Thermal and Mechanical Properties of Polyurethane–Diacetylene Segmented Copolymers. 1. Molecular Weight and Annealing Effects

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ABSTRACT: The thermal transitions and mechanical properties of a number of segmented polyurethanes containing diacetylene groups within their hard segments were evaluated. The ultimate tensile properties of these materials were found to be strongly dependent on their overall molecular weight and thermal history. In all cases, increased molecular weight resulted in improved mechanical properties. Annealing treatments were also found to dramatically improve the mechanical properties of these elastomers. Thermal analysis revealed that annealing increased the cohesive forces of the hard domains, thereby increasing their mechanical integrity. The effect that annealing had on the mechanical behavior was found to be highly dependent on the particular mechanism of deformation active in these segmented copolymers. Two distinctly different modes of deformation were observed in the polyurethane–diacetylene elastomers.

I. Introduction and Background

Over the past decade, a great deal of research has focused on the goal of identifying the key structural and morphological parameters necessary for high strength and toughness in phase-separated segmented polyurethanes. It is now well recognized that the enhanced mechanical properties of these materials are a direct result of their two-phase microstructures.[1,2] Typically, these materials consist of discrete or semicontinuous glassy or crystalline "hard" segment domains dispersed throughout a continuous rubbery "soft" segment amorphous phase. The flexible, rubbery soft segment domains impart elastomeric properties to the copolymer whereas the more rigid hard segment domains restrict viscous flow and act to mechanically reinforce the copolymer. By suitable variation in chemical structure, composition, and processing history, it is possible to obtain tough, high-strength elastomers with an extremely wide range of thermal–mechanical properties. In fact, it is this tremendous ability to readily modify the properties of these materials by variation in chemical structure and composition that has stimulated the enormous technological and scientific interest in these polymers. Thus, in principle, it is possible to tailor the thermal, mechanical, and optical properties of these segmented copolymers to meet specific performance criteria. In addition, many of the fundamental issues concerning structure–property relationships in two-phase systems can be readily addressed by suitable engineering of the molecular structures of these materials.

Many parameters are known to influence the mechanical behavior of these materials.[2] For example, factors such as the soft segment molecular weight and glass transition temperature, strain-induced crystallization of the soft segments, the hard segment structure, weight fraction, and state of organization, the degree of phase separation, interfacial thickness, cross-linking (in either phase), and the overall molecular weight have all been implicated as being important in determining the mechanical behavior of segmented elastomers. In order to clearly establish how these numerous factors combine to produce high strength in phase-separated elastomers, it is necessary to understand the mechanisms of deformation that the various microstructures of these materials can undergo. It has long been recognized that the exception-

ally high strength and toughness of these materials are related to the ability of the hard domains to readily dissipate strain energy as they undergo molecular reorganization and deform plastically under high-stress conditions.[3] An understanding of how these mechanically reinforcing hard domains respond to an applied stress is therefore a key to the understanding of the mechanical behavior of these materials.

In past years, researchers have systematically varied the chemical structure, composition, and molecular weight of both the soft segment and hard segment components of these segmented copolymers in an attempt to modify their properties as well as to gain an insight into their deformation mechanisms and basic structure–property relationships. For the soft segments, most of the work has focused on polar low molecular weight macrodiols such as polyethers or polyesters although a great deal of attention has recently been paid to nonpolar soft segments based on prepolymers such as polybutadiene,[4] polyisobutylene,[5] and poly(dimethylsiloxane).[6] The hard segments, on the other hand, are typically created from aromatic or aliphatic diisocyanates chain extended with low molecular weight diols or diamines. Although such studies have provided us with a good understanding of some of the key structural parameters that determine the mechanical and thermal behavior of these materials, the incredible variety found in the morphologies and superstructures of the resultant materials makes it extremely difficult to assess the relative importance of any of these factors. In other words, each time a chemical modification is made to the copolymer structure in order to study its impact on a specific property, the morphology of the material can change dramatically, making it difficult to determine what really influenced the material's behavior. This is particularly true in copolymer systems in which a delicate balance exists between phase separation and phase mixing such as in segmented copolymers containing polar soft segments capable of hydrogen bond formation with the hard segments. Thus, one would like to identify a segmented copolymer system in which structural modifications could be systematically introduced without creating major changes in the morphology of the material. In such a case, it would be possible to truly determine the impact of such a structural change on the properties of interest.

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A parameter of interest in this research is the influence of hard segment domain cohesion and rigidity on the thermal–mechanical properties of segmented polyurethanes. The nature and type of inter- and intramolecular interactions within the hard segment domains has been identified as an important factor in determining the physical properties of these materials. Since the hard domains are usually only held together by relatively weak secondary bonds as opposed to covalent linkages, it is possible to thermally overcome these interactions and hence process these materials at elevated temperatures. As a result of this, they are frequently referred to as thermoplastic elastomers. The presence of these weakly associated hard segments, however, also limits the useful temperature range of the copolymers as a significant deterioration of the mechanical properties naturally occurs as the temperature approaches the softening or melting temperature of the hard domains. Other less desirable properties such as mechanical hysteresis and stress softening are also believed to be linked to these weak interchain hard segment interactions that allow chain slippage, molecular relaxation, and plastic deformation to occur within the hard domains.[7] The importance of hard segment domain cohesion was recently noted by workers at the University of Wisconsin[8] where it was found that an enhancement of hard segment domain cohesion obtained by the development of either hard domain crystallinity or ionic aggregation resulted in a significant increase in the ultimate tensile strength, rubbery plateau modulus, and Young's modulus of poly(dimethylsiloxane)–polyurethane segmented polymers.

Many researchers have attempted to examine the influence of hard domain cohesiveness on the thermal–mechanical properties of segmented polyurethanes by introducing chemical cross-links into the hard segment domains. For example, various cross-linking agents such as peroxides and trifunctional chain extenders have been utilized to chemically modify the hard domain cohesiveness via chemical cross-links.[9-12] In all cases, however, this approach results in significant modifications of the packing and organization of the hard segment domains and often times reduced ultimate tensile properties. Specifically, it has been found that only a slight amount of cross-linking introduced in this manner can be tolerated before the hard domain organization is disturbed and the material's properties are significantly diminished. Cross-linking has also been accomplished by utilizing an excess of the diisocyanate component to promote allophonate-type linkage.[13,14] In this case, in addition to variations in the hard segment packing and organization, the presence of additional hard segment material also changes the hard domain volume fraction and hence the interconnectivity of the hard domains. Thus to date, a segmented copolymer system has not been identified in which primary covalent cross-links can be selectively and controllably introduced into the hard domains without major modifications in the state of organization of the hard segments and the polymer's morphology.

In addition to chemical cross-linking, increased hard segment intermolecular interactions can also be obtained by utilizing hard segments with stronger nonbonded interactions. For example, significant improvements in many of the properties sensitive to weak interchain forces within the hard domains can be realized by introducing more strongly associating polar groups into the hard segments such as urea linkages, which, in general, tend to improve the degree of microphase separation of the system and increase the hard domain softening temperature.[15,16] However, this also makes it more difficult to melt process the copolymer since the higher temperatures required to soften the hard domains and induce plastic flow can also result in chemical degradation of the polymer chain. Thus, it can be generally stated that variations in the chemical structure of the hard segments that tend to favor higher temperature stability of the hard domains also significantly reduce the ease in which the copolymer can be processed as a thermoplastic. Similarly, random covalent cross-links introduced into the hard domains during synthesis or processing of the elastomers can also severely compromise their processing characteristics.[17] It should also be reemphasized that many studies on the influence of hard segment domain cohesion have been complicated by the fact that chemical modifications introduced during synthesis or postcure processing steps can dramatically alter the state of organization of the hard segments within the hard domains and the morphology of the polymer.

Clearly a highly desirable polyurethane elastomer would be one that could be molded at fairly low temperatures into a desired form with a well-defined morphology and subsequently chemically modified in the solid state to improve the thermal–mechanical stability of the hard domains. If the chemistry used to modify the hard domain structure could be initiated without significant changes in the organization of the hard domains or morphology and superstructure of the copolymer, then such an elastomer would serve as an ideal system in which to study the influence of hard domain cohesion and rigidity on the mechanical and thermal properties of segmented copolymers. We have found that it is possible to obtain such a system by combining the novel chemistry of the diacetylenes with the well established chemistry of the segmented polyurethanes.

Polyurethane–diacetylene block copolymers are a new class of elastomers[18-20] essentially described as conventional polyurethanes containing diacetylene units within their hard segments. They consist of alternating blocks of soft segments comprised of poly(tetramethylene oxide) and hard segments based on aromatic or aliphatic diisocyanates. The diacetylene unit lies along the polymer backbone, within the hard segment, and is introduced via the chain extender. The physical and mechanical properties of these elastomers bear close resemblance to those of traditional segmented polyurethanes. Specifically, they have a two-phase microstructure resulting from the thermodynamic incompatibility of the hard and soft segments, which consists of isolated or interconnected hard domains dispersed in a continuous or semicontinuous elastomeric soft phase. In addition to sharing the properties of traditional polyurethanes, the polyurethane–diacetylene block copolymers exhibit several unique characteristics directly attributable to the reactive diacetylene units residing within their hard segments. For example, the diacetylene units residing in the hard domains can undergo solid-state polymerization upon exposure to heat or radiation, causing the formation of a networklike structure in the hard domains comprised of polydiacetylene chains running perpendicular to the original host polymer chains. The solid-state polymerization of diacetylene groups is a topochemical, lattice-controlled, diffusionless process, which takes place with minimal disruption of the host chain environment.[21] Thus, cross-polymerization increases the rigidity of the hard domains without inducing significant changes in other parameters such as the packing and organization of the hard segments, the degree of phase separation, or the polymer's morphology.

The polydiacetylene backbone that forms as a result

Chart I
Hard Segment Structures of the Polyurethane–Diacetylene Elastomers

MDI-2,4

MDI-5,7

HDI-2,4

HDI-5,7
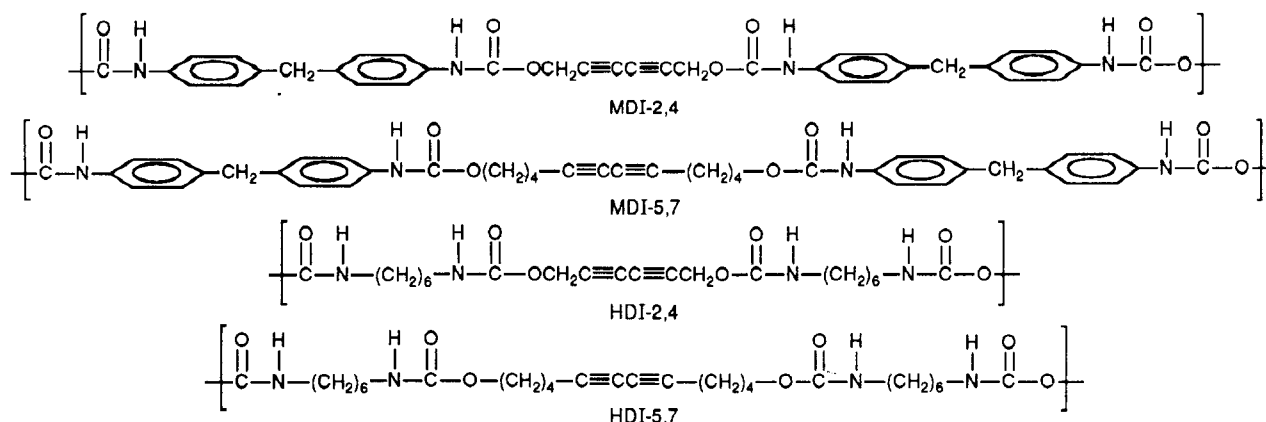
of diacetylene cross-polymerization is highly conjugated and absorbs in the visible region of the spectrum, the shape and position of the resultant absorption bands being highly dependent on the effective conjugation length, which is determined by the local environment of the chain. It is due to this dependence that polydiacetylene-based elastomers exhibit thermochromism and mechanochromism, which are color changes that occur under the influence of heat and stress, respectively.[22] Thus, the sensitivity of the polydiacetylene backbone to its local environment can be employed to detect changes in the hard domain organization as a function of stress. The diacetylene units therefore provide an indication of the order within the hard domains by means of their reactivity and can increase the rigidity of the hard domains in a systematic fashion by undergoing cross-polymerization, while the polydiacetylene backbone serves as a molecular probe that can be utilized to monitor changes in the hard domain organization during deformation.

The polyurethane–diacetylene segmented copolymers are clearly ideally suited for mechanical property studies since, as mentioned previously, the cohesion and rigidity of the hard segment domains can be selectively increased in the solid state without significant changes in the morphology of the material. Although the topochemical polymerization of the diacetylene groups is best facilitated in a crystalline environment, we have found that this chemistry can also be effectively initiated in poorly ordered paracrystalline environments. In the crystalline hard domains, cross-polymerization of the diacetylene groups will produce polydiacetylene chains that, in principle, could span the length of the entire hard domain. In the less ordered hard domain materials, on the other hand, polydiacetylene chains will link together fewer hard segments per conjugated chain, producing a hard domain that is still capable of some molecular mobility. This gives one an opportunity to examine how two quite different hard domain structural modifications will influence the tensile behavior of these materials. It should be mentioned that the ultimate tensile properties of polyurethane elastomers are strongly linked to the deformability of the microstructure. Excessively rigid hard segment domains, therefore, could severely compromise the strength and extensibility of the elastomers. Since modification of the mechanical properties results from a selective hardening of the hard domains, particular attention has been paid to the trade-off between the thermal–mechanical stability and structural integrity of the hard domains and the tensile strength of the elastomers.

This paper and the one that follows describe the results

of our current studies on the influence of hard segment structure and cohesion on the mechanical behavior of the diacetylene-containing segmented polyurethanes. During the process of evaluating these materials, it was found that their ultimate tensile properties were highly sensitive to a number of fundamental variables, such as molecular weight of the copolymer and postprocessing annealing treatments. These latter variables were also found to dramatically influence the effect that diacetylene cross-polymerization within the hard domains had on the mechanical behavior. Thus, to truly understand how the mechanical properties of these materials were modified by this chemistry, it was necessary to first establish the role that these key variables, which are common to all segmented polyurethanes, played in determining their ultimate tensile properties. The first paper of this series describes the effects that molecular weight and annealing history have on the ultimate tensile properties of the diacetylene elastomers. The second paper, on the other hand, describes the influence that diacetylene cross-polymerization has on the mechanical properties of many of the various materials discussed in this paper.

II. Experimental Section

Synthesis. The polyurethane–diacetylene segmented copolymers were synthesized by solution polymerization using the standard two-step reaction commonly employed for segmented polyurethanes. The details of the synthesis can be found in our previous publications.[20] 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 in the elastomers is approximately 2:1:1. The chain extenders contain the diacetylene functionality and introduce it into the block copolymer, where it remains dormant until exposed to radiation, heat, light, etc. The hard segment structures of the elastomers are shown in Chart I. 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 MDI-5,7-2000 refers to an elastomer synthesized from MDI, 5,7-dodecadiyne-1,12-diol, and PTMO of molecular weight 2000. In the "5,7" series there are four carbons separating the diacetylene group from the urethane group, whereas in the "2,4" series there is only one carbon between the diacetylene functionality and the urethane group. In general, this results in the "5,7" series having more ordered hard domains than the corresponding "2,4" series as the additional carbon atoms increase

the flexibility and, hence, crystallizability of the chains (Chart I).

The molecular weights of the elastomers were varied by introducing slight variations in the stoichiometry: the proportion of the diisocyanate was varied from 1.95 to 2.05 as opposed to keeping it constant at 2. It was found that the molecular weights of the elastomers were very sensitive to the stoichiometry, with stoichiometries slightly deficient in the diisocyanate yielding significantly lower molecular weights than those with a slight excess of the diisocyanate. A comparison of the elemental analysis of the lower molecular weight samples with the higher molecular weight samples revealed that they were identical in elemental composition, indicating that they contained the same percentage of hard segments relative to soft segments. This latter fact was also confirmed by infrared analysis. Infrared analysis also indicated that the slight stoichiometric imbalance utilized to vary the molecular weight did not introduce any detectable allophanate linkages into the polymers. Hence the only significant differences between these materials are their molecular weights. Samples of the same elastomer with different molecular weights are distinguished by an extension of their designations with the letters "A", "B", "C", or "D", with "A" representing the highest molecular weight followed in order by "B", "C", and "D".

Sample Preparation. Samples for stress–strain and other measurements 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 for 2 days) under a flow of nitrogen. Both, MDI-5,7-1000 and MDI-5,7-2000 were cast from a mixture of 25% toluene and 75% tetrahydrofuran, while MDI-2,4-1000 was cast from a mixture consisting of 50% toluene and 50% THF. All the HDI-based elastomers were generally cast from a mixture of 75% toluene and 25% THF. The casting solvent greatly influences the morphology of polyurethanes and hence the same casting solvent composition was consistently used for a particular elastomer. 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 cut into strips 0.25 or 0.375 in. wide and 3–4 in. long for tensile testing.

Stress–Strain Measurements. Stress–strain testing was done on an Instron Model 1122, using elastomeric or pneumatic grips to prevent slippage of the samples. Strain was measured with the help of an incremental extensometer, which 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 on the basis of the initial cross-sectional area. On average, at least four stress–strain curves were generated for each material. Generally, the maximum standard deviation among the different samples was less than 5%. In each case the stress–strain curve most representative of its class has been displayed in the figures, though the values for the ultimate tensile strength and strain at failure reported in the tables are an average of four or five curves.

DSC. Differential scanning calorimetry was carried out on a Du Pont 9900 thermal analyzer equipped with a DSC module. Samples were run at 10 °C/min in nitrogen, using 9–12 mg of sample per run. Melting points were taken as the minimum in the endothermic peak and glass transition temperatures determined by the intersection method as the onset of the transition.

Molecular Weight Determination. Molecular weights were determined on a Waters high-pressure liquid chromatograph equipped with two Waters ultrastyragel columns (1000 and 10^4 Å) in series. THF at room temperature, at a flow rate of 1 mL/min, was used as the eluent. The samples were detected by a refractive index detector. Monodisperse polystyrene standards were used for calibration. It should be noted that the molecular weights are reported as weight averages (M_w) and are obtained as relative values in terms of equivalent molecular weight polystyrene standards with the same retention volume and thus are more useful for comparisons rather than as absolute values. The number-average molecular weights of HDI-

5,7-1000 and MDI-5,7-1000 were also determined by osmometry and were found to be consistently less by about 15% as compared to those determined by GPC. Thus, an estimate of the true molecular weights of these materials can be obtained by correcting the reported GPC data downward by about 15%. These results are consistent with the findings of Cooper et al.,[23] who reported that molecular weights determined via GPC using polystyrene equivalents are an upper bound on the true molecular weights, generally being higher by about 20% than the absolute value.

WAXS. X-ray diffraction was performed on a Rigaku RU-200B diffractometer on solvent-cast films using Cu Kα radiation.

III. Results and Discussion

1. Material Characterization. Previous characterization[20] of the polyurethane–diacetylene segmented copolymers has revealed that the elastomers derived from the aliphatic diisocyanate HDI are more phase separated and exhibit substantially more ordered hard segment domains than the MDI-based materials. The samples evaluated during this initial characterization were prepared by either compression molding techniques or solution casting techniques. It was noted in this earlier work that the morphology and molecular organization of the diacetylene-containing segmented copolymers are highly sensitive to the methods used to process these materials. Thus, although the general features that characterize these copolymers remain essentially the same, specific details about their molecular organizations and hence macroscopic properties will most assuredly be influenced by the techniques used to manipulate them into forms suitable for mechanical property evaluation. Since the elastomers described in this study were formed into films by using a different solvent system and casting technique than previously described, it is worth briefly noting some of their relevant structural features.

An example of how variations in casting solvent can influence the behavior of these materials is provided by MDI-2,4-1000. It is previously reported[22] that when MDI-2,4-1000 is formed into films by casting from pure THF or compression molding it does not undergo cross-polymerization when exposed to UV radiation. However, when cast into films by using the toluene/THF solvent mixture described in this paper, MDI-2,4-1000 readily undergoes cross-polymerization as is indicated by the elastomer turning a deep blue color when exposed to UV radiation. This occurs because THF is a good solvent for the hard segments of MDI-2,4-1000 and is also much more volatile than toluene. Thus, films cast from pure THF are formed by very quick evaporation and the time available is simply not sufficient for the system to develop well-ordered hard segment domains. The presence of toluene slows down the evaporation process and also facilitates the development of enhanced hard segment ordering as this solvent is a relatively poor solvent for the hard segments, which means they will start interacting with each other in a mobile state long before the solvent system has evaporated. In general, we find that the casting conditions used in this present study produce materials with much more highly ordered hard domains and, for samples capable of developing long-range crystallinity, more crystalline hard domains.

As evidence for this latter point, we present the WAXS patterns of select solvent-cast polyurethane–diacetylene elastomers in Figure 1. The solvent-cast films of HDI-5,7-1000 and HDI-2,4-1000 exhibit sharper, more intense crystalline peaks at a two θ value of 24° and display a significantly higher ratio of crystalline to amorphous scattering as compared to the same polymers formed into
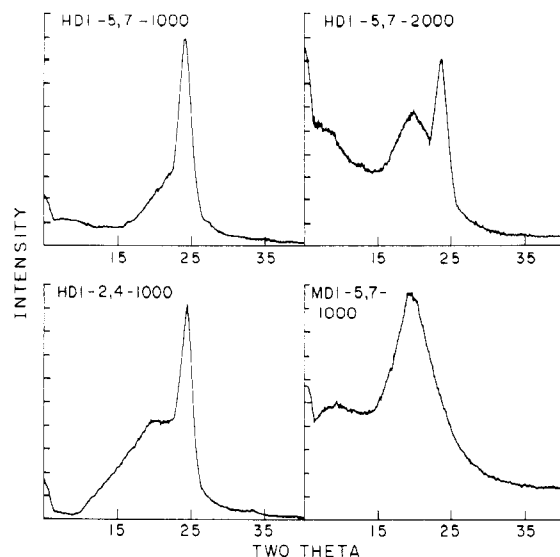
Figure 1. Wide-angle X-ray scattering patterns of the solvent-cast polyurethane–diacetylene elastomers.

films by the original techniques.[20] HDI-5,7-2000 also exhibits a sharp crystalline peak at 24° but its amorphous halo centered at 20° is larger and more prominent when compared to that of HDI-5,7-1000. This is expected due to the larger proportion of amorphous soft segments present in the former material. As found before, the MDI-based elastomers do not exhibit evidence for crystalline hard domains as indicated by the occurrence of only a single, broad amorphous halo centered at about 20° for MDI-5,7-1000 (similar curves were obtained for MDI-5,7-2000 and MDI-2,4-1000). However, as mentioned above, higher order within the hard domains of the MDI-based materials is indicated by the dramatically enhanced reactivity of MDI-2,4-1000 to the UV radiation initiated topochemical polymerization of the diacetylene groups found in the hard domains. This nicely illustrates how the reactivity of the diacetylene groups present in the hard segments can be used to probe changes in the level of hard segment ordering due to the fact that this topochemical process is highly sensitive to the local molecular environment of the diacetylenes. In this case, improved ordering occurs within hard domains exhibiting paracrystalline organizations and produces correlated stacks of hard segments better organized for the solid-state diacetylene polymerization to occur. The creation of very small crystallites in these materials, however, cannot be ruled out by X-ray analysis. In summary, the hard domains of the HDI-based copolymers currently under investigation are highly crystalline as opposed to the MDI-based materials that exhibit only paracrystalline hard domains or weakly developed hard segment crystallinity. Similar results were obtained in earlier work, although the current film-forming technique dramatically improved the hard segment ordering in all of the elastomers discussed in this paper.

The DSC thermograms of the solvent-cast segmented copolymers exhibit features similar to those of the previously reported copolymers, namely, the glass transition temperature of the PTMO soft segments in the low-temperature regime and both hard segment endothermic and exothermic activity in the high-temperature region. The behavior of the elastomers based on PTMO-2000 is similar to that of the PTMO-1000 series elastomers except in the low-temperature regime as demonstrated in Figure 2. These elastomers, in addition to the soft segment glass transition, exhibit endotherms centered at approx-
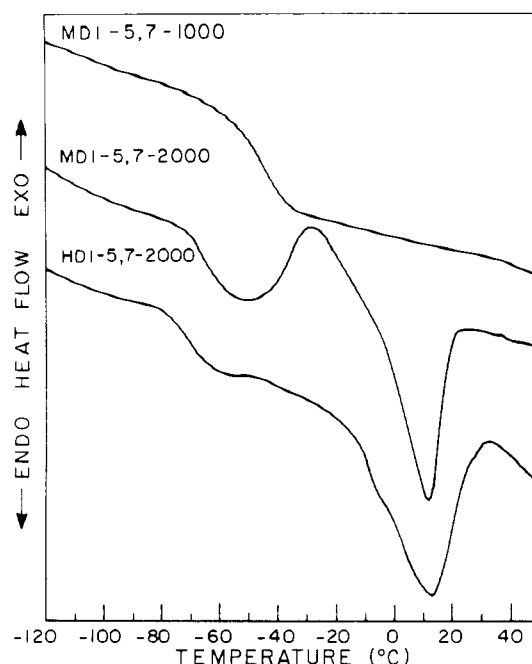

Figure 2. DSC thermograms of select solvent-cast polyurethane–diacetylene elastomers.

Table I
Thermal Transitions of the Polyurethane–Diacetylene Elastomers

material	annealing treatment	low-temp DSC (T_g, T_{exo}, T_{endo}), °C	endotherms, °C	exotherms, °C
MDI-5,7-1000-(D)	90 °C, 45 min	−54, none, none	none, 103 (122)[a]	321
MDI-5,7-2000	90 °C, 45 min	−72, −28, 11	64, 107	315
HDI-5,7-1000	90 °C, 45 min	−73, none, none	46, 107	319
HDI-5,7-2000-(C)	90 °C, 45 min	−76, none, 13	none, 103	331
HDI-2,4-1000	90 °C, 45 min	−73, none, none	45, 94	219

[a] Represents weak high-temperature shoulder.

imately 15 °C, which are attributed to the melting of a crystalline PTMO phase.[24] An exotherm is observed at −28 °C for MDI-5,7-2000, which arises due to cold crystallization of PTMO segments and has also been reported by Wang and Cooper[25] for elastomers derived from PTMO soft segments with molecular weights of 2000 or greater.

The thermal transitions of all of the elastomers whose mechanical properties are currently under investigation are presented in Table I. As can be seen, for the PTMO-1000 series, the HDI-based elastomers consistently display a lower glass transition temperature (about −72 °C) than the MDI-based materials (about −55 °C). Increasing the molecular weight of the PTMO soft segment from 1000 to 2000, however, lowers the glass transition temperature of MDI-5,7-2000 to a value in the same range as that of the HDI-based copolymers. Thus, for elastomers synthesized from PTMO-1000, it is clear that, in addition to more ordered hard domains, the HDI-based materials are more phase separated than the MDI-based materials. Evidence for the higher degree of phase separation in the HDI-based systems is also provided by IR data as reported earlier.[20] This difference in phase mixing is essentially eliminated when these same polymers are created from the higher molecular weight PTMO-2000, which, as discussed repeatedly in the literature,[2]
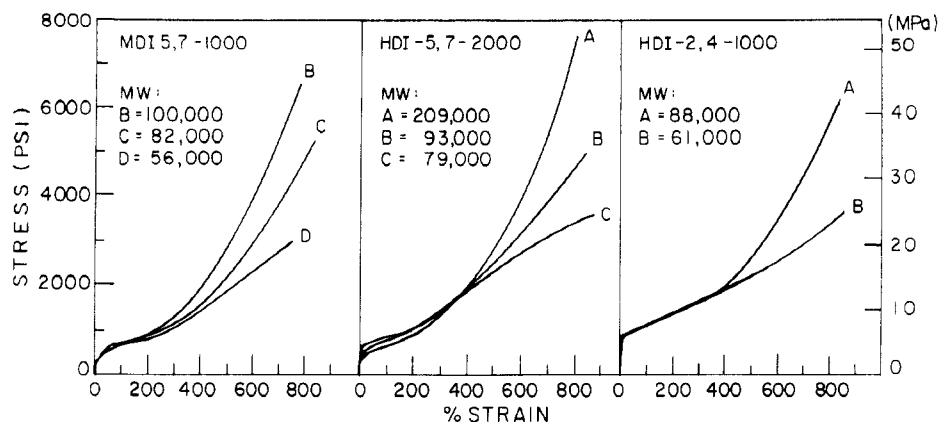
Figure 3. Stress–strain curves of the polyurethane–diacetylene elastomers with different molecular weights. The MDI-5,7-1000 and HDI-5,7-2000 samples were annealed at 90 °C for 45 min while the HDI-2,4-1000 samples were annealed at the same temperature for 4 h.

Table II
Molecular Weight and Ultimate Tensile Properties of the
Polyurethane–Diacetylene Elastomers

material	M_w	annealing treatment	UTS, psi	% strain at failure
MDI-5,7-1000-(A)	107 000	95 °C, 1 h	5800	710
MDI-5,7-1000-(B)	100 000	90 °C, 45 min	6500	760
MDI-5,7-1000-(C)	82 000	90 °C, 45 min	5300	850
MDI-5,7-1000-(D)	56 000	90 °C, 45 min	2400	700
HDI-5,7-2000-(A)	209 000	90 °C, 45 min	7700	820
HDI-5,7-2000-(B)	93 000	90 °C, 45 min	5000	840
HDI-5,7-2000-(C)	79 000	90 °C, 45 min	3500	840
HDI-2,4-1000-(A)	88 000	90 °C, 4 h	6100	820
HDI-2,4-1000-(B)	61 000	90 °C, 4 h	2900	920
HDI-5,7-1000	91 000	90 °C, 45 min	3700	790

promotes better phase separation in segmented copolymers and allows soft segment crystallization to occur.

2. Mechanical Properties—Molecular Weight Effects. The influence of molecular weight on the stress–strain behavior of select polyurethane–diacetylene elastomers is displayed in Figure 3. In all three cases shown, the ultimate tensile strength increases significantly due to an increase in the molecular weight, while, in general, the strain-to-failure decreases only slightly. The small strain modulus of these materials, on the other hand, remains essentially unchanged with increasing molecular weight. It is well-known that the mechanical properties of polymers change with increasing molecular weight up to a threshold value, beyond which they remain essentially constant.[26] Experimental verification of this fact has been provided in the literature[2,27,28] for a number of segmented polyurethanes, which implies that a low molecular weight can significantly reduce the mechanical properties of these polymers. It is clear from Figure 3 that the overall molecular weight of the diacetylene-containing segmented polyurethanes dramatically influences the mechanical properties of these materials. These results therefore reinforce the importance of evaluating materials of equivalent molecular weight when comparing the mechanical properties of various segmented polyurethanes. Since the molecular weights of conventional polyurethane elastomers discussed in the literature are frequently not reported, it is not always clear whether improved properties for samples made by different polymerization techniques or with different molecular structures are related to molecular and/or morphological parameters or are solely due to variations in molecular weight.

It has been reported that, for most conventional polyurethanes based on either polyester or polyether soft segments, the samples prepared by bulk polymerization have

higher molecular weights and better mechanical properties than those prepared by solution polymerization.[2] The ultimate tensile strengths (see Table II) of the higher molecular weight samples of this study are approaching the values reported for bulk-polymerized PTMO-based segmented polyurethanes of similar molecular weights. In addition, the magnitude of the increase in ultimate tensile strength with increasing molecular weight for all the elastomers is very similar to that reported by Schollenberger et al.[28] for segmented polyurethanes of varying molecular weights synthesized via a bulk polymerization technique. The polydispersities of the latter bulk-polymerized materials (PDI's ranging from 6 to 17), however, were significantly greater than those of the polymers discussed in this work (PDI's ranging from 1.5 to 3.5). Probably because in bulk polymerization there can be cross-linking as well as phase separation of the reactants causing different stoichiometries in different regions and hence compositional and structural variations across the material; features that are not probable in solution polymerization. It is clear, however, that the ultimate tensile properties of the polyurethane–diacetylene copolymers are comparable to those of bulk-polymerized conventional polyurethanes of equivalent molecular weight.

The hard segment content of the elastomers presented in this paper is, in general, lower than that found in many of the elastomers whose mechanical properties are discussed in the literature. An increased hard segment content would also be expected to increase the ultimate tensile strength of the elastomer.[29] Thus, caution must be exercised whenever comparisons are made between materials with differences that go well beyond a simple comparison of the weight-average molecular weights of the polymers. In any event, it is clear that molecular weight is a major factor in determining the ultimate tensile properties of segment copolymers made by a variety of polymerization techniques.

A number of molecular weight dependent variables have been identified that could be responsible for the variations in mechanical properties observed with increasing molecular weight. For example, the number of hard and soft segments that have one end free, i.e., not chemically bound on both ends, the number of hard domains a single chain passes through, the molecular packing and ordering within the hard domains, and the number of trapped chain entanglements and interlocking loops existing in the soft phase are all believed to play an important role. All of these variables could, in turn, influence the elastomer's ability to hold off catastrophic failure long enough to allow other reinforcing mechanisms such as chain ori-

entation and strain-induced crystallization of the soft segments to occur at higher strains. In order to explain the dependence of mechanical properties on the molecular weight of polyurethanes, Speckhard and Cooper[2] postulated that the number of bonds in the interfacial area and the number of domains a single elastomeric chain passes through are important, as these factors would be decreased by a reduction in molecular weight. In addition, the number of trapped chain entanglements and interlocking loops existing in the soft phase would also be of significance, because any change in molecular weight would clearly effect this number, which is known to have an effect on mechanical properties. Thus, to a first approximation, changes in all of these parameters can be responsible for the molecular weight dependence found in segmented polyurethanes.

In the case of the polyurethane–diacetylene elastomers, it can be seen that, at high strains, the effect of increasing the molecular weight is to increase the level of stress needed to achieve a given level of strain. This effect manifests itself as a distinct upturn in the stress–strain curve, which is most dramatic in the higher molecular weight samples. Strain hardening effects of this type have been typically attributed to either limited chain extensibility, which results when portions of the soft segments with ends firmly anchored in the matrix become fully extended, or strain induced crystallization of the soft segments, which creates additional plastic domains that can mechanically reinforce the polymer. Both of these processes will be facilitated by the development of a more effective network structure that restricts the amount of chain slippage and molecular relaxation that can occur in the copolymer. These latter effects would prevent the chains from becoming highly aligned or extended during stretching. Thus, as the molecular weight of the copolymer increases, the elastic network becomes more firmly established due to the development of more effective virtual cross-linking by the hard domains and the concomitant increase in physical chain entanglements.

It is unclear at this point whether the upturn in the stress–strain curves, which is most pronounced in the higher molecular weight samples, is related to limited chain extensibility, strain-induced crystallization, or both. In the case of HDI-5,7-2000, however, we have found that strain-induced crystallization does play an important role in determining the mechanical behavior of this material. Indirect evidence for this is provided by the unusually large level of plastic deformation (permanent set) found in the higher molecular weight samples of this material after stretching. This indicates that some of the crystalline regions created by strain-induced crystallization of the soft segments during stretching remain intact when the sample is relaxed to its unstrained state, thereby preventing elastic recovery. Although plastic deformation associated with irreversible hard domain orientation and deformation is quite common in these materials, the level far exceeds that expected for a material with such a low hard segment content (about 22 wt % hard segments). Direct evidence for this comes from WAXS data generated from high molecular weight samples that were stretched to high strains and relaxed back to an unstrained state. As can be seen in Figure 4, these samples develop an intense, well-defined reflection at a 2θ value of 19.8° and a smaller peak at 37.4°, which have previously been attributed to the formation of a crystalline PTMO phase in the copolymer.[30] The presence of strain-induced crystallization in segmented polyurethanes based on PTMO soft segments with molecular weights greater than 2000 is well documented in the literature, as is its effect on
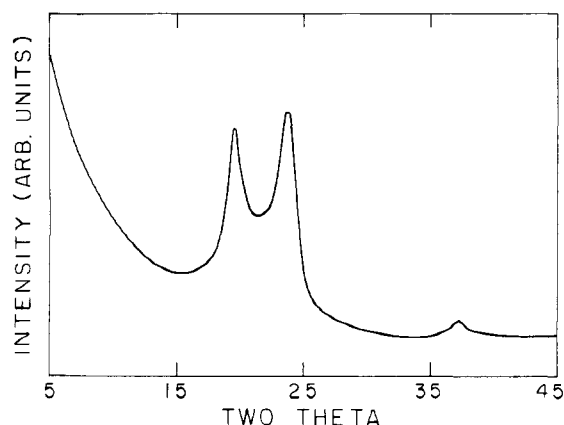

Figure 4. Wide-angle X-ray scattering pattern of HDI-5,7-2000 recorded in the relaxed state after stretching a sample to a strain of about 600%.

increasing the level of residual deformation remaining after stretching.[31] The fact that the soft segments exist in an environment that is conducive to crystallization is supported by the presence of a soft segment melting endotherm in the DSC curve (see Figure 2), which is not completely cleared until about 30 °C. Thus, strain-induced crystallization is clearly indicated for HDI-5,7-2000. For the elastomers based on PTMO soft segments with a molecular weight of 1000, it is reasonable to conclude that the upturn is related to limited chain extensibility and possibly strain-induced crystallization. Preliminary optical studies indicate that the higher molecular weight MDI-based copolymers with PTMO-1000 soft segments also undergo strain-induced crystallization. To date, no evidence for strain-induced crystallization in the HDI-based PTMO-1000 materials has been found.

In conclusion, it can be stated that the overall molecular weight of the polyurethane–diacetylene segmented copolymers plays a significant role in the determination of their ultimate tensile properties. The increase in ultimate tensile strength that occurs with increasing molecular weight is a direct result of the presence of more highly entangled polymer chains, which, due to restrictions on their long-range mobility imposed by the two-phase domain morphology, i.e., by having more hard segments per chain anchored in hard domains, can act as effective cross-link junctions. The next paper in this series will show that the response of the mechanical properties of these polymers to diacetylene cross-polymerization is also strongly influenced by variations in molecular weight.

3. Thermal Properties—Effects of Annealing. If one accepts the premise that the mechanical properties of segmented polyurethanes are strongly linked to the two-phase microstructure of these materials and the level of ordering (both molecular and supermolecular) present within the polymer, then it stands to reason that it should be possible to modify the relevant mechanical properties of these polymers by inducing changes in these parameters. To examine this feature in the diacetylene-containing segmented polyurethanes, we set out to investigate the influence of annealing on their mechanical and thermal properties. In those cases that annealing produced changes in the thermal properties of the elastomers, significant changes in the ultimate tensile properties were also observed. Needless to say the changes due to annealing are highly dependent on the temperature and duration of the treatment. The following discussion will focus on the effects of annealing on the mate-
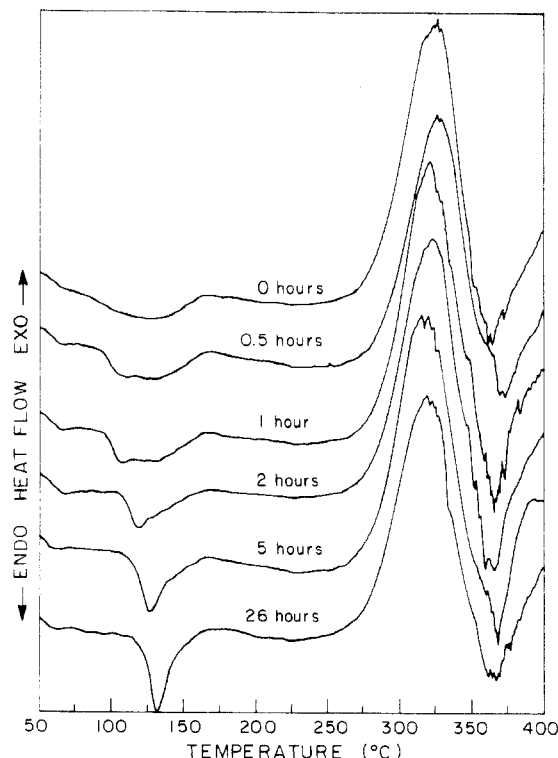
Figure 5. DSC thermograms of MDI-5,7-1000 (M_w = 107 000) as a function of annealing time at 95 °C.

rials that showed the most dramatic changes as a result of this treatment.

The DSC thermograms of MDI-5,7-1000-(A) (M_w = 107 000) as a function of annealing time at a temperature of 95 °C are presented in Figure 5. The DSC trace of the as-cast, unannealed elastomer exhibits two broad ill-defined endotherms and a large exotherm. The exotherm, which appears at about 320 °C, results from a liquid-phase thermal polymerization and degradation of the diacetylene groups.[20] The weak lower temperature endotherm (60 °C) is commonly attributed to the thermal disruption of hard domains with only limited short-range ordering, as is frequently observed[32,33] in conventional MDI-based segmented polyurethanes. The response of this peak to annealing and its shape and breadth, however, suggest that it may in fact be the glass transition temperature of the amorphous regions of the hard domains. The broad, higher temperature endotherm extending from approximately 90 to 160 °C is due to the disruption of hard domains with longer range order and possibly small crystallites not detectable by WAXS techniques. Annealing the material does not seem to have any significant effect on the lower temperature endotherm, with the exception of moving it around by a few degrees. The higher temperature endotherm, on the other hand, is dramatically changed with annealing as it becomes better defined and shifts systematically to higher temperatures with longer annealing times.

The breadth of this endotherm can be explained by the existence of a distribution of hard domains of various sizes within which the hard segments achieve various states of short-range paracrystalline order. Upon heating, disruption of these ordered regions occurs over a wide range of temperature, with the smaller, less ordered regions within the hard domains disordering before the larger, more ordered regions due to surface and internal energy effects. By annealing at temperatures near the onset of this transition, the more disordered regions of the hard

domains are slowly transformed into larger, more ordered regions.

Examination of the carbonyl and N–H stretching regions of this material as a function of annealing by infrared analysis[34] revealed that the percentage of interurethane hydrogen bonding did not change significantly during this process. It was observed, however, that interurethane hydrogen bonds associated with ordered regions of the hard domains did increase at the expense of interurethane hydrogen bonds associated with disordered regions of the hard domains. The interpretation of the infrared data was based on the recent work of Painter et al.,[35] which shows that, in addition to determining the amount of nonbonded urethane carbonyl groups, it is possible to distinguish between hydrogen-bonded carbonyls present in either ordered or disordered regions of the polymer. Thermal analysis revealed that the glass transition temperature of the PTMO soft segments does not change appreciably on annealing, thus also indicating that the degree of phase separation is not effected by the thermal treatment. In fact, the soft segment glass transition temperature increased slightly due to a small amount of increased phase mixing that inevitably accompanies annealing at high temperatures. These results indicate that the size of the hard domains (and related interfacial area) remains essentially constant during the annealing process, suggesting that changes are, for the most part, only taking place within the existing hard domains and are not related to the diffusion of hard segments dissolved in the soft segment matrix into the hard domains. This effect has also been reported by other researchers and is believed to lead to an increase in long-range ordering within these materials.[32,33,36]

More recent studies on segmented polyurethanes employing small-angle X-ray scattering[37] to investigate the effects of annealing report increased phase separation and an increase in the size of the hard domains due to annealing. However, the changes are most significant in the case of less phase-separated systems such as the polyester-based polyurethanes as compared to more phase-separated systems such as the polyether-based systems where the changes at the best are very slight. Hence, it seems reasonable to conclude that the major effect of annealing is improved ordering within the hard domains. We cannot, however, rule out the possibility that some of the hard domains have merged to form larger domains.

The general effect of annealing the MDI-5,7-1000 materials is to ultimately convert a very broad endotherm centered about 120 °C into an intense, well-defined endotherm centered at about 130 °C. These changes reflect a transition within the hard domains from a state of poorly developed order to a state of well-developed longer range order. As to be expected, the time it takes to complete this transition depends strongly on the annealing temperature, with higher temperatures and the associated increased hard segment mobility producing the fastest approach to this near equilibrium state of improved order. For example, for samples annealed at 90 °C, the changes in the endotherm follow a similar pattern as seen in Figure 5, although the material never quite develops the sharp endotherm observed at about 130 °C even after an annealing time of 26 h. Annealing samples at 105 °C, on the other hand, very quickly generates (usually within 45 minutes) a sharp, well-defined endotherm at about 130 °C that is very similar in breadth and intensity to the endotherm created after annealing for 26 h at 95 °C. It should be noted at this time that annealing the MDI-5,7-1000 samples does not change their WAXS patterns, which,
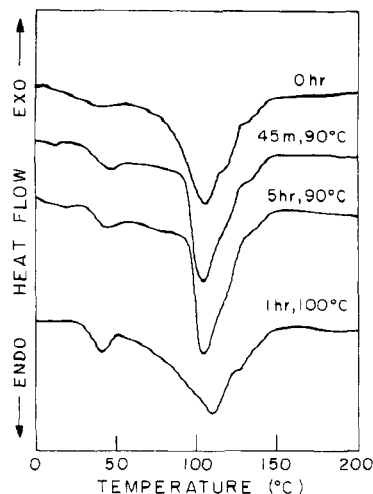
Figure 6. DSC thermograms of HDI-5,7-1000 as a function of annealing time and temperature.

Figure 7. Stress–strain curves of MDI-5,7-1000 (M_w = 82 000) and HDI-5,7-1000 as a function of annealing time and temperature.

as discussed earlier, display only an amorphous scattering peak. This indicates that improved ordering takes the form of long-range paracrystalline order and not true crystalline order. The existence of very small crystallites, of course, cannot be completely ruled out by X-ray techniques.

The DSC thermograms obtained from samples of HDI-5,7-1000 after annealing at either 90 or 100 °C are presented in Figure 6. Annealing at 90 °C results in a narrowing of the melting endotherm centered around 107 °C and a intensification of the small endotherm at about 45 °C. However, no significant changes occur in the DSC traces when the annealing time is increased from 45 min to 5 h at this temperature. It might be expected from our MDI-5,7-1000 results that annealing HDI-5,7-1000 at the higher annealing temperature of 100 °C would yield a more intense, well-defined endotherm shifted to an elevated temperature. However, in contrast to this, a broad and ill-defined endotherm is obtained after annealing at 100 °C, although the peak does shift to a higher temperature and develops a shoulder at a still higher temperature.

