Thermal and Mechanical Properties of Polyurethane–Diacetylene Segmented Copolymers. 2. Effects of Diacetylene Cross-Polymerization

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ABSTRACT: Selective cross-linking of the hard domains of segmented polyurethanes via the radiation-induced solid-state reaction of diacetylene groups was utilized to ascertain the influence of hard domain cohesion and rigidity on the mechanical properties of these materials. The rigidity and mechanical integrity of the hard segment domains were found to play an extremely important role in determining their mechanical behavior. The specific influence exerted by the hard domains was found to be strongly dependent on molecular weight, the level and type of hard segment ordering, and the microstructure of the material. In all cases, the effect of diacetylene cross-polymerization was to increase the modulus and decrease the ultimate tensile strain. The ultimate tensile strength was found to initially increase, reach a maximum, and eventually decrease upon exposure to high-energy electrons. Disruption and reorganization of the hard domain system at high stress levels was verified as an important strengthening mechanism in segmented polyurethanes.

I. Introduction

In the preceding paper, it was argued that improved hard segment ordering brought about by suitable annealing treatments can significantly increase the mechanical integrity and cohesion of the hard domains of diacetylene-containing segmented polyurethanes. This, in turn, dramatically enhances the ultimate tensile properties of these materials in a way that is strongly dependent on the specific mode of deformation active in the copolymer. Although thermal analysis indicated that the primary effect of annealing was to improve ordering within the hard domains, it is not possible to completely rule out the possibility that morphological changes, such as changes in the size and/or shape of the hard domains, also occur during annealing. These latter effects make it difficult to directly relate the observed mechanical property changes to a specific structural modification.

In the diacetylene-containing segmented polyurethanes, hard domain cohesion can also be increased by radiation-induced cross-polymerization of the diacetylene groups present in the hard segment domains. In this case, cross-polymerization creates a networklike structure in which hard segments are linked together by the covalent bonds of the resultant polydiacetylene backbone. This process is illustrated in Scheme I for a single stack of hard segments. Since the polymerization reaction is a topochemical diffusionless process, improved hard segment cohesion takes place without significant changes in the size, shape, or ordering of the hard domains. This means that it is possible to introduce well-defined cross-links into the hard domains without disruption of the copolymer's morphology. In addition, since increased hard segment cohesion is accomplished by the development of a cross-linked hard domain structure, the resultant structural modifications are permanent as opposed to the temporary state (in terms of mechanical stability) of improved hard domain ordering that results from annealing.

In this paper, we explore the influence of diacetylene cross-polymerization on the mechanical properties of these new materials. As will be discussed, there are many similarities as well as important differences between the effects of annealing and the effects of cross-polymerization on

**Scheme I
Schematic Representation of Diacetylene
Cross-Polymerization within the Hard Domains**
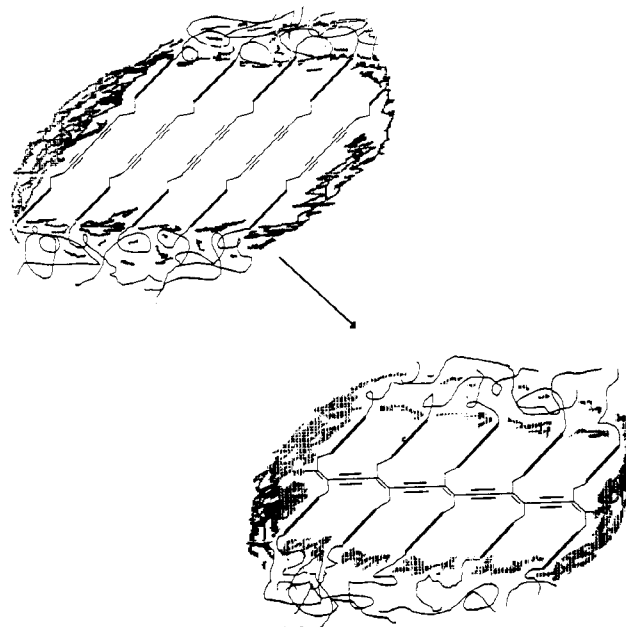
the mechanical behavior of the diacetylene-containing copolymers.

