Registry No. 1, 1107-00-2; **4a** (*n* = 1), 102852-94-8; **4a**, 102920-40-1; **4b**, 102920-41-2; **4c**, 102920-42-3; **6a**, 102920-39-8; **6b**, 102920-38-7; $(Ph_3P)_2Ni(CO)_2$, 13007-90-4; $C_6H_5NH_2$, 62-53-3.

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Synthesis and Characterization of Polyurethane–Diacetylene Segmented Copolymers

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ABSTRACT: Polyurethane segmented copolymers containing the reactive diacetylene group within the hard segments were synthesized from three basic monomers: a low molecular weight hydroxyl-terminated polyether, a diacetylenediol, and a diisocyanate. Thermal and spectroscopic analysis revealed a two-phase domain structure in which the diacetylene groups reside in hard-segment domains dispersed throughout a continuous matrix of the flexible soft-segment material. In such an arrangement, the diacetylene units can be cross-polymerized to the poly(diacetylene) form within these domains (via heat or radiation) without disruption of the flexible nature of the elastomeric phase. The result is a material that exhibits the optical properties of a poly(diacetylene) and the mechanical properties of a tough highly extensible elastomer. The thermal–mechanical properties of the elastomers could be dramatically modified by cross-polymerization of the diacetylene groups. The polyurethane–diacetylene elastomers represent a new class of materials with a unique combination of mechanical and optical properties.

I. Introduction

The topochemical solid-state polymerization of diacetylene monomers to fully conjugated polymers with extended chain geometries has been exploited with increasing zeal over the past 10 years in an effort to prepare polymeric systems with novel electrical, optical, and mechanical properties.[1] The fully extended unsaturated backbone of the poly(diacetylenes) gives rise to many of the novel properties of these materials such as their nonlinear optical properties,[2] thermochromic properties,[3] and highly anisotropic mechanical properties.[4] Although the backbone structure is primarily responsible for the optical and electrical properties of these unique materials, it is becoming increasingly more evident that dramatic changes in the behavior of these polymers can be introduced by the manipulation of the structure of their side groups. Thus, by varying the composition and organization of the side groups, it is possible to obtain a wide variety of diacetylene polymers with a broad range of physical properties. However, even with this tremendous capability to molecularly engineer the properties of the poly(diacetylenes) via manipulation of their side groups, the construction of a poly(diacetylene) with the optimum combination of optical, mechanical, and processing behaviors has not been realized. Indeed, a highly desirable material would be a polymer exhibiting the novel optical properties of a poly(diacetylene) and the mechanical behavior of a tough, highly extensible elastomer or fiber.

In addition to the polymerization of the monomeric diacetylenes, it has been demonstrated that the diacetylene functionality can be incorporated in the repeat structure of a polymer backbone and will undergo solid-state cross-polymerization on exposure to suitable radiation or by annealing at elevated temperatures.[5-8] In this case, the resultant side groups are actually polymer chains connecting the poly(diacetylene)-conjugated backbones in a networklike structure. These materials have recently been referred to as macromonomers[7] due to the systematic polymerization of the diacetylene units within the backbone of the host polymer, giving rise to this final networklike structure. The term cross-polymerized[7] is used to indicate that polymer chains are formed at regular intervals along the original polymer backbone as opposed to the typical random cross-linking that many polymers undergo when exposed to radiation. Recently, this approach has been extended to segmented copolymers[9,10] in which the cross-polymerization reaction can be restricted to phase-separated domains containing the diacetylene groups. While a number of different macromonomers have been synthesized and subsequently cross-polymerized, a detailed investigation of the structure–property relationships in these novel materials has not emerged. This is unfortunate since it is expected that with the right combination of structure and molecular organization, these materials would exhibit extremely interesting optical properties and novel mechanical behavior. The properties

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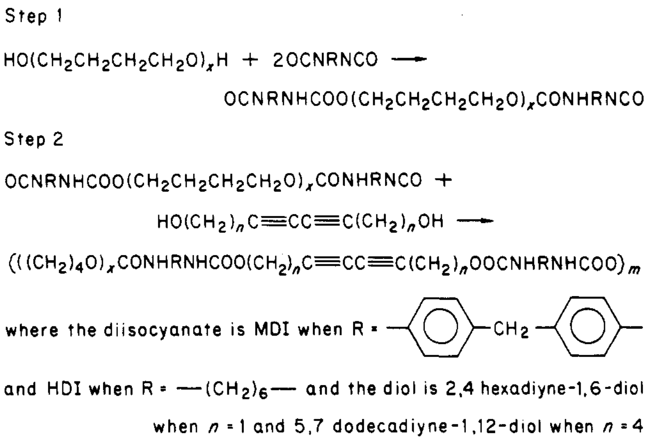
Scheme I



of these polymers could also be readily modified by controlling the extent of cross-polymerization of the diacetylene groups.

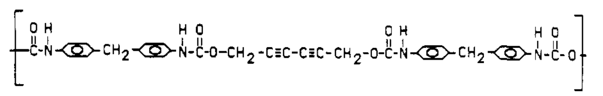
In order to obtain polymeric systems that exhibit the desired combination of optical and mechanical properties, we have incorporated the reactive diacetylene functionality in the hard-segment structure of polyurethane segmented block copolymers. The characteristic properties of polyurethane elastomers in general can be attributed directly to the morphology of the polymer which consists of microphase-separated domains of the hard segments distributed throughout a matrix of a soft-segment material with a low glass transition temperature.[11] In the case of the polyurethane–diacetylene elastomers discussed in this paper, the polymer is composed of long flexible "soft" poly(tetramethylene oxide) segments alternating with "hard" urethane–diacetylene-based segments. The incompatibility of the hard and soft segments results in aggregation of the diacetylene-based segments into a separate phase. It is within these isolated domains that cross-polymerization of the diacetylene groups converts the hard domains into a poly(diacetylene) networklike structure.

These materials exhibit the mechanical behavior of polyurethane segmented copolymers and the optical properties of the poly(diacetylenes). In this paper, the synthesis and characterization of these novel materials will be described with an emphasis on their polyurethane-like properties. Specifically, the effects of cross-polymerization on the thermal–mechanical properties of the elastomers will be examined. The following paper will describe the optical properties of these materials and how they are influenced by temperature and stress.

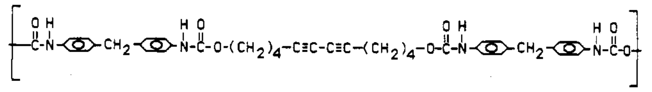
II. Experimental Section

A. Synthesis of Polyurethane–Diacetylene Segmented Copolymers. 1. Preparation of Reactants. Poly(tetramethylene oxide) (PTMO) (Quaker Oats Co.) was dried under vacuum (1 μm) at 80 °C for 3 days to remove water. 4,4′-Methylenebis(phenyl isocyanate) (MDI) (Eastman Kodak) was vacuum distilled at 150 °C (20 μm) and stored under dry nitrogen. Hexamethylene diisocyanate (HDI) (Polysciences) was vacuum distilled at 90 °C (10 μm) and stored under dry nitrogen. 2,4-Hexadiyne-1,6-diol (Farchan Laboratories) was recrystallized from toluene at about 70 °C and vacuum dried for 4 h prior to use. 5,7-Dodecadiyne-1,12-diol synthesized from 5-hexyn-1-ol (Farchan Laboratories) according to the procedure of Hay[12] was recrystallized from ethyl ether at 0 °C and vacuum dried for 4 h prior to use. Toluene was distilled over sodium metal under dry nitrogen. Dibutyltin bis(2-ethylhexanoate) (Eastman Kodak) was used as received. All manipulations of reagents were carried out under a dry inert atmosphere with vacuum-line techniques.

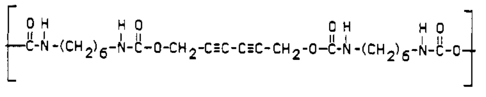
Table I
Hard-Segment Structures of the Polyurethane–Diacetylene Segmented Copolymers



MDI-2,4-1000

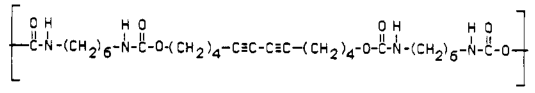


MDI-5,7-1000



$$\left[-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-CH_2-C\equiv C-C\equiv C-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\right]$$

HDI-2,4-1000



$$\left[-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\right]$$

HDI-5,7-1000

2. Synthesis of the Polyurethane–Diacetylene Elastomers by the Multistep Method. The polyurethane–diacetylene segmented copolymers were prepared from three basic monomers: a low molecular weight hydroxyl-terminated polyether, a diacetylenediol, and a diisocyanate. The synthetic route used to prepare the elastomers is illustrated in Scheme I. In the first step, a hydroxyl-terminated poly(tetramethylene oxide) (PTMO) prepolymer of average molecular weight 1000 is encapped with isocyanate groups with a 2:1 mole ratio of diisocyanate to PTMO. The second step is a stepwise reaction of the isocyanate groups with a diol containing the diacetylene functionality within the molecule. This so-called chain-extension step increases the molecular weight of the polymer as the newly formed urethane linkages join the molecules together. The diisocyanates used were 4,4′-methylenebis(phenyl isocyanate) (MDI) and hexamethylene diisocyanate (HDI). The diols used were 2,4-hexadiyne-1,6-diol and 5,7-dodecadiyne-1,12-diol. From this point on, materials will be designated by the monomers used to synthesize the elastomers. For example, MDI-2,4-1000 refers to an elastomer prepared from MDI, 2,4-hexadiyne-1,6-diol, and PTMO of average molecular weight 1000. The anticipated hard-segment structures of the polyurethane–diacetylene segmented copolymers are shown in Table I. The soft-segment structure is $(CH_2CH_2CH_2CH_2O)_x$ in which x equals on the average about 14.

3. Synthetic Procedures. a. MDI-2,4-1000 was prepared as follows: to a three-neck round-bottom flask equipped with a mechanical stirrer, addition funnel, and nitrogen purge was added 0.005 mol (1.29 g) of MDI with 30 mL of dry toluene, and the mixture warmed to 70 °C. This was followed by the slow addition of 0.00257 mol (2.577 g) of PTMO (average molecular weight 1000) in 30 mL of toluene (added over 1 h). The resultant solution was then refluxed for 3 h at 80 °C. The solution was then cooled to room temperature and 0.00257 mol (0.2827 g) of 2,4-hexadiyne-1,6-diol was added followed by heating at 60 °C for 3 h. When the reaction was complete, the elastomer was precipitated in methanol, washed to remove unreacted impurities with 1000 mL of methanol, and finally vacuum dried for 36 h at room temperature.

b. MDI-5,7-1000 was prepared by the same procedure given in (a) except 0.00257 mol (0.5 g) of 5,7 dodecadiyne-1,12-diol was added in place of 2,4 hexadiyne-1,6-diol.

c. HDI-2,4-1000 was prepared with the procedure given in (a) except 0.005 mol (0.84 g) of HDI was added in place of MDI.

d. HDI-5,7-1000 was prepared with the procedure given in (a) except 0.00257 mol (0.5 g) of 5,7-dodecadiyne-1,12-diol was added in place of 2,4-hexadiyne-1,6-diol and 0.005 mol (0.84 g) of HDI was used in place of MDI.

For the polymerization of the HDI-based copolymers, dibutyltin bis(2-ethylhexanoate) was added to the initial solution as a catalyst

Table II
Elemental Compositions of the Polyurethane–Diacetylene Segmented Copolymers

sample	% C theor	% C exptl	% H theor	% H exptl	% O[a] theor	% O[a] exptl	% N theor	% N exptl	wt % hard segments
MDI-2,4-1000	67.46	67.76	8.59	8.97	20.50	19.43	3.43	3.84	38.6
MDI-5,7-1000	68.35	68.49	8.88	8.87	19.49	19.46	3.27	3.18	41.6
HDI-2,4-1000	63.53	63.50	9.83	10.51	22.79	22.18	3.82	3.81	31.7
HDI-5,7-1000	64.73	64.70	10.08	10.36	21.55	21.38	3.61	3.56	35.4

[a] Oxygen by difference.

Table III
Molecular Weight Averages and Distributions of the Polyurethane–Diacetylene Segmented Copolymers

sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
MDI-2,4-1000	27 500	66 900	2.43
MDI-5,7-1000	57 400	118 000	2.05
HDI-2,4-1000	37 600	96 400	2.56
HDI-5,7-1000	59 000	128 000	2.17

to compensate for the lower reactivity of the aliphatic isocyanates. In all cases, yields in excess of 70% were obtained of white translucent rubbery powders. The elastomers were stored at 0 °C in the dark to prevent cross-polymerization by room light.

B. Characterization of the Segmented Copolymers. 1. Elemental Analysis. The elemental compositions of the polyurethane–diacetylene segmented copolymers are presented in Table II along with their respective theoretical values based on the assumption that polymerization proceeds with the formation of only linear copolymer as outlined in Scheme I. The theoretical hard-segment weight percents are also given in Table II. The good agreement between the experimental compositions and the theoretical values indicates that linear polyurethane–diacetylenes are the predominate species formed during polymerization. This implies that one diacetylene functionality exists per hard segment as shown in Table I. However, as pointed out by Miller et al.,[13] the formation of longer oligomers during the first step of the multistep method leads to a distribution of hard-segment sequence lengths in the final polymer. Thus, the composition of the hard segments shown in Table I represents the average structure of the hard segments. The polyurethane–diacetylene segmented copolymers are all soluble in solvents such as THF, indicating that extensive cross-linking via, for example, allophanate linkages or by cross-polymerization of the diacetylene groups did not occur to any appreciable extent during formation of these macromolecules.

2. Molecular Weight Determinations. Molecular weights were measured with a Waters Associates high-pressure liquid chromatograph (HPLC) equipped with E-125, E-500, and E-Linear μBondagel columns. The eluent was THF run at a flow rate of 1 mL/min at room temperature. Samples were detected with a Model R401 refractive index detector or when possible (MDI-based copolymers) with a Model 440 UV detector at a wavelength of 254 nm. Narrow molecular weight polystyrene standards were used to calibrate the system. Table III lists the molecular weight averages and the polydispersities of the polyurethane–diacetylene copolymers as determined by size exclusion chromatography. Since this technique actually measures the hydrodynamic volume of a polymer molecule rather than its molecular weight directly, differences in polymer–solvent interactions (which modify the dimensions of the molecule) between the polystyrene standards and the samples under analysis can result in inaccurate determinations of the molecular weight. Therefore, the molecular weights given in Table III are more useful for comparative purposes rather than as absolute values.

It can be seen that the copolymers synthesized by chain extension with 5,7-dodecadiyne-1,12-diol exhibit higher molecular weights and a slightly lower polydispersity than the copolymers extended with 2,4-hexadiyne-1,6-diol. These differences are due primarily to the presence of a more pronounced low molecular weight shoulder in the GPC curves of the polymers prepared with 2,4-hexadiyne-1,6-diol, indicative of a slightly larger fraction of low molecular weight species in these materials. This most likely reflects the lower nucleophilicity and hence reactivity of the –OH group in this diol due to its closer proximity to the unsaturated diacetylene group. Lower reaction rates (with isocyanates) have previously been reported[14] for unsaturated diols such as 1,4-butynediol compared to their saturated analogues, which is consistent with this interpretation. The similar molecular weights obtained for the HDI-based copolymers and the MDI-based copolymers demonstrate the utility of the tin catalyst in increasing the reaction rates of the normally less reactive aliphatic isocyanates. The molecular weight averages and the polydispersities obtained for the diacetylene elastomers using the GPC technique are within the range of values reported for other polyurethane elastomers such as MDI–butanediol–PTMO-based polyurethanes which, as determined by GPC, fall within the range 30 000–100 000 for M_n values.[11,13] The general conclusion that can be made from these data is that there are no major differences in the molecular weights or molecular weight distributions of these new copolymers, and, hence, differences in properties of these materials cannot be attributed to molecular weight differences.

3. Thermal Analysis. Differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) were performed with Du Pont 1090 and 990 thermal analyzers equipped with DSC and TMA modules, respectively. Melting points were taken as the maximum in the endothermic peak, and glass transition temperatures (T_g) were determined by the intersection method. For the DSC, samples were run at 10 °C/min in nitrogen, using 10–15 mg of sample per run. For the TMA, 1-mm-thick molded samples were run at 10 °C/min in the penetration mode with a 20-g load.

4. Infrared and Raman Spectroscopy. Infrared spectra were recorded on a Nicolet 20 DX Fourier transform infrared spectrophotometer (FTIR). Temperature studies were conducted with a heated precision cell equipped with a Fenwal Model 550 temperature controller (temperature range, 25–200 °C). Absorption ratios and peak areas were recorded after the peaks reached a constant value of absorbance (typically after 5 min at a given temperature). Raman scattering experiments were performed at room temperature with a Brewster angle back-scattering geometry. Incident radiation of 6328 Å at about 0.2 mW was provided by a He–Ne laser. A cylindrical focusing lens was used to minimize sample heating by the laser. The scattered radiation was collected at 90° to the sample surface, analyzed by a Spex double-grating monochromater, and detected by a RCA photomultiplier tube.

5. X-ray Diffraction. X-ray diffraction patterns were recorded with a Philips vertical diffractometer (Cu Kα radiation) equipped with an IBM Series 1 X-ray analyzer.

III. Results and Discussion

A. Thermal Analysis. The DSC scans of the as-prepared polyurethane–diacetylene segmented copolymers are shown in Figure 1. In the low-temperature regime (−100 to 0 °C), the glass transition of the PTMO soft segments is clearly observable. In the high-temperature regime (0 to 400 °C), both endothermic and exothermic transitions are present in all samples with the exception of MDI-2,4-1000, which only exhibits exothermic activity. Table IV summarizes the thermal transitions of the elastomers as determined by DSC. Glass transition temperatures obtained by TMA are also presented for comparison.

The higher temperature endotherms of the elastomers result from thermal disruption of hard-segment crystalline domains (verified by other techniques to be discussed). HDI-5,7-1000 exhibits the most pronounced melting endotherm and also the lowest soft-segment glass transition

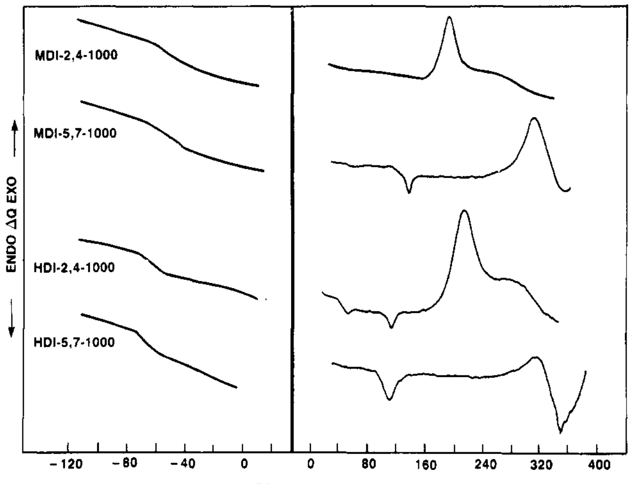


Figure 1. DSC thermograms of the as-prepared polyurethane–diacetylene segmented copolymers.

Table IV
Thermal Transitions of the Polyurethane–Diacetylene Segmented Copolymers

material	T_g(DSC), °C	T_g-(TMA), °C	endotherms,[a] °C	exotherms, °C
MDI-2,4-1000	-54	-53	none	200
MDI-5,7-1000	-52	-50	138 (65)	317
HDI-2,4-1000	-69	-74	116 (50)	218
HDI-5,7-1000	-71	-77	112 (50)	312

[a] Values in parentheses represent weak endotherms.

temperature. The lack of an observed melting endotherm for MDI-2,4-1000 indicates that no extensive three-dimensional crystalline ordering has occurred in the hard domains of this material. MDI-based polyurethanes chain extended with butanediol with similar hard-segment weight fractions also show no indication of hard-segment crystalline organization.[13] This has been attributed to restricted hard-segment mobility, which inhibits the crystallization of hard segments containing fewer than three MDI units. The greater flexibility of the hard segments of MDI-5,7-1000 resulting from the additional methylene groups surrounding the diacetylene functionality seems to promote some crystallization within the hard domains of this elastomer as evidenced by its melting endotherm. In addition, it is expected that nonbonded interactions between diacetylene groups will provide an additional driving force for crystallization in all of the elastomers.

The more diffuse lower temperature endotherms exhibited by the elastomers MDI-5,7-1000, HDI-5,7-1000, and HDI-2,4-1000 are believed to be morphological in origin and, as discussed by many researchers,[15,16] arise due to different degrees of short-range ordering within the hard domains. As a result, their existence is highly dependent on the thermal history of the sample. DSC showed no indication of soft-segment crystallinity, which typically gives rise to melting endotherms below 30 °C.[17] This is not surprising since crystallinity in PTMO does not usually develop in polyurethane elastomers containing lower molecular weight (less than 2000) PTMO soft segments.[17]

The exothermic transitions observed for all of the elastomers are due to a combination of thermally induced liquid-phase cross-polymerization and degradation of the diacetylene groups within the hard segments. This process is accompanied by charring of the samples and some loss in weight. It is interesting to note that the temperature of this transition (see Table IV) is determined by the immediate molecular structure surrounding the diacetylene groups. For the elastomers extended with 2,4 hexadiyne-1,6-diol, the transition occurs at about 200 °C, whereas for the elastomers chain extended with 5,7 dodecadiyne-1,12-diol the transition is centered at about 300 °C. Thus, the high-temperature exothermic transitions are controlled by the molecular structure of the diacetylene portion of the hard segment rather than the structure of the entire hard segment. Similar high-temperature exotherms have been reported for both diacetylene monomers[18] and diacetylene macromonomers.[8] In a former publication, the magnitude of the exotherm was found to be related to the diacetylene monomer concentration. A similar relationship exists in the case of the polyurethane–diacetylene elastomers and can be used to approximate the extent of cross-polymerization of the diacetylene units by suitable integration techniques (Table V).

Table V
Heats of Transition for the High-Temperature Exotherm of the Segmented Copolymers after Various Treatments

	ΔH, J/g		
sample	as molded	annealed 64 h at 90 °C	exposed to γ radiation for 2 weeks
MDI-2,4-1000	256	190	125
MDI-5,7-1000	221	157	166
HDI-2,4-1000	260	135	48
HDI-5,7-1000	149	63	0

Thermal analysis has been used extensively to estimate the degree of phase separation within polyurethane segmented copolymers. For example, it has been clearly established that phase mixing increases the glass transition temperature of the PTMO soft segment from its pure value of around −80 °C to higher temperatures as the degree of phase mixing increases.[17] In addition, the observation of thermal transitions related to hard-segment crystallinity can be used as a strong indication of a phase-separated morphology. By these criteria, it is clear that the HDI-based polyurethane–diacetylene copolymers are highly phase separated with soft-segment glass transition temperatures approaching the value of a pure PTMO segment. The MDI-based copolymers, on the other hand, are less phase separated, as indicated by their higher glass transition temperatures. The values obtained here for the MDI-based elastomers are close to the values reported for MDI-based polyurethanes chain extended with butanediol.[13] Thus, the presence of the diacetylene groups within the hard segments does not seem to appreciably influence the compatibility of the hard and soft segments of MDI-based polyurethanes. It should be pointed out that the MDI-based polyurethane–diacetylene elastomers that are clearly more phase mixed than the HDI-based elastomers are nevertheless two-phase systems. The strong tendency of the aliphatic hard segments of the HDI-based elastomers to crystallize accounts, in part, for the greater phase separation observed in these copolymers.

The presence of the reactive diacetylene groups within phase-separated domains of the elastomers affords a relatively easy way to modify the thermal–mechanical properties of these materials by controlling the extent of cross-polymerization of the diacetylene units. To examine the influence of cross-polymerization on the thermal properties of the elastomers, samples were compression molded at 600 psi and between 100 and 120 °C for 10 min into strips 1 mm in thickness. These samples were then exposed to either thermal or radiation treatment (^{60}Co γ radiation) to initiate cross-polymerization of the diacetylene groups.

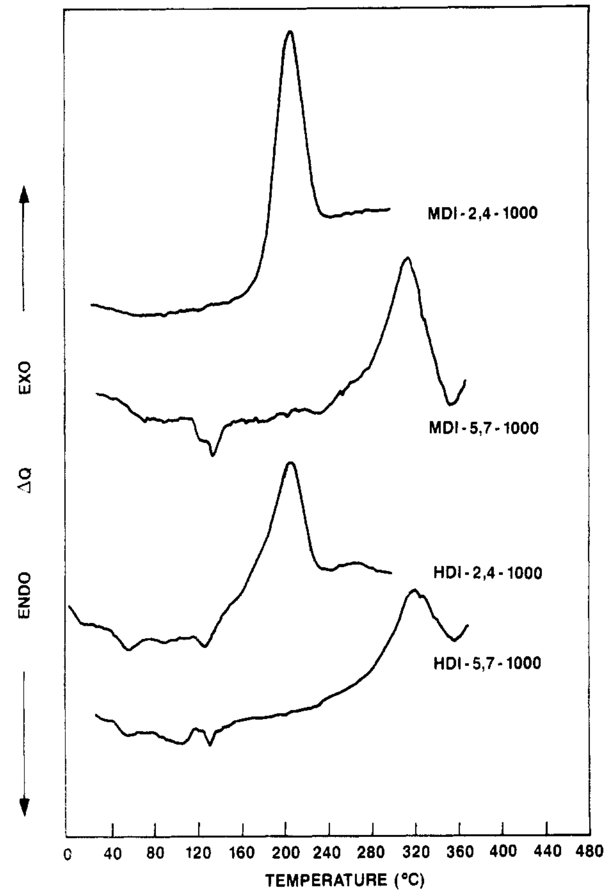


Figure 2. DSC thermograms of molded polyurethane–diacetylene segmented copolymers.

The DSC scans of the molded elastomers are shown in Figure 2. Comparison of these scans with those of the as-prepared elastomers (Figure 1) clearly indicates that the temperatures of the endothermic thermal transitions of the elastomers are highly dependent on the thermal history of the sample. For the molded elastomers, the melting endotherms occur at slightly higher temperatures and additional new endotherms are apparent in MDI-5,7-1000 and HDI-5,7-1000. These changes reflect differences in the long- and short-range order of the hard-segment domains introduced by the molding operation. Figure 3 shows the DSC scans of the molded elastomers after thermal annealing at 90 °C for 64 h under nitrogen. During this process, the colors of the elastomers change dramatically from translucent white to dark red or blue (depending on the particular elastomer) as cross-polymerization of the diacetylene groups generates the conjugated backbone of a poly(diacetylene) within the hard domains. Figure 4 shows the DSC scans of the molded elastomers after exposure to ^{60}Co γ radiation for 2 weeks. Again, the color of the elastomers changes dramatically as cross-polymerization occurs, in this case, initiated by γ radiation.

The conversion of the diacetylene units into poly(diacetylene) network chains was estimated by integrating the area under the high-temperature exotherm, which is proportional to the number of unreacted diacetylene groups in the copolymer. The energy values representing the heats of this transition are found in Table V for the molded elastomers subjected to the various treatments. This technique is only semiquantitative due to the complex shapes of the exotherms resulting from a combination of different processes taking place during this irreversible transition. It does, however, provide a relative technique

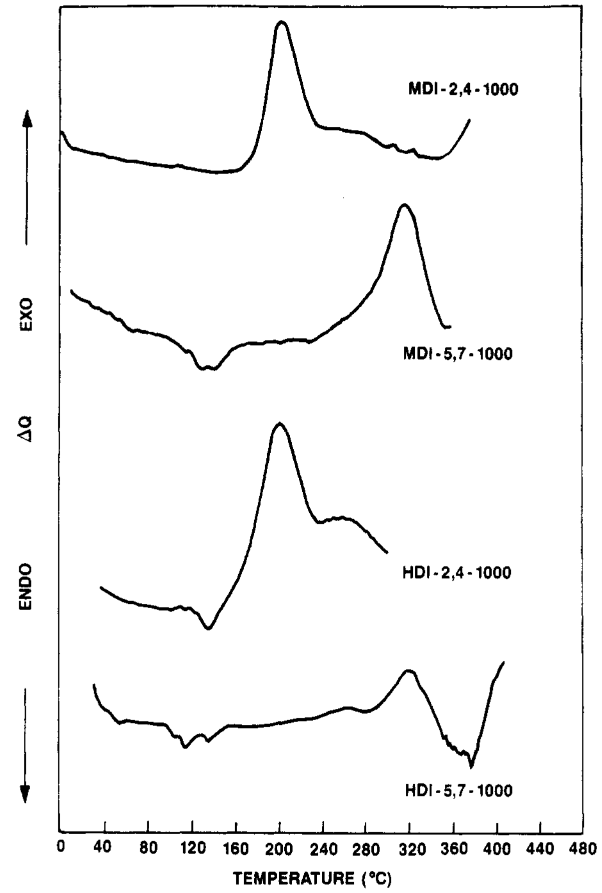


Figure 3. DSC thermograms of polyurethane–diacetylene segmented copolymers annealed for 64 h at 90 °C.

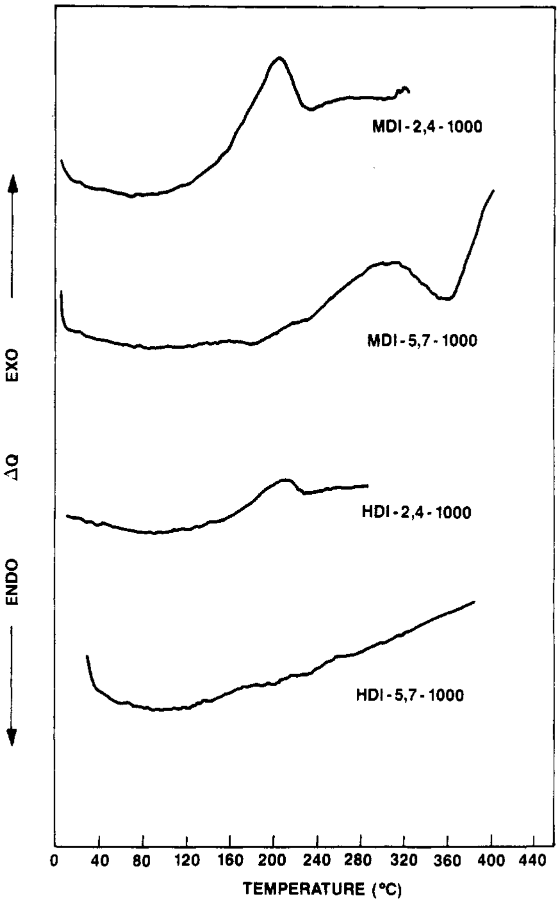


Figure 4. DSC thermograms of polyurethane–diacetylene segmented copolymers exposed to γ radiation for 2 weeks.

for estimating the extent of cross-polymerization of the diacetylene groups.

The DSC scans of the thermally annealed elastomers still exhibit the endothermic transitions characteristic of the molded samples. In the case of MDI-5,7-1000, HDI-5,7-1000, and HDI-2,4-1000, the melting endotherms have been raised to slightly higher temperatures, indicating improved ordering of the hard domains resulting from the annealing process. Also, for the elastomers exhibiting lower temperature endotherms, annealing at 90 °C has either eliminated or raised the temperatures of these transitions. This is consistent with the behavior of other polyurethane elastomers[15,16] that have been annealed to improve the short-range order of their hard domains. The existence of these hard-domain transitions after annealing indicates that thermal cross-polymerization of the diacetylene groups is not an efficient process. Indeed, it has been found that, with the exception of MDI-2,4-1000, cross-polymerization of the elastomers by thermal means is highly dependent, in a nonpredictable way, on the history of the sample, including the amount of time it has been exposed to ambient light. In some cases it was found that thermal cross-polymerization of these materials was not a homogeneous process resulting in large portions of the sample still unreacted. MDI-2,4-1000, on the other hand, is uniformly cross-polymerized by using heat in a highly reproducible manner. Comparison of the heats of transitions of the thermally cross-polymerized elastomers (Table V) shows that the HDI-based elastomers, which are more phase separated, are cross-polymerized to a greater extent than the MDI-based elastomers under the same conditions. The more extensive hard-domain crystallinity of the HDI-based elastomers (see the section on X-ray diffraction) also accounts for their greater conversion to the poly(diacetylene) network chains.

In contrast to the thermally cross-polymerized elastomers, the DSC scans of the elastomers cross-polymerized by γ radiation exhibit no endothermic transitions. In addition, the exothermic transition of the HDI-based elastomers is either nonexistent (HDI-5,7-1000) or very small (HDI-2,4-1000). Thus, for the HDI-based elastomers, cross-polymerization of the diacetylene groups within the hard domains via γ radiation results in nearly complete conversion to the poly(diacetylene) network structure. This, in turn, modifies the thermal behavior of these domains as they become rigid infusible entities. As was the case in the thermal cross-polymerization of the elastomers, it can be seen from Table V that the HDI-based elastomers undergo a greater conversion to the poly(diacetylene) newtwork than the MDI-based elastomers. The presence of a greater percentage of hard segments dissolved in the soft-segment domains as indicated by the lesser phase separation of the MDI-based elastomers precludes the possibility of complete conversion in these copolymers. The topochemical cross-polymerization process is also best facilitated in a crystalline environment,[1] as demonstrated by the apparent complete conversion of the diacetylene groups of HDI-5,7-1000 to the poly(diacetylene) network.