Recall that HDI-5,7-1000 is comprised of highly crystalline hard segment domains as indicated by WAXS data. Thus, annealing at 90 °C, which is just below the melting point of the majority of the crystallites, has the effect of eliminating defects within the crystalline regions and improving the overall order of smaller, less defined crystalline domains. In this case, it is probable that the smaller crystallites that are melted during the annealing treatment are reformed and combined with the larger more stable crystallites. From these results, it appears that the improved order that accompanies this process is achieved very quickly at 90 °C. As the annealing temperature moves closer to the melting point of the hard domains (annealing at 100 °C), thermal disruption and melting of larger crystalline regions takes place, which is accompanied by additional phase mixing of the soft and hard segments. This latter effect is known to occur in polyurethanes with hard segments forming paracrystalline domains[38] and is believed to result from the enhanced thermodynamic compatibility of the hard and soft segments at elevated temperatures. Thus, upon cooling from this pseudomelt, some of the larger more robust hard domains can reform into more crystalline entities, whereas a significant portion of the hard segment material will not be able to reestablish a crystalline organization over the time period that the sample cools to room tempera-
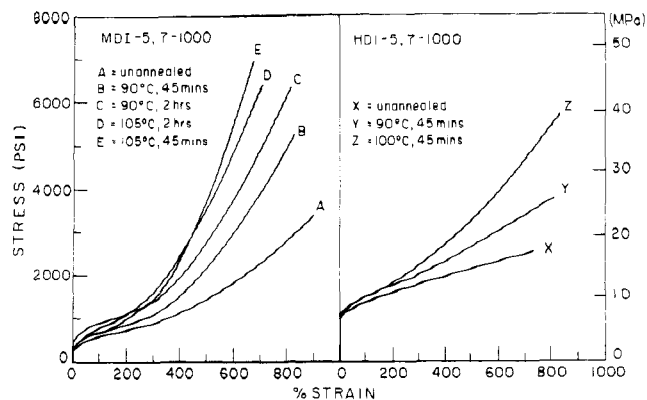
ture. The net result is a material that is comprised of a wide range of different crystalline orders and crystallite sizes and is overall in a more more disordered state. A comparison of the WAXS data of the unannealed HDI-5,7-1000 with that of the material annealed for 1 h at 100 °C indicates a significant increase in the amount of amorphous scattering upon annealing at this temperature. Thus, WAXS results support the conclusion that annealing at 100 °C causes a majority of the hard domains to melt thereby producing a more disordered material upon cooling to room temperature that is comprised of a wide range of crystalline regions of various levels of order.

In summary, annealing of these two particular elastomers at elevated temperatures results in improved ordering within the hard domains, which, in turn, would be expected to increase the mechanical integrity of the hard domains due to the enhanced hard segment cohesion that results from having more optimized hard segment organizations with fewer defects. For materials that exhibit true crystalline order within the hard domains, annealing at temperatures very close to the melting point can also introduce disorder into the material. We now turn our attention to how these various annealing treatments influence the mechanical behavior of the segmented copolymers.

4. Mechanical Properties—Effects of Annealing. The stress–strain curves of MDI-5,7-1000-(B) (M_w = 82 000) and HDI-5,7-1000 (M_w = 91 000) obtained after various annealing treatments are presented in Figure 7. As can be seen, annealing of these elastomers has a very dramatic effect on their ultimate tensile properties. For HDI-5,7-1000 annealed at 90 and 105 °C and MDI-5,7-1000-(B) annealed at 105 °C, it was found that the most significant changes in the ultimate tensile properties occurred during the initial hour of annealing at the given temperatures. Thereafter, upon further annealing, the tensile strength of the polymer remained essentially the same or actually decreased by a small amount. For MDI-5,7-1000-(B) annealed at 90 °C, however, it was found that optimum ultimate tensile properties were obtained only after at least 2 h of annealing. These observations are consistent with DSC results which show that the major changes in the endotherms associated with hard segment ordering of both HDI-5,7-1000 annealed at 90 and 105 °C and MDI-5,7-1000-(B) annealed at 105 °C occur during the first hour of annealing, whereas, the changes in the endotherm of MDI-5,7-1000-(B) annealed at 90 °C follow a more gradual response to annealing time. This latter effect is particularly prevalent during the annealing of a higher molecular weight sample, MDI-5,7-1000-
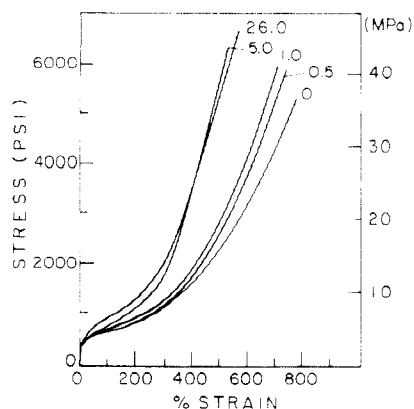
Figure 8. Stress–strain curves of MDI-5,7-1000 ($M_w = 107\,000$) as a function of annealing time at 95 °C. Numbers indicate annealing time in hours.

(A) ($M_w = 107\,000$), at 95 °C, where it was found that the maximum ultimate tensile properties were obtained after about 5 h of annealing (see Figure 8). As can be seen in Figure 5, the endotherms of this material show a gradual time-dependent response to annealing. Thus, the major changes in the DSC thermograms of these materials brought about by annealing all correlated well with the changes observed in their ultimate tensile properties.

Specifically, for MDI-5,7-1000, it was found that annealing treatments that most effectively shift the DSC endotherm to its highest temperature position (about 130 °C) and simultaneously decreased the breadth of this transition produce the most dramatic improvements in tensile strength. Thus, annealing at 90 °C for long times is not as effective as annealing at 105 °C for shorter times. This latter treatment very quickly establishes improvements in the long-range ordering within the hard domains (as evidenced by DSC) and produces the most dramatic changes in the tensile strength. Annealing at intermediate temperatures (such as 95 °C), which more slowly shifts the endotherm to its maximum value of about 130 °C, ultimately produces changes in the tensile strength comparable to the higher temperature annealed material. In all cases, once an optimum annealing time at a given temperature is surpassed, the material shows no significant improvement in properties (in some cases, a slight decrease actually occurs after this point), even though the DSC endotherm may continue to show modest changes with further annealing.

In the case of the MDI-5,7-1000 segmented copolymer, we explain the changes in ultimate tensile properties brought about by annealing in the following way. First, it is to recognized that the major effects of annealing are to (a) increase the amount of stress required to produce a given value of strain, (b) decrease the overall strain-to-failure, and (c) increase the small strain modulus of the material. In essence, annealing shifts the point at which the upturn of the stress–strain curve appears to slightly lower strains and dramatically increases the tensile strength of the system. As indicated by DSC analysis, annealing promotes improved ordering within the hard domains and eliminates many of the weakly associated hard segment regions of the copolymer. Thus, the overall effect of annealing is to increase the mechanical integrity of the hard domains by optimizing the range of interactions between hydrogen-bonded hard segments thereby improving the strength of intermolecuar forces operating within the hard domains. This improved hard domain cohesion, in turn, reduces the amount of stress bias molecu-

lar relaxation that can take place during the initial stages of elongation. Molecular relaxation from locally high stresses can take a number of different forms, such as the pulling of individual hard segments out of the hard domains by soft segments that have reached the limit of their extensibility or the localized deformation of larger regions of the hard domains. In both cases, these processes would become more difficult since the more strongly interacting hard segments offer a greater resistance to chain slippage and plastic deformation. Thus, the more cohesive hard domains remain intact during the early stages of stretching, allowing the soft segment phase to reach a state of full extension and orientation at lower strains. The net effect is that the two-phase microstructure requires more energy to deform and is significantly less extensible.

The situation for HDI-5,7-1000 appears to different from that of the MDI-5,7-1000 material. In this case, as can be seen in Figure 7, annealing increases the ultimate tensile strength of the elastomer but does not reduce the strain to failure of the material. In fact, it tends to increase the ultimate strain by a modest amount. To understand this fundamental difference, the mechanism of deformation of this material must be considered.

Looking first at the unannealed material, it can be seen that the stress–strain curve displays a distinct lack of any upturn at higher strains as was clearly observed with the MDI-5,7-1000 family of copolymers. The small strain modulus of this material is also significantly larger than that of its MDI counterpart. This latter observation indicates that the crystalline hard domains of HDI-5,7-1000 form a semicontinuous, highly interconnected hard domain morphology, which means that the hard domains are capable of opposing deformation of the microstructure and supporting load even at small strains. This type of morphology is a direct consequence of the high degree of phase separation exhibited by this material and the corresponding increase in hard domain volume fraction that accompanies such a state. In other words, with fewer hard segments dissolved in the soft segment matrix, the effective volume occupied by the hard domains increases relative to a less phase separated system with a similar hard segment content. The higher level of hard domain content and interconnectivity found in this material, coupled with the high degree of crystallinity of its hard domains, apparently restricts the ability of the soft segments to become highly oriented and severely limits the amount of strain-induced crystallization that can occur at high strains. Thus, at low strains, the hard domains offer a high resistance to deformation and remain essentially intact, possibly becoming partially oriented during tensile elongation. This results in a material with a high initial modulus. Beyond a critical stress level, strain softening occurs at the hard domains begin to irreversibly and gradually deform in response to higher stress levels. This latter mode of deformation takes place in such a way as to prevent the soft segments from becoming fully extended or crystallizing. The basic features of this mechanism of deformation are consistent with previously reported optical studies on this material.[22]

For the HDI-5,7-1000 sample annealed at 90 °C for 45 min, the effect of annealing is to again improve hard domain cohesion, in this case by eliminating defects within the larger crystalline domains by reforming the smaller, less ordered domains into more structurally intact entities (see DSC section). Improved ordering within the hard domains, therefore, creates a microstructure that requires a higher level of stress to obtain a given state of strain

and, hence, the modest increase in tensile strength observed in this copolymer. Since the primary mechanism of deformation for this material centers on a gradual deformation and restructuring of the microstructure with limited opportunities for extensive soft segment orientation or soft segment crystallization to take place, the strain to failure is not influenced by improvements in hard segment cohesion. In other words, the material still elongates by an irreversible deformation of the hard domains, it just takes more energy to overcome the stronger secondary forces holding the hard domains together.

The HDI-5,7-1000 sample annealed at 100 °C for 45 min displays a remarkable improvement in ultimate tensile strength and also exhibits a pronounced upturn in its stress–strain curve at higher strains (about 200%). It is clear that annealing this material at a temperature very close to its melting temperature dramatically improves its ultimate tensile strength. As the DSC data for this sample show that this particular annealing treatment introduces substantial disorder into the material, it is not unreasonable to conclude that its morphology and domain microstructure have been significantly altered during annealing. This, most likely, is also accompanied by increased phase mixing of the soft and hard segments at the domain boundaries. Increased phase mixing at the domain interfaces, in turn, would be expected to improve the adhesion between the normally highly incompatible hard domains and soft segment matrix, thereby improving the strength of the material. Many researchers believe that diffuse interfacial zones are preferred over sharp boundaries for enhanced mechanical properties.[2] In addition, it appears that the morphology has been modified in such away as to allow some of the soft segments to become aligned during stretching. All of these changes could combine to create a much stronger material further reinforced by additional strengthening mechanisms such as strain-induced crystallization of the soft segments, which was not possible in the unannealed material. Clearly, more work is needed to establish the origin of this material's dramatic change in mechanical properties upon annealing.

Preliminary annealing studies were also conducted on HDI-2,4-1000, which, as anticipated, exhibited very similar behavior to HDI-5,7-1000 in terms of the response of its mechanical properties to annealing. Recall that HDI-2,4-1000 also exhibits a well-phase-separated domain morphology with highly crystalline hard segment domains. The stress–strain curves of this material found in Figure 3 show that suitable annealing treatments (and molecular weight) can also produce a strain hardening effect, albeit at much higher strains than that observed in the MDI-based polymers. It should also be noted that annealing of any of the elastomers at temperatures that did not significantly alter their DSC thermograms (typically temperatures below 70 °C) did not create any significant changes in their stress–strain behavior. This latter observation confirms that the effects of annealing are not due to simply removing residual solvent trapped in the material during solvent casting.

IV. Conclusions

The obtainment of high strength and good extensibility in segmented polyurethanes requires the development of a firmly established network structure comprised of strongly interacting hard segments aggregated into separate domains and a soft segment phase containing highly entangled soft segments. Optimum properties are realized when the cohesive forces holding the hard segment domains together are strong enough to resist large-scale, stress-biased molecular relaxations in the form of chain slippage and hard domain disruption, which would be expected to decrease the effectiveness of the network structure created by the existence of the phase-separated hard domains. In those cases where hard domain reorganization is the primary mode of deformation, stronger hard domains increase the tensile strength by offering more resistance to their disruption. If, on the other hand, the primary mode of deformation is related to a significant extension of the soft segment phase, increased tensile strength results when more cohesive hard domains remain intact longer during stretching, allowing the soft segment phase to reach a state of full extension and orientation at lower strains. The latter mode of deformation creates the strongest materials as it allows other mechanisms of reinforcement such as strain-induced crystallization of the soft segment to take place.

In this study, we have found that the ultimate tensile properties of diacetylene-containing segmented polyurethanes depend strongly on the overall molecular weight of the copolymer and its particular thermal history. In all cases, increased molecular weight produces a much stronger material with a more pronounced upturn observed in its stress–strain curve at lower strains. These observations were attributed to the development of a copolymer with more mechanically stable cross-links resulting from the more elastically effective entangled state created by the presence of longer chains capable of contributing more hard segments per chain to the phase-separated hard domain structure. The mechanical properties of the higher molecular weight copolymers examined in this work were found to be comparable to those of conventional segmented polyurethanes believed to exhibit exceptional mechanical properties.[2]

Annealing treatments were found to dramatically improve the mechanical properties of the elastomers. Thermal analysis revealed that annealing at suitable temperatures increased the cohesive forces operating between the hard segments, thereby improving the structural integrity of the hard domains. This effect typically manifested itself as a shifting of the endotherm associated with the level of order within the hard domains to higher temperatures accompanied by a narrowing of this peak indicating improved hard segment ordering within the hard domains. In all cases where annealing resulted in more ordered hard domains and, hence, improved hard domain cohesion, the ultimate tensile properties were found to increase significantly. The particular effect that annealing had on the mechanical properties was highly dependent on the mechanism of deformation operating in the copolymer. In some cases, annealing significantly decreased the strain to failure of the material, whereas in others, it remained essentially constant.

Two distinctly different mechanisms of extension were observed in the polyurethane–diacetylene copolymers. For materials containing highly crystalline hard domains and well-phase-separated morphologies, it was found that the primary mode of deformation required continuous disruption and reorganization of the hard domains. For elastomers based on PTMO soft segments with an average molecular weight of 1000, this process takes place without the benefits of significant soft segment extension and/or strain-induced crystallization as evidenced by the lack of a significant upturn in the stress–strain curves. In this case, it is believed that the higher hard domain content that results from a more phase-separated domain morphology creates a more interconnected hard domain microstructure, which increases the small strain modu-

lus of the material and effectively inhibits the development of highly extended soft segments. Alternatively, it is possible that the shapes (and possibly sizes) of the crystalline hard domains create a nonuniform loading of the material resulting in locally high stress concentrations during stretching that can only be alleviated by plastic deformation of the hard domains. In either case, it is clear that tensile elongation is only achieved by significant disruption of the hard domains. This type of behavior was observed in both HDI-5,7-1000 and HDI-2,4-1000. Annealing of these copolymers causes an improvement in tensile strength due to the increased resistance of their hard domains to mechanical disruption brought about by improved hard domain cohesion. No significant decrease in the strain to failure of these materials was observed as a result of annealing.

The second mechanism of deformation, which was observed in the less phase-separated MDI-5,7-based materials, involves tensile elongation primarily by extension of the soft segments, which, for samples annealed to create improved hard domain cohesion, occurs, at least during the early stages of elongation, without extensive disruption of the hard domains. In this case, improved hard domain cohesion limits the amount of hard domain disruption and chain slippage that can take place at low strains therefore allowing the soft segments to reach the limit of their extensibility and perhaps crystallize at much lower strains. The overall effect of annealing for these materials is to increase the ultimate tensile strength and decrease the ultimate strain to failure.

We believe that the conclusions drawn from this work are not unique to the diacetylene elastomers but rather are applicable to the general behavior of segmented polyurethanes with similar hard segment contents, degrees of phase mixing, hard segment crystallinity, etc. The following paper reinforces these conclusions by showing that systematic increases in the hard domain cohesion of segmented polyurethanes introduced by cross-polymerization of diacetylene groups in the hard domains has an effect on the mechanical properties similar to that of annealing, which is also dependent on the basic mechanism of deformation active in the copolymer. The essential features of the two different mechanisms of deformation have also been verified by visible dichroism studies of partially cross-polymerized materials, which will be presented in a future publication.

Registry No. (MDI-5,7)(PTMO) (block copolymer), 109327-11-9; (MDI-2,4)(PTMO) (block copolymer), 107702-75-0; (HDI-5,7)(PTMO) (block copolymer), 116076-21-2; (HDI-2,4)(PTMO) (block copolymer), 107702-72-7.

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