II. Experimental Section

The polyurethane–diacetylene elastomers used in this study were prepared as described in a previous publication.[1] In all cases, the mole ratio of diisocyanate, poly(tetramethylene oxide) (PTMO), and chain extender was maintained at 2:1:1. The details concerning the experimental procedures and equipment used to characterize the elastomers can be found in the Experimental Section of the preceding paper.

Samples were prepared by the solvent casting technique described in the preceding paper and thereafter irradiated by exposure to high-energy electrons from a Van de Graff electron accelerator operated at 2.6 MeV. In those cases where high radiation dosages were employed, incremental dosage treatments were applied to ensure that excessive sample heating did not occur. In all cases, the temperature of the samples did not
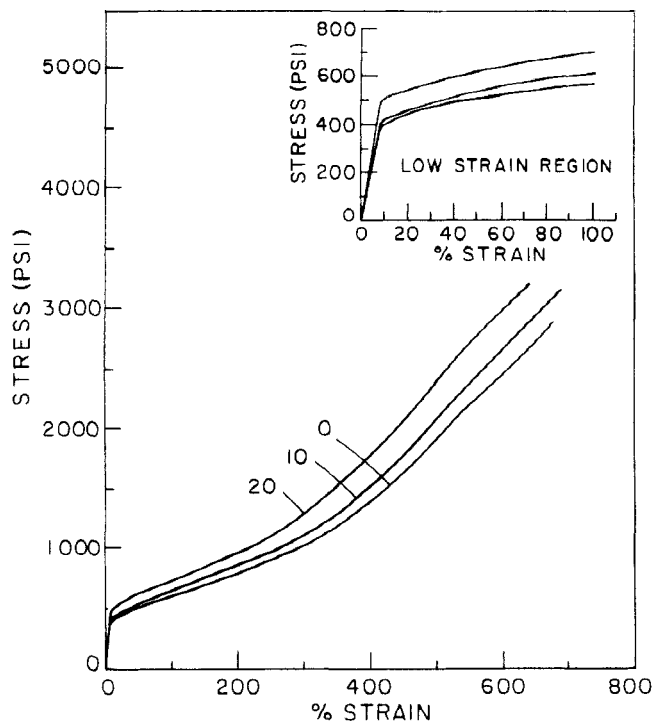
Figure 1. Stress–strain curves of MDI–butanediol–PTMO as a function of radiation dosage. Numbers indicate radiation dosage in megarads.

Table I
Properties of MDI–Butanediol–PTMO as a Function of Radiation Dosage

radiation dosage, Mrad	M_w	T_g, °C (onset, midpoint, end)	modulus, psi 10%	100%
0	109 000	−54, −48, −39	4000	570
10	118 500	−55, −47, −39	4170	620
20	148 500	−55, −48, −37	5000	700

rise above 50 °C. All samples were annealed at 90 °C for 45 min prior to irradiation unless otherwise noted. The mechanical testing procedures used were identical with those employed in the preceding paper.

III. Results and Discussion

1. Effects of β-Radiation on Conventional Segmented Polyurethanes. Before discussing the effect that diacetylene cross-polymerization has on the thermal and mechanical properties of the various diacetylene-containing segmented polyurethanes, it is appropriate to comment on how these same properties are modified when segmented polyurethanes that do not contain the reactive diacetylene group are exposed to high-energy electrons. In order to accomplish this, a conventional segmented polyurethane synthesized from 4,4′-methylene-bis(phenyl isocyanate) (MDI), butanediol, and PTMO-1000 (MDI-BD-1000) in a fashion similar to that adopted for the diacetylene elastomers was analyzed after various exposures to electron beam radiation. These experiments were conducted to ensure that the dramatic changes in mechanical and thermal properties observed after radiation treatment of the diacetylene-containing segmented copolymers were not simply due to the creation of radiation-induced cross-links randomly introduced into either the soft segment or hard segment phase.

Figure 1 shows the stress–strain curves of MDI-BD-1000 after exposure to a 0, 10, and 20 Mrad dosage of electron radiation. Table I lists the values of select properties of this material after radiation treatment. As can

be seen, the 10 Mrad dosage produces only a slight improvement in the tensile strength of the copolymer and no significant change in its ultimate strain. