this model, the soft segments take the form of randomly coiled macromolecules spaced between the hard domains. When the elastomer is stretched, stress is transmitted to the hard domains via the soft segments and the long axes of the lamellae are forced to orient into the stretch direction, i.e, the hard segments line up perpendicular to the stress direction. The hard domains that are oriented into the stretch direction are placed under tension, thus producing a tensile (or shearing) stress on the poly(diacetylene) chains. This tensile stress is clearly observed as a shift in the absorption band to higher energies with increasing strain level. It is also responsible for the mechanically induced phase transition observed in the HDI-based elastomers. The hard domains oriented perpendicular to the stretch direction, on the other hand, are subjected to a different stress field and may even be placed into a slight compressive mode. This latter effect would explain the fact that the excitonic peak observed with horizontally polarized light for the HDI-based materials continuously shifts to lower energies with increasing strain level. At strains greater than ca. 300%, the lamellae start to break up and orientation of the hard segments into the stretch direction may occur.

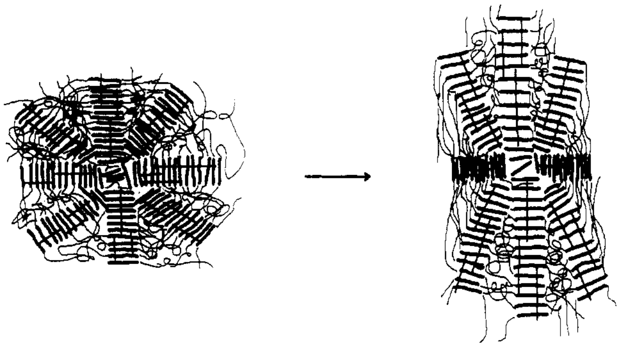

Figure 9. Schematic representation of a proposed model of deformation.

It is possible that the lightly cross-polymerized regions of the hard domains behave differently than the non-cross-linked regions. If this were the case, the linked hard segments could respond to stress by orienting into the stretch direction as structurally intact units (negative hard-segment orientation), whereas the nonlinked hard segments would be free to break away from the hard domain and orient independently into the stretch direction (positive hard-segment orientation). Since we are only probing the orientation of the poly(diacetylene) chains, it is not possible to observe this latter mode of orientation. Infrared dichroism experiments are currently underway to confirm that the majority of the hard segments do indeed initially orient transverse to the stretch direction.

The poly(diacetylenes) are well-known for their thermochromic transitions and the dramatic color changes that accompany these temperature-induced phase transtions. Mechanically induced chromic transitions in poly(diacetylenes), however, are much less frequently observed. In fact, the authors are only aware of one reported case in which a true crystallographic phase transition was induced in a poly(diacetylene) single crystal via the application of stress. This particular phase transition was not reversible and resulted in the coexistence of two separate phases within the mechanically stressed crystal.[15] The unique two-phase microstructure of the diacetylene-containing segmented polyurethanes allows the hard domains of these materials to be subjected to stress levels sufficient to induce a variety of reversible and irreversible chromic transitions. In MDI-2,4-1000, the color changes observed during tensile elongation are simply due to a mechanically induced disordering of the hard domains and the creation of highly disordered poly(diacetylene) chains. This type of behavior would be expected in any poly(diacetylene) material subjected to disorder-inducing stress levels. For the HDI-based materials, however, the stresses that are transmitted to the hard domains during elongation actually induce a structural phase transition that is completely reversible as long as a critical strain level is not exceeded. Thus, this represents the first report of a fully reversible mechanically induced phase transition in a poly(diacetylene). It also provides direct evidence that reversible mechanically induced phase transitions are possible within the hard domains of segmented polyurethanes.

The mechanically induced optical transition of the HDI-based segmented copolymers is very similar to the thermochromic transition also exhibited by these materials.[1] Typically, they change in color from blue to yellow at temperatures greater than 90 °C. The spectral changes associated with the thermochromic transition also involve the elimination of the original blue-phase absorption band and the development of a new yellow-phase absorption band with a peak at 510 nm. The thermochromic transition is reversible only if the material is not heated above ca. 130 °C. In this case, however, the absorption band of the newly formed yellow phase (at room temperature) is unusually narrow and exhibits well-defined vibronic sidebands suggesting the existence of a very well ordered phase. The broad nature of the absorption band of the mechanically induced yellow phase (see Figure 7b) indicates that this transition is also accompanied by a fair amount of disordering at high strain levels.

The thermochromic transition of the HDI-based materials has been attributed to a conformational rearrangement of the methylene groups attached to the poly(diacetylene) backbone that takes place without changes in the level of hydrogen bonding of the side chains.[1,16] Given the similarities in optical properties, it is reasonable to conclude that mechanical stress induces the same kind of hard-domain molecular reorganization as the thermal process. A clue to the types of conformational changes induced by either heat or stress in the poly(diacetylene) elastomers is provided by recent NMR studies[17] of the thermochromic transition of poly(ETCD) [poly[*N*,*N*′-diethyl(dodeca-5,7-diynylene dicarbamate)]]. This particular poly(diacetylene) has a side group structure very similar to that of the HDI-5,7-based elastomers (there are four methylene groups between the poly(diacetylene) backbone and the urethane group) and displays similar spectral changes during its thermochromic transition. In this case, the thermochromic transition has been shown to involve a gauche to trans conformational transition of the methylene groups in the poly(ETCD) side groups. The unit cell of the polymer also undergoes an abrupt volume expansion during the transition which appears to be a true first-order crystallographic phase transition.[18]

In summary, it has been demonstrated that the unique optical properties of selectively engineered poly(diacetylene) chains can be utilized to examine the influence of tensile strains on the orientation and order of hard domains in segmented polyurethanes. These materials also exhibit novel reversible mechanochromic behavior, observed as dramatic color changes during stretching. Thus, in addition to providing new insights into the mechanisms of deformation active in segmented polyurethanes, diacetylene-containing polyurethanes display very novel optical properties.

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Registry No. HDI-5,7-1000 (block copolymer), 116076-21-2; MDI-2,4-1000 (block copolymer), 107702-75-0.