The DSC results show that it is possible to modify the thermal behavior of the elastomers by changing the structure of the hard domains via cross-polymerization of the diacetylene units. With HDI-5,7-1000 as an example, it can be seen that cross-polymerization by γ radiation changes the elastomer from a material that melts at around 110 °C to a material with no observable thermal transitions in the higher temperature regime. How these changes influence the thermal–mechanical properties of the elastomers and, in particular, the glass transition temperature of the soft segments will now be discussed.

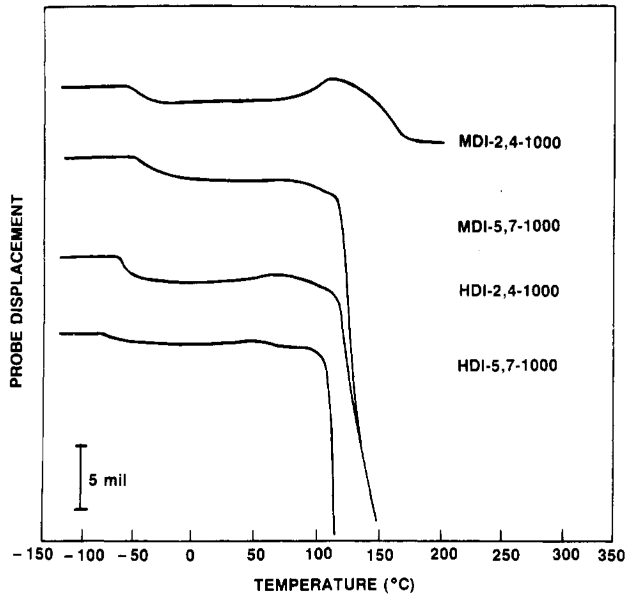


Figure 5. TMA scans of molded polyurethane–diacetylene segmented copolymers.

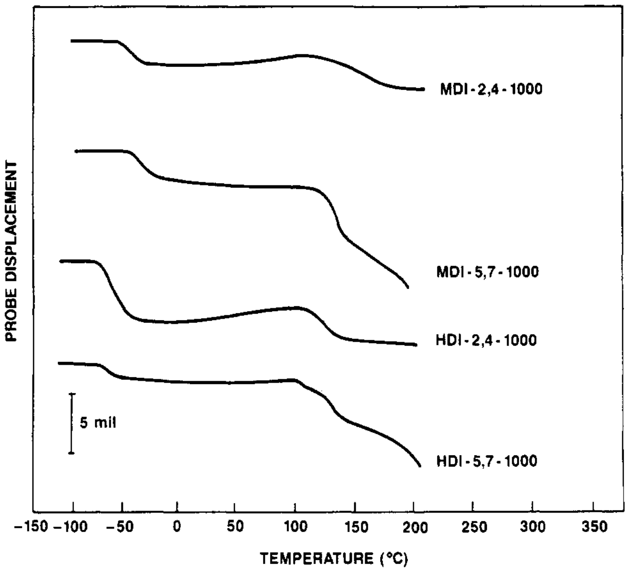


Figure 6. TMA scans of polyurethane–diacetylene segmented copolymers annealed for 64 h at 90 °C.

In order to examine the influence of cross-polymerization of the diacetylene groups on the glass transition temperature of the soft segments, thermal mechanical analysis (TMA) was performed on samples prepared in the same manner as for the DSC studies. The technique comprises placing a weighted probe on the sample and monitoring the penetration (or expansion) of the probe into the material as a function of temperature. The probe was loaded with a 20-g weight to enhance penetration into the sample at softening points of the copolymer. This technique has been shown[19] to be a reliable method for the determination of thermal transitions in polyurethane elastomers. It should be pointed out that, in this study, values of the glass transition temperature obtained by DSC and TMA were consistently in good agreement (within about 5 °C), as can be seen in Table IV for the as-prepared elastomers.

The TMA scans of the as-molded polyurethane–diacetylene elastomers are found in Figure 5. The scans of the thermally annealed elastomers and of the γ-irradiated elastomers are found in Figures 6 and 7, respectively. Two

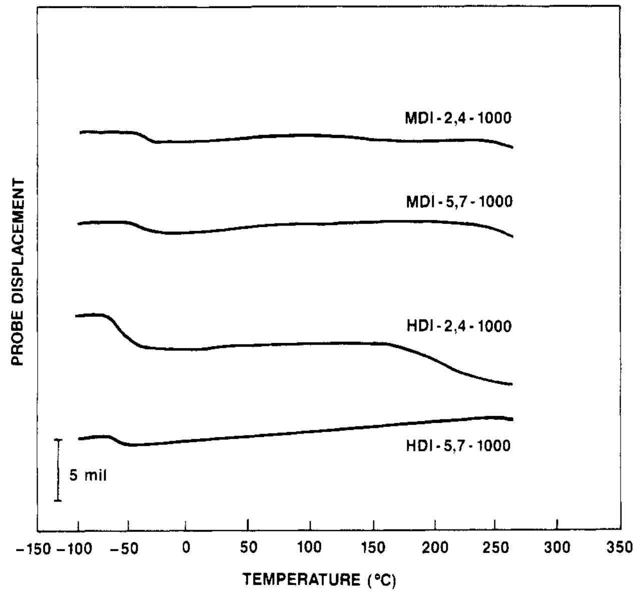


Figure 7. TMA scans of polyurethane–diacetylene segmented copolymers exposed to γ radiation for 2 weeks.

major penetrations were observed for all as-molded elastomers. The first low-temperature penetration can be attributed to the glass transition temperature of the soft PTMO segments of the copolymers. The second penetration is due to a softening of the hard domains. For the elastomers MDI-5,7-1000, HDI-2,4-1000, and HDI-5,7-1000, the values of the latter transition corresponded exactly with the higher temperature melting endotherms observed by DSC. The magnitude of these transitions and visual observations reveal that extensive viscous flow has occurred during the transition, which is consistent with the interpretation of this transition as a melting of the copolymers. Thus, these materials exhibit the processing characteristics of many other thermoplastic elastomers. MDI-2,4-1000, which does not exhibit a melting endotherm, shows a smaller penetration at its softening point relative to the other elastomers. The minor penetrations occurring below the softening points of the elastomers between 50 and 100 °C corresponded fairly well with the lower temperature endotherms observed by DSC. The exception to this was MDI-2,4-1000, which exhibited a minor penetration at about 60 °C and no endothermic activity by DSC.

The TMA scans of the cross-polymerized elastomers show that the glass transition temperatures of the PTMO soft segments are essentially unaffected by cross-polymerization of the diacetylene groups within the hard domains for both the thermally cross-polymerized elastomers and γ cross-polymerized elastomers (values in Table VI). The fact that this transition remains unchanged during the cross-polymerization of the diacetylene units indicates that this chemistry is restricted to the phase-separated hard domains of the copolymers. Thus, any modification of the thermal–mechanical behavior of the elastomers resulting from cross-polymerization involves changes in the structure and modulus of the hard domains and not changes in the soft-segment domains or hard segment–soft segment compatibility.

The TMA scans of the thermally annealed elastomers still show the higher temperature penetrations due to softening of the hard domains, although they are significantly less pronounced and cover a broader temperature range than the original as-molded samples. These results are consistent with the DSC results, which clearly indicate the presence of a large percentage of hard domains containing unreacted diacetylene groups. The TMA scans of the γ cross-polymerized elastomers, on the other hand, show no major softening of the elastomers up to temperatures of about 250 °C (175 °C for HDI-2,4-1000). In this case, sufficient conversion of the diacetylene groups to the poly(diacetylene) network structure has occurred within the hard domains to render them infusible. To insure that these dramatic changes in the thermal–mechanical behavior of the elastomers were not the result of random cross-linking initiated by the highly ionizing γ radiation, a control sample of a conventional polyurethane segmented copolymer was subjected to similar treatment. A polyurethane segmented copolymer prepared from MDI, butanediol, and PTMO was synthesized by the same methodology used to prepare the polyurethane–diacetylene copolymers. After 2-week exposure of a molded sample of this material to the γ source, the thermal mechanical behavior remained unchanged. Specifically, the major softening point of this material detected by TMA at about 120 °C was unchanged by the radiation treatment. The dramatic modification of the thermal behavior of the polyurethane–diacetylene copolymers is therefore due to cross-polymerization of the diacetylene groups and the formation of the poly(diacetylene) network.

Table VI
Soft-Segment Glass Transition Temperatures of the Segmented Copolymers after Various Treatments

	glass transition temp, °C		
sample	as molded	annealed 64 h at 90 °C	exposed to γ radiation for 2 weeks
MDI-2,4-1000	−53	−52	−48
MDI-5,7-1000	−50	−46	−49
HDI-2,4-1000	−74	−73	−71
HDI-5,7-1000	−77	−73	−74

B. Infrared and Raman Spectroscopy. 1. Infrared Spectroscopy. Infrared spectroscopy has proven to be a valuable technique for the investigation of hard–soft-segment molecular interactions in many phase-separated copolymers.[15,20] This technique was used in the present study to investigate the degree of phase mixing in the polyurethane–diacetylene copolymers and to examine changes in hydrogen bonding that occur during phase transitions in both the copolymers and their cross-polymerized products. In the latter case, FTIR temperature studies were performed to probe the role of hydrogen bonding in the temperature-dependent properties of the elastomers.

Figures 8 and 9 present the FTIR spectra of solution-cast films of the MDI-based and HDI-based polyurethane–diacetylene elastomers, respectively. The spectra of the elastomers show the absorption bands characteristic of polyurethane–PTMO segmented copolymers with the expected differences arising from the portion of the hard segments derived from the diisocyanates (HDI and MDI) used to build the macromolecules. The diacetylene group is infrared inactive and therefore does not contribute to the spectra of the elastomers. Of particular interest are the absorption bands of the carbonyl stretching region around 1700 cm^{-1} and the NH stretching region around 3300 cm^{-1}.

Whenever there exists the opportunity for hydrogen bonding in polymeric systems, it is of interest to explore the influence of these highly directional secondary bonds on the relevant properties of the material. In the case of the polyurethane–diacetylene copolymers, there is one NH proton donor within the urethane linkage of the hard segment and two possible proton acceptors: the carbonyl oxygen of the urethane group and the ether oxygen of the

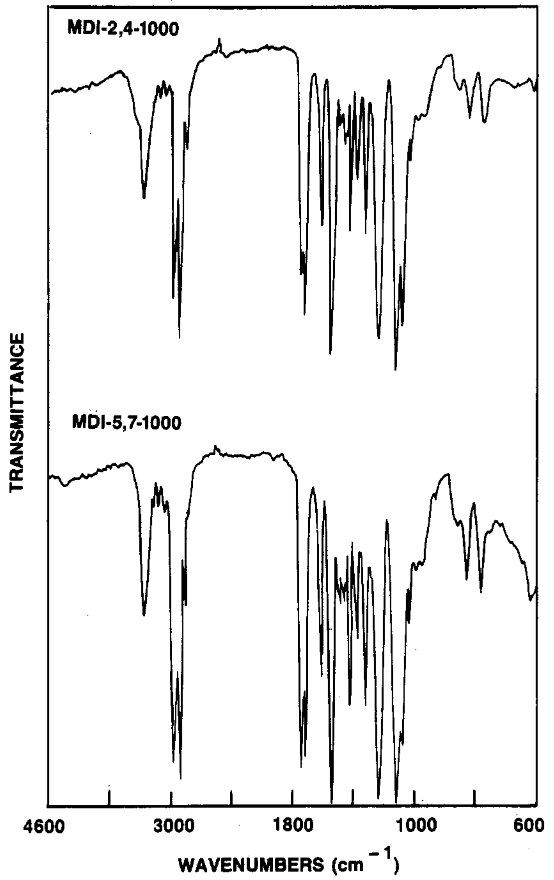


Figure 8. FTIR spectra of MDI-based polyurethane–diacetylene segmented copolymers.

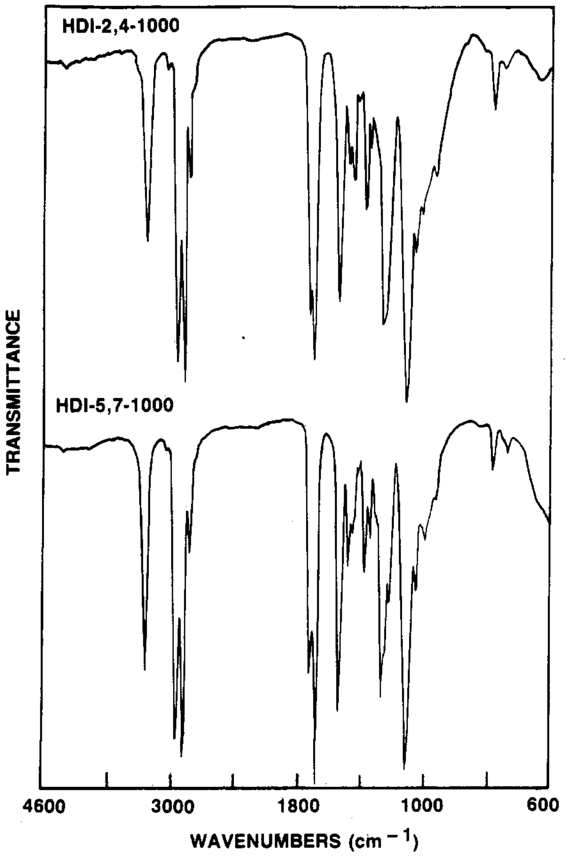


Figure 9. FTIR spectra of HDI-based polyurethane–diacetylene segmented copolymers.

Table VII
Fraction of Interurethane Hydrogen Bonding of the Copolymers Based on the Carbonyl Region

sample	fraction of interurethane bonded carbonyl[a] solvent-cast films	maximum fraction[b]
MDI-2,4-1000	0.551	0.560
MDI-5,7-1000	0.491	0.571
HDI-2,4-1000	0.570	0.682
HDI-5,7-1000	0.712	0.862

[a] $ABS_{bonded}/[ABS_{bonded} + ABS_{free}]$. [b] Annealed at 90 °C for 2 h.

PTMO soft segment. Hydrogen bond formation between the urethane NH and the ether oxygen of PTMO occurs either at domain interfaces or when phase mixing of the hard and soft segments occurs at the molecular level. Interurethane hydrogen bonding, on the other hand, results from hard-segment interactions within the phase-separated hard domains. Thus, the amount of interurethane bonding serves as an approximate measure of the extent of phase separation in these copolymers. This parameter can be obtained by absorbance measurements in the carbonyl region which consists of two peaks centered at about 1700 and 1730 cm^{-1} due to bonded carbonyl and free carbonyl, respectively.[20] The ratio of the absorbances of these two peaks has been used as an "hydrogen bonding index" to estimate the extent of interurethane hydrogen bonding.[20] Alternatively, the fraction of interurethane bonded carbonyl, defined as the absorbance of the bonded carbonyl divided by the sum of this quantity, and the absorbance of the free carbonyl has been used to estimate this parameter.[13] It should be kept in mind that hydrogen bonding between the soft segments and hard segments at the domain interfaces is an important component of this parameter and without knowledge of domain surface areas and topography its influence cannot be evaluated.

It can be seen in Figures 8 and 9 that the solution-cast films (THF) of the elastomers exhibit both free and bonded carbonyl peaks in the region between 1750 and 1650 cm^{-1}. The fractions of interurethane bonded carbonyl (defined as above) calculated from these absorption bands for the solution-cast films of each copolymer are found in Table VII. From these data it is clear that the HDI-based elastomers have a higher percentage of interurethane bonding than the MDI-based elastomers. It was found, however, that the values obtained for the amount of interurethane bonding were highly dependent on the type of solvent used to cast the films and on the thermal history of the sample. For example, HDI-based elastomers cast from toluene consistently exhibited higher values of interurethane bonding compared to castings from THF or DMF. This observation reminds us of how sensitive the morphology and domain organization of segmented copolymers are to their processing history. Annealing the films at elevated temperatures resulted in an increased percentage of interurethane bonding for all of the elastomers except MDI-2,4-1000, which was only slightly affected by thermal treatment. Annealing studies revealed that the maximum improvement in the percentage of interurethane bonding and, hence, phase separation occurred when the samples were annealed at 90 °C for 2 h. Annealing of the films at this temperature for longer than 2 h resulted in a significant decrease in the percentage of interurethane bonding. For example, for a sample of HDI-5,7-1000 the fraction of interurethane bonding decreased from a value of 0.775 to 0.421 after 20 h of annealing. Clearly, at these higher temperatures near the melting points of the elastomers, in addition to improved hard-domain ordering, there is a tendency for increased phase mixing as this process becomes more thermodynamically favorable. Thus, annealing is a balance between two opposing processes. It should be pointed out that annealing of these solvent-cast thin films for extended periods did not result in any cross-polymerization of the diacetylene groups, as evidenced by the lack of color changes characteristic of poly(diacetylene) formation.

The maximum fractions obtained for the copolymers after annealing at 90 °C for 2 h are also presented in Table VII. These data again show that the HDI-based elastomers are more phase separated than the MDI-based elastomers as indicated by their greater fraction of interurethane bonding after annealing with the exception of MDI-2,4-1000, which remains essentially unchanged. This material seems to behave in a similar manner to MDI-based polyurethanes chain extended with butanediol (of the same hard-segment weight fraction), which show similar degrees of phase separation and are only weakly responsive to annealing.[13] In addition, there is no evidence for crystalline organization within the hard domains of MDI-2,4-1000 in contrast to the other elastomers, which exhibit some degree of hard-segment crystallinity. Annealing therefore promotes additional crystallization and ordering of the hard segments of these copolymers, resulting in greater phase separation. This conclusion is supported by both DSC and X-ray diffraction studies of annealed films. For MDI-2,4-1000, the lower flexibility and mobility of its hard segments inhibits this process at these temperatures. Closer examination of the data from the annealed elastomers reveals that the fraction of interurethane bonding correlates well with the glass transition temperatures of the elastomers as determined by DSC or TMA. Comparison of these data shows that copolymers with the lower glass transition temperatures also have the greater amount of interurethane bonding. From these data it can be concluded that HDI-5,7-1000 is the most extensively phase-separated copolymer followed by HDI-2,4-1000 and finally by the MDI-based elastomers, which are about at the same level of phase separation.

The NH region of the spectra indicates nearly complete hydrogen bonding for all of the elastomers at room temperature, as indicated by the presence of only the bonded NH stretching band at around 3300 cm^{-1}. MDI-2,4-1000, however, exhibits a pronounced shoulder centered at about 3420 cm^{-1}, which is the region characteristic of the free NH stretching band.[21] Annealing of this material at 90 °C for periods as short as 1 h was found to almost completely eliminate any nonbonded NH. The presence of nonbonded NH in MDI-2,4-1000 was also found to be dependent on sample preparation. Thus, although annealing does not increase the extent of phase separation within MDI-2,4-1000, it does produce a fully hydrogen bonded material.

The influence of hydrogen bonding on the physical and mechanical properties of polymeric systems has been the focus of much attention in past years. In the case of segmented polyurethane elastomers, it has been convincingly argued[15,16] that the thermal and mechanical properties of these materials are determined by the morphological features of the copolymer rather than by the presence of hydrogen bonding or its thermal disruption at higher temperatures. Certain polyurethane–urea segmented copolymers, on the other hand, do show[22] a correlation between the thermal properties and hydrogen bonding activity of these materials. This issue is complicated by the presence of varying degrees of ordering within the phase-separated hard domains of these copolymers ranging from short-range order to three-dimensional crystallinity. Thus, the thermal–mechanical behavior of these copolymers is controlled by a number of different order–disorder transitions resulting from the varied organizations present in the materials. The key question then becomes which of these transitions are accompanied by thermal disruption of hydrogen bonding and what effect do they have on the relevant properties of these materials. For the poly(diacetylenes), it is of interest to establish the role of hydrogen bonding in the reversible and irreversible thermochromic phase transitions exhibited by some of these conjugated polymers. These unique transitions, which are characterized by dramatic visually observable color changes, have been attributed to both order–disorder transitions involving thermal disruption of hydrogen bonding[23] and to crystal-phase transitions,[3] depending on the particular poly(diacetylene) under consideration. Since the polyurethane–diacetylene elastomers exhibit the properties of both the segmented copolymers and the poly(diacetylenes) it is appropriate to examine the influence of hydrogen bonding on the properties of these unique materials.

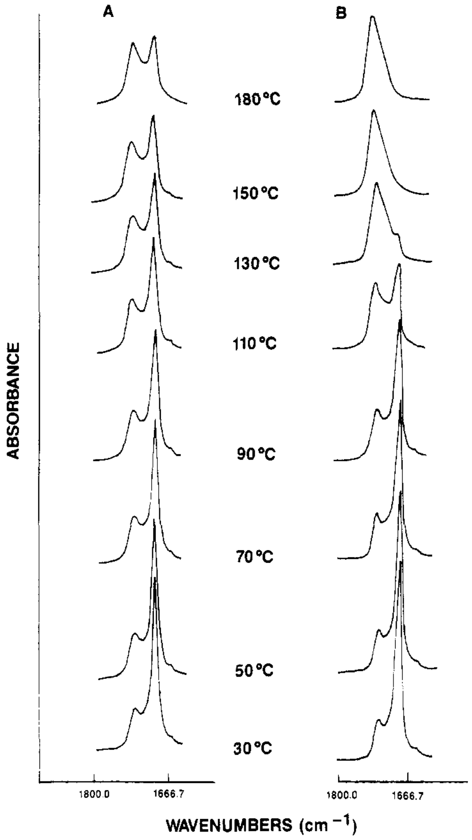


Figure 10. Effect of temperature on the carbonyl region of HDI-5,7-1000: (A) cross-polymerized thin film, and (B) as-prepared thin film.

Infrared thermal analysis was used to probe the extent of hydrogen bonding as a function of temperature for the segmented copolymers. Thin films of the elastomers were cast from solution and subsequently annealed for 2 h at 90 °C to insure maximum phase separation and complete removal of solvent. Column B of Figure 10 shows the carbonyl region of a thin film (cast from toluene) of the elastomer HDI-5,7-1000 as a function of temperature. The absorption bands in column A are from a similarly prepared sample of HDI-5,7-1000 that has been cross-polymerized by a 30-min exposure to UV light of 3 MW/cm^2 intensity at 254 nm. As will be discussed in the following paper, this exposure time results in the maximum conversion of the diacetylene groups to poly(diacetylene) chains within the hard domains.

For the as-cast film (column B), it an be seen that the absorption band characteristic of bonded carbonyl centered

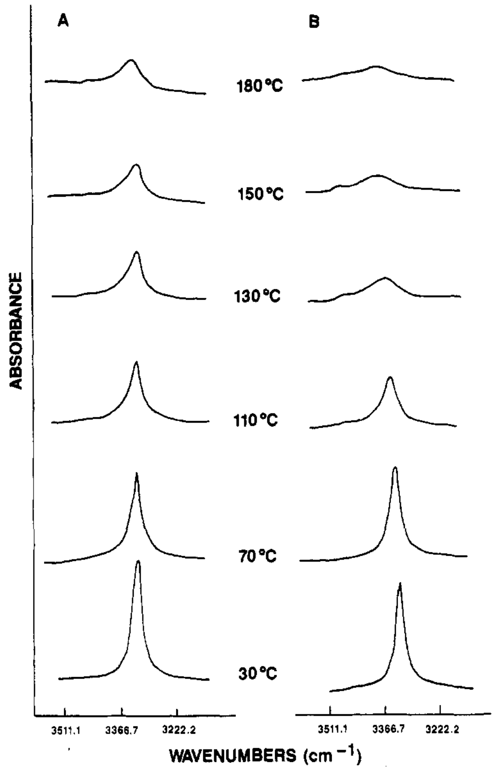


Figure 11. Effect of temperature on the NH stretching region of HDI-5,7-1000: (A) cross-polymerized thin film, and (B) as-prepared thin film.

at about 1696 cm^{-1} for this copolymer starts to decrease dramatically when the temperature exceeds 90 °C and is nondetectable above 150 °C. In this same temperature range, the nonbonded carbonyl absorption band centered at about 1720 cm^{-1} increases and eventually becomes the dominate absorption band in this region. These changes result from extensive thermal disruption of interurethane hydrogen bonding occurring over this temperature range. Similar observations can be made by examining the temperature dependence of the NH stretching region, which is shown in Figure 11 for HDI-5,7-1000 for both the as-cast film (B) and the cross-polymerized film (A). For the as-cast film (column B), the bonded NH stretch centered at 3320 cm^{-1} becomes increasingly broader and less intense and develops a pronounced shoulder due to nonbonded NH (above 3400 cm^{-1}) as the temperature is raised above 90 °C. Similar changes have been attributed to hydrogen bond breaking in other polyurethane[15] and polyamide[24] macromolecules and arise, in part, due to the large difference in dipole moments and force constants of the bonded and free state of the NH stretch. Thus, both the NH region and carbonyl region show considerable hydrogen bond dissociation at temperatures above 90 °C for HDI-5,7-1000.

The above changes in hydrogen bonding can be represented graphically by calculating the percentage of interurethane bonded carbonyl as a function of temperature. Since this parameter is derived from the carbonyl bond of the urethane group, it gives us direct information on the extent of hydrogen bonding in the phase-separated hard domains. Figure 12 shows the percentage of interurethane bonded carbonyl as a function of temperature for HDI-5,7-1000 and the other copolymers that were examined with the same procedures. In the case of the MDI-based elastomers, thin films were cast from THF instead of toluene, which was used for the HDI-based elastomers. Using these data, it is possible to detect thermally induced transitions of the hard domains that involve changes in either the rate of hydrogen bond dissociation, the thermal coefficient of expansion of the material, or the amount of hydrogen bonding. In the amorphous regions of the hard domains, hydrogen bonding dissociation will be governed by chain-segment mobility and the rotational freedom of the hard segments. Increasing temperatures are expected to increase the average kinetic energy of the molecules, shifting the equilibrium to the left as the chains overcome rotational barriers to achieve their nonbonded conformations. In the crystalline regions of the hard domains, disruption of hydrogen bonds occurs only during melting of these ordered regions, as indicated by an abrupt change in the extent of hydrogen bonding. The contribution of both of these behaviors in addition to the effects of thermal expansion, which result in changes in the local environment and strength of the hydrogen bonds via changes in the urethane–urethane contact distance, accounts for the shape of the curves shown in Figure 12. The latter effect can also be used to detect transitions when changes in the thermal coefficient of expansion of the material occur during the transition.

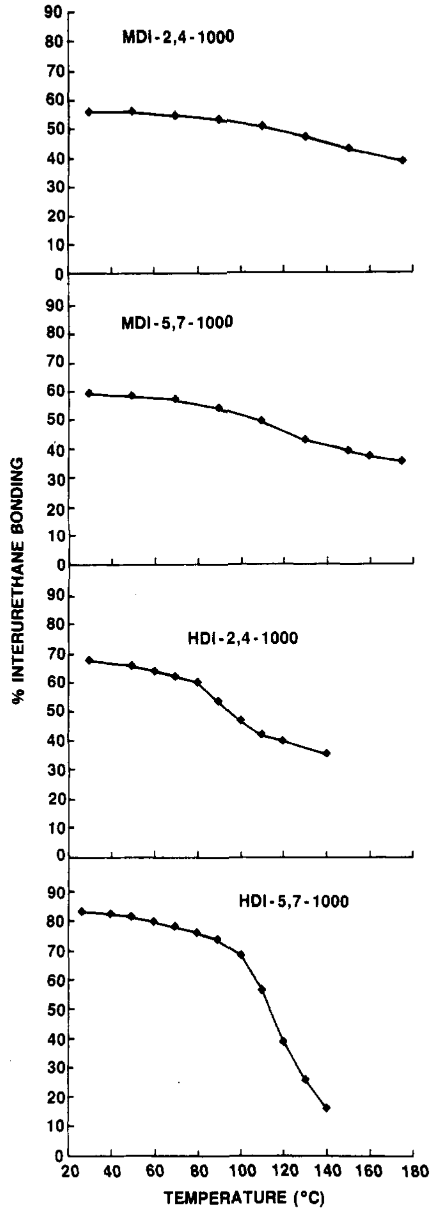


Figure 12. Percentage of interurethane bonding as a function of temperature for the polyurethane–diacetylene segmented copolymers.

MDI-2,4-1000 shows a negligible loss in the extent of interurethane hydrogen bonding until about 80 °C, above which point there is a small but steady decrease in the amount of hydrogen bonding with increasing temperature. This transition is about 30 °C below the major softening point of the elastomer as determined by TMA. It is tempting to ascribe this change in slope to the onset of molecular motion in the amorphous hard domains, that is, the glass transition temperature of the hard domains. The glass transition temperature of the hard domains of MDI-based polyurethanes chain extended with butanediol, determined by similar methods, was also found to be around 80 °C.[15] Molecular motion of the hard segments is therefore controlled by the MDI moieties of the hard segment and not the diacetylene portion. To further pursue this point, a polyurethane segmented copolymer prepared from MDI, butanediol, and PTMO was synthesized with the same two-step polymerization technique used to prepare the polyurethane–diacetylene elastomers. A TMA of this material run under the same conditions as the diacetylene elastomers showed a major softening at about 120 °C but no activity in the region of the glass transition temperatre. The thermal behavior of MDI-2,4-1000 and the more conventional MDI-based polyurethanes is clearly very similar. It is therefore reasonable to assume that the transition observed by FTIR is of a similar origin.

As can be seen in Figure 12, the copolymers that exhibited melting behavior also exhibit more pronounced infrared thermal transitions that are comprised, in contrast to the transition of MDI-2,4-1000, of three distinct slope changes. The magnitude of the loss of interurethane hydrogen bonding during these transitions is much greater for the HDI-based copolymers than for MDI-5,7-1000 with HDI-5,7-1000, showing the most extensive hydrogen bond disruption during this transition. These abrupt changes in the extent of hydrogen bonding can be attributed to the melting of crystalline hard domains with the concomitant thermal disruption of their hydrogen bonded networks. On the basis of this interpretation, it appears that the hard domains of HDI-5,7-1000 are highly crystalline and become completely disordered with limited hydrogen bonding after melting. The temperature of this order–disorder transition corresponds with the melting temperature of HDI-5,7-1000 as determined by both DSC and TMA (about 110 °C). In the case of HDI-2,4-1000, the infrared transition temperature (onset 80 °C) is lower than the melting temperature determined by TMA and DSC (onset 110 °C). This discrepancy may be due to differences in domain organization and order brought about by the different sample preparations used for each method. In other words, casting HDI-2,4-1000 from solvent may have resulted in more disordered hard domains with depressed melting temperatures. The relatively smaller changes in the extent of interurethane hydrogen bonding occurring during the transition of MDI-5,7-1000 indicates a significantly lower degree of hard-segment crystallinity in this material. In addition, it is possible that a greater amount of hydrogen bonding is retained in the melt state of this copolymer due to the lower segmental mobility of the MDI units. The infrared transition temperature of MDI-5,7-1000 was also found to be lower than the melting temperature as determined by DSC or TMA. The presence of a significant amount of amorphous organization within the hard domains of MDI-5,7-1000 makes it difficult to distinguish between transitions resulting from melting behavior and transitions related to activity in the amorphous regions.

Similar data can be generated by following changes in the NH stretching region as a function of temperature. By integrating the total area of both the bonded and free NH absorptions, it is possible to observe changes in the amount of hydrogen bonding in the copolymers.[15] Since the bonded NH absorption is much more intense than the nonbonded absorption, the integrated intensity of both absorption bands will decrease as the amount of hydrogen bonding throughout the entire copolymer decreases. The integrated absorbance of the NH region (normalized to the room temperature value) as a function of temperature for the various copolymers is shown in Figure 13. In addition to the decrease in intensity due to hydrogen bond breaking, the effects of reduced intermolecular interactions occurring with increasing temperature also contribute to the slopes of these curves.[25] Thus, an absolute measure of the extent of hydrogen bonding is not possible. It is possible, however to determine the presence of thermally induced transitions by the observation of abrupt slope changes in these curves. It should also be pointed out that, unlike the measurements of the carbonyl region, the NH region is influenced by hydrogen bonding to both the urethane hard segments and ether soft segments.

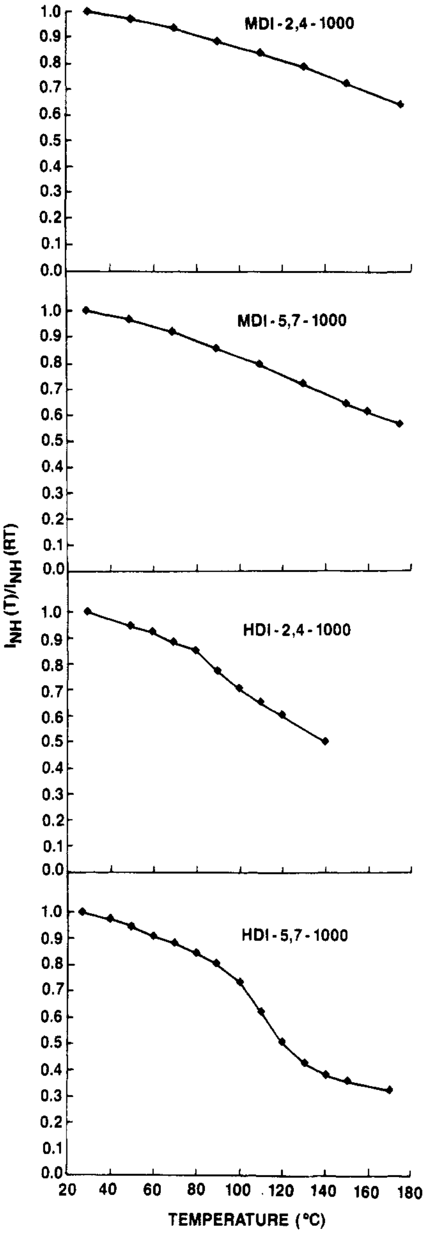


Figure 13. Integrated NH absorbance (normalized to room temperature) as a function of temperature for the polyurethane–diacetylene segmented copolymers.

The general features of the curves generated with this technique are similar to the features of the curves obtained by monitoring the carbonyl region. MDI-2,4-1000 again shows a slope discontinuity at about 80 °C. Both of the HDI-based elastomers exhibit pronounced transitions at the same temperatures revealed by monitoring the carbonyl region. The transition observed in MDI-5,7-1000, however, is barely detectable with this approach due to a greater degree of phase mixing that tends to obscure its weaker hard-domain melting transition. It is to be expected that the copolymers with the least amount of phase mixing and greatest degree of hard-segment crystallinity will exhibit the more pronounced infrared transitions. Thus, from these data it can be concluded that the high-temperature thermal transitions of the copolymers HDI-5,7-1000 and HDI-2,4-1000 observed by TMA and DSC are a result of melting of the hard domains and extensive thermal disruption of hydrogen bonds. For the MDI-based elastomers, on the other hand, it is not clear what role if any the relatively smaller amount of hydrogen bond disruption plays in determining the thermal and mechanical behavior of these materials. In this case, the morphology of the copolymers may be the dominant factor in determining these properties as has been pointed out by Seymour and Cooper.[15]

For the cross-polymerized copolymers, it can be seen in column A of Figure 10 that the conversion of the diacetylene units within the hard domains to the poly(diacetylene) network has dramatically changed the thermal behavior of HDI-5,7-1000. The lower energy absorption due to bonded carbonyl remains strong up to temperatures of 180 °C, indicating only minor changes in the extent of interurethane hydrogen bonding with increasing temperature. This same behavior can be observed in the NH region as shown in column A of Figure 11. Again it can be seen that, in contrast to the original copolymer (column B), the characteristics of a extensively hydrogen bonded material are retained to much higher temperatures. This is to be expected since both TMA and DSC results clearly indicated no melting activity after HDI-5,7-1000 has been cross-polymerized. Graphs of the percentage of interurethane hydrogen bonding vs. temperature and the normalized integrated NH absorbance vs. temperature derived from these spectra are presented in Figures 14 and 15. Similar data generated from HDI-2,4-1000 is also given in these figures. In both cases, a plot of the material before cross-polymerization is included for direct comparison.

The graphs reveal that the cross-polymerized copolymers do not exhibit the thermal transitions characterized by abrupt hydrogen bond disruption. This is most clearly seen in the plots of percent interurethane bonding vs. temperature which represent only the changes in hydrogen bonding taking place in the hard domains. Note that in the case of HDI-5,7-1000, cross-polymerization does not influence the degree of phase separation or domain surface area as indicated by the similar level of interurethane bonding before and after cross-polymerization. For HDI-2,4-1000, however, the topochemical polymerization process results in a significant decrease in this value, indicating perhaps a change in domain shape taking place during cross-polymerization. For both materials, formation of the poly(diacetylene) network structure within the hard domains stabilizes the hydrogen bonded network by restricting the segmental mobility of the urethane segments.

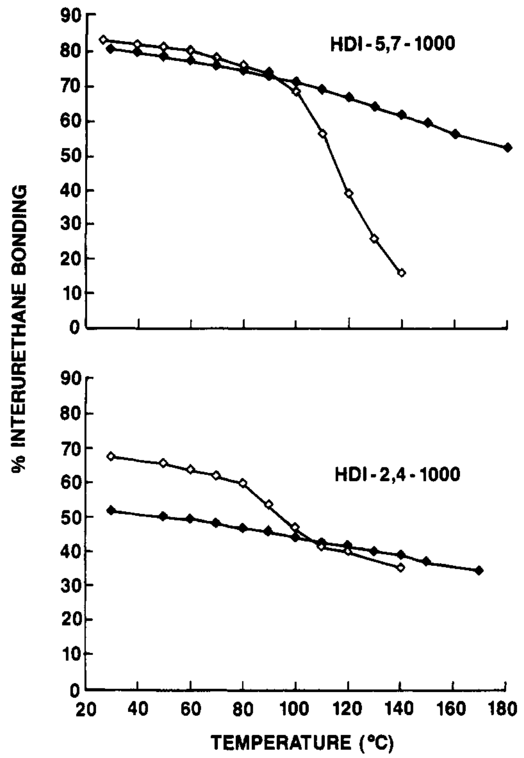


Figure 14. Percentage of interurethane bonding as a function of temperature for HDI-5,7-1000 and HDI-2,4-1000. Open circles represent as-prepared films, and closed circles represent UV cross-polymerized films.

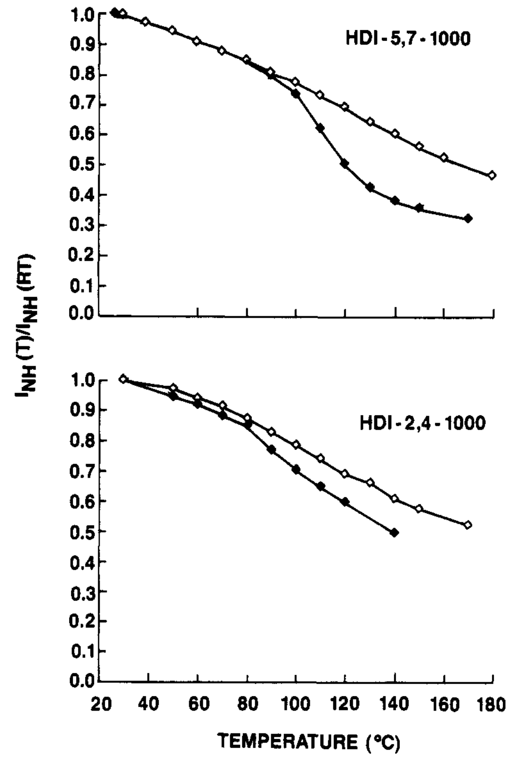


Figure 15. Integrated NH absorbance (normalized to room temperature) as a function of temperature for HDI-5,7-1000 and HDI-2,4-1000. Closed circles represent as-prepared films, and open circles represent UV cross-polymerized films.

Many urethane-substituted poly(diacetylenes) exhibit reversible thermochromic behavior that is related to the sensitivity of the conjugated backbone to changes in the organization and packing of their side groups. The exact origin of this phenomenon is still unclear, and many studies have been aimed at elucidating the mechanism of these rather dramatic changes which occur with heating. In some cases, it has been reported[23] that the thermochromic transitions are accompanied by extensive hydrogen bond disruption that allows the conjugated backbone to adopt a less planar conformation with more localized valence electrons. There are also examples of poly(diacetylenes) in which the thermochromic transitions occur without disruption of hydrogen bonds.[3] As will be discussed in greater detail in the following paper, cross-polymerized HDI-5,7-1000 exhibits a thermochromic transition with an onset at about 90 °C. The data presented here clearly demonstrate that this transition is not the result of an order–disorder transition involving thermal disruption of the interurethane hydrogen bonded network. Indeed, this transition is accompanied by only a slight decrease in interurethane bonding. Close examination of the data in either Figure 14 or 15, however, reveals a clear slope discontinuity occurring at the temperature of the thermochromic transition of cross-polymerized HDI-5,7-1000. It is believed that this change in slope results from the different temperature-dependent behavior of the high-temperature phase of this copolymer. Slope changes of this type related to changes in the thermal expansion coefficient of a material that take place during a phase transition have been well documented.[25] It is also possible that the slope change is due to melting of residual unreacted diacetylene-containing segments still present in the hard domains. Cross-polymerized HDI-2,4-1000, however, which does not exhibit thermochromic behavior and would be expected to contain larger amounts of unreacted diacetylene groups as indicated by thermal analysis of cross-polymerized samples, does not exhibit a similar slope change on heating. It therefore seems reasonable to attribute this abrupt change in slope to the phase change that accompanies the thermochromic transition. The full implications of these results will be discussed in the following paper where the temperature-dependent optical properties of the cross-polymerized elastomers will be examined in greater detail. FTIR temperature studies were not performed on the MDI-based copolymers due to the difficulty of cross-polymerizing solvent-cast thin films of these materials with UV radiation.

2. **Raman Spectroscopy.** Resonance Raman spectroscopy (RRS) has been used extensively to study the vibrational and electronic properties of the conjugated backbone of the poly(diacetylenes).[26] Unlike infrared spectroscopy, which is insensitive to backbone-related vibrations, RRS probes only those vibrational modes that are coupled to the electronic states of the conjugated backbone. Thus, by exciting an electronic transition of the π-electron system of the backbone, it is possible to resonantly enhance the intensity of Raman bands associated with the part of the molecule giving rise to the electronic transition. This resonance effect dramatically increases the Raman intensity of backbone-related vibrations, making it possible to examine the conjugated backbone of the poly(diacetylenes).

Figure 16 displays the room temperature Raman spectra (excitation wavelength 632.8 nm) of the polyurethane–diacetylene copolymers. The spectra were obtained on molded samples of the elastomers cross-polymerized for 2 weeks with ^{60}Co γ radiation. In the case of HDI-2,4-1000, a large fluorescent background prevented the obtainment of an acceptable spectrum of this material. Cross-polymerization of films of HDI-2,4-1000 by UV radiation, however, resulted in materials that did not exhibit this phenomenon. The broad fluorescent background of HDI-2,4-1000 cross-polymerized by γ radiation indicates that extensive disordering has occurred during polymerization by this highly ionizing radiation.[26] The samples polymerized by UV radiation apparently were less susceptible to this and hence were used for the Raman studies.

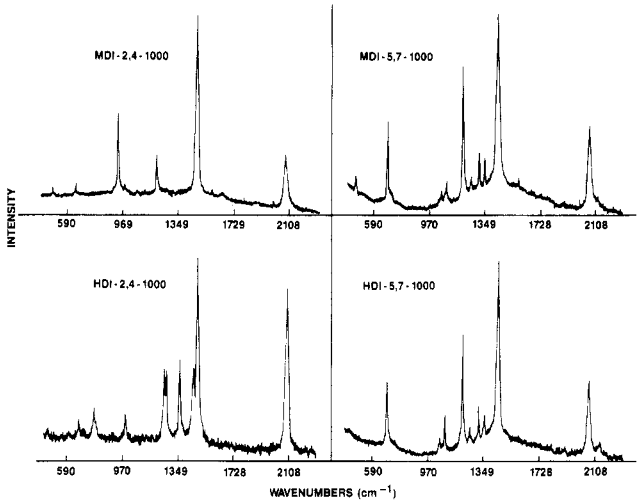


Figure 16. Raman spectra of the polyurethane–diacetylene elastomers.

The Raman data clearly show that cross-polymerization of the diacetylene units within the hard domains produces the poly(diacetylene) conjugated backbone expected from the 1,4 addition polymerization of these reactive groups. The Raman bands characteristic of the carbon–carbon double bond and triple bond vibrations of the conjugated backbone of the cross-polymerized elastomers are found around 1450 and 2050 cm^{-1}, respectively. The exact frequencies of these vibrations are determined by the extent of electron delocalization along the conjugated backbone.[27] At greater extents of delocalization, the frequency of the vibration becomes lower since delocalization tends to lower the effective bond stretching force constants.

Variations in the Raman spectra result from a coupling of the motion of the side-group atoms with the motion of the backbone atoms.[28] The spectra of HDI-5,7-1000 and MDI-5,7-1000 are therefore very similar since the sequence of atoms closest to the backbone is identical, with the differences resulting from the different diisocyanate residues being too far from the backbone to influence it. The copolymers chain extended with 2,4-hexadiyne-1,6-diol, on the other hand, exhibit quite different spectra due to the influence of the atoms nearest the backbone, which now includes the structure of the diisocyanate residues (only one carbon atom away from the backbone).

C. **Wide-Angle X-ray Diffraction.** The wide-angle X-ray diffraction patterns of the polyurethane–diacetylene segmented copolymers are shown in Figure 17. Unless otherwise stated, samples for diffraction studies were prepared by hot pressing the elastomers into films at 110 °C and 600 psi. The MDI-based elastomers show no indication of hard-segment crystallinity as evidenced by the occurrence of only a broad amorphous halo centered at about 20° (2θ). The HDI-based elastomers, on the other hand, exhibit both amorphous and crystalline reflections. In the case of HDI-5,7-1000, an intense relatively narrow crystalline diffraction peak centered at about 24° overlaps the amorphous halo centered at about 20.5°. HDI-2,4-1000 exhibits a much less intense crystalline diffraction peak also centered at about 24° and an amorphous halo centered at about 20.5°. The presence of hard-segment crystallinity is therefore indicated for the HDI-based elastomers.

These results confirm the conclusions drawn from the thermal and infrared studies that indicated that hard-segment crystallinity is most developed in HDI-5,7-1000 and HDI-2,4-1000. Recall that the magnitude of hydrogen bond disruption occurring during the high-temperature

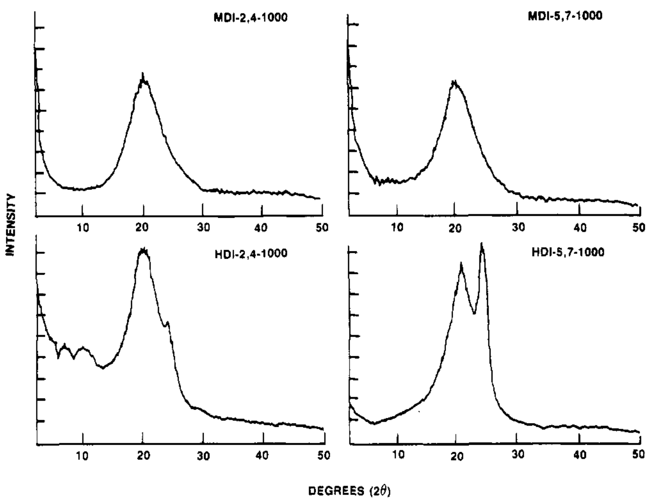


Figure 17. X-ray diffraction patterns of the polyurethane–diacetylene elastomers.

thermal transitions detected by FTIR temperature studies was largest in HDI-5,7-1000, followed by HDI-2,4-1000, and finally by MDI-5,7-1000, which exhibited a barely detectable transition. No evidence for hard-domain crystallinity was provided for MDI-2,4-1000 by either DSC or FTIR. The diffraction results are completely consistent with the results obtained by the other techniques with the exception of MDI-5,7-1000, which exhibited a crystalline melting endotherm by DSC and no indication of crystallinity by X-ray diffraction. Considering the weak transition observed by infrared thermal analysis, it is not surprising that crystallinity in MDI-5,7-1000 is not detectable by X-ray diffraction. This implies that the extent of crystallinity in MDI-5,7-1000 is low and the crystallite size is small.

The hard-segment crystallinity of HDI-5,7-1000 was found to vary considerably with sample preparation. For example, samples prepared by casting films from DMF solutions were less crystalline than samples prepared by hot pressing films, as indicated by a less intense crystalline diffraction peak. Annealing these films at 90 °C for 2 h, however, resulted in an increased intensity and, hence, improved hard-domain crystallinity. To examine the effect of cross-polymerization on the crystallinity of HDI-5,7-1000, a film was cross-polymerized by exposure to ^{60}Co γ radiation for 2 weeks and then subjected to X-ray analysis. Figure 18 shows the diffraction patterns of a film of HDI-5,7-1000 (a) as-formed, (b) cross-polymerized, and (c) cross-polymerized and heated to 140 °C. The cross-polymerized film still retains its intense crystalline diffraction peak although it has been diminished slightly by the polymerization process. Cross-polymerization of the diacetylene units therefore proceeds with retention of hard-segment crystallinity as is frequently encountered in the topochemical polymerization of diacetylene monomers to poly(diacetylenes). The final diffraction peak in Figure 18c shows that crystallinity is not completely lost when a cross-polymerized film is heated to the thermochromic transition and cooled to room temperature. The decrease in peak intensity indicates that some amount of disorder is introduced during this transition.

IV. Conclusions

The incorporation of reactive diacetylene groups in the hard-segment structures of polyurethane elastomers has resulted in materials whose thermal, mechanical, and optical properties can be readily modified by controlling the solid-state reaction of these groups. The unique properties of the polyurethane–diacetylene elastomers result from a two-phase domain structure in which the diacetylene groups reside in hard-segment domains dispersed throughout a continuous soft-segment phase. Evidence for the existence of a two-phase domain morphology has been provided by thermal analysis, infrared analysis, and wide-angle X-ray diffraction. These techniques revealed that the polyurethane–diacetylene segmented copolymers derived from the aliphatic diisocyanate HDI were more phase separated than the MDI-based diacetylene copolymers, as evidenced by their lower soft-segment glass transition temperatures and higher degrees of interurethane hydrogen bonding. The HDI-based polyurethane–diacetylene copolymers were found to contain crystalline hard domains in contrast to the MDI-based materials in which hard-segment crystallinity was only weakly developed in MDI-5,7-1000. Infrared thermal analysis showed that the high-temperature thermal transitions of the HDI-based elastomers are related to a disordering of the hard domains resulting in extensive thermal disruption of hydrogen bonds.

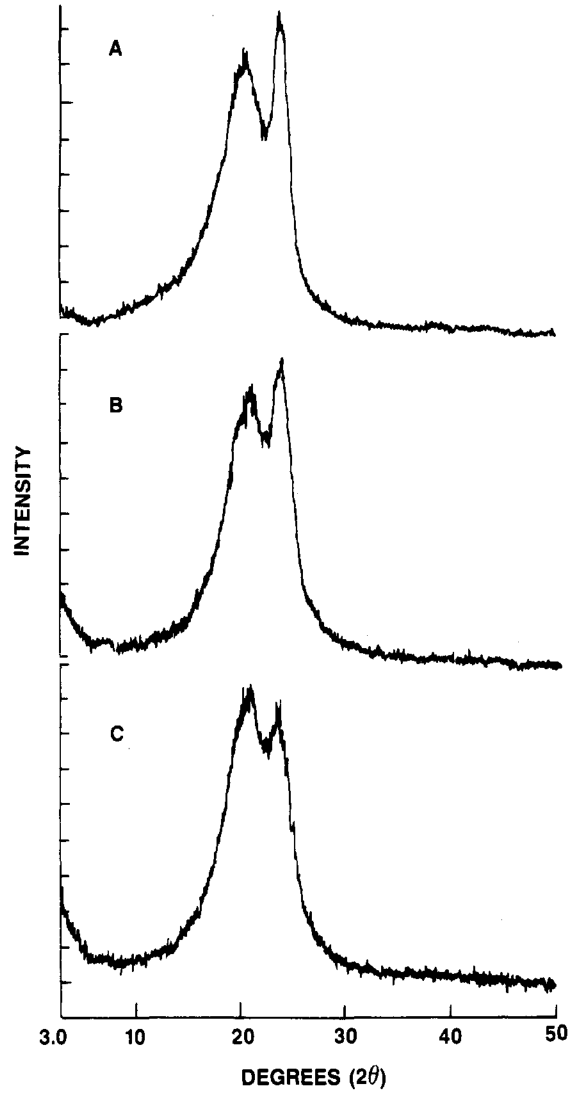


Figure 18. X-ray diffraction patterns of HDI-5,7-1000: (A) as-molded film; (B) cross-polymerized; (C) cross-polymerized, heated to 140 °C, and cooled to room temperature.

The polyurethane–diacetylene segmented copolymers exhibit the physical and mechanical properties of traditional polyurethane elastomers. Most notably, the thermal behavior of MDI-2,4-1000 was found to be very similar to MDI-based polyurethanes chain extended with butanediol.

However, it was shown that the thermal–mechanical properties of the elastomers could be dramatically modified by initiating cross-polymerization of the diacetylene groups residing in the hard domains. Raman spectroscopy revealed that cross-polymerization was accomplished by the expected solid-state 1,4 addition polymerization of the diacetylene groups, resulting in the formation of the conjugated poly(diacetylene) backbone. Thermal mechanical analysis indicated that this chemistry was restricted to the hard domains. The most extensive conversion of the diacetylene groups to the poly(diacetylene) network structure was found in HDI-5,7-1000, which exhibited the least amount of phase mixing and the greatest degree of hard-segment crystallinity. This is to be expected since the cross-polymerization reaction is a topochemical process that is best facilitated by highly crystalline organizations that allow for optimum packing of the diacetylene groups. The successful cross-polymerization of the diacetylene groups of the MDI-based elastomers, however, indicates that the reaction can proceed in systems with limited long-range order. In this case, the local geometric arrangement of the diacetylene groups is sufficient for the topochemical reaction to occur.

For all of the elastomers, cross-polymerization by γ radiation resulted in materials that were infusible, and insoluble and exhibited limited thermal activity up to temperatures of about 250 °C. Thus, it was demonstrated that the elastomers could be molded at temperatures near their melting or softening points (between 100 and 125 °C) and subsequently cross-polymerized to obtain materials that retained their mechanical integrity to much higher temperatures. Since cross-polymerization only takes place in the hard domains, the flexible elastomeric nature of the soft segments is unaffected by the formation of the poly(diacetylene) backbone. This allows one the ability to study changes in the mechanical behavior of segmented polyurethanes resulting from an in situ modification of the structure of the hard domains. For elastomers such as HDI-5,7-1000, this occurs without any changes in the degree of phase separation or domain surface area, eliminating many variables that normally make such an analysis difficult. In other words, modification of the mechanical behavior of the elastomers proceeds without any major changes in their morphology. Clearly, the resultant changes in the mechanical properties of the elastomers will depend on how the two phases are organized, i.e., if the two phases are continuous or if one phase is isolated and dispersed in a continuous phase of the other. The full implications of this are currently under investigation.

In addition to changes in the mechanical behavior of the elastomers, cross-polymerization results in materials that exhibit the optical behavior of the poly(diacetylenes). For example, cross-polymerized HDI-5,7-1000 displays a thermochromic transition at about 100 °C. This transition was shown to proceed without thermal disruption of hydrogen bonds as is the case for some thermochromic poly(diacetylenes). The optical properties of the polyurethane–diacetylene copolymers and the influence of temperature and stress on these properties will be the subject of the next paper in this series.

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Registry No. MDI-2,4-1000, 98973-17-2; MDI-5,7-1000, 98973-19-4; HDI-2,4-1000, 98973-18-3; HDI-5,7-1000, 98973-20-7.

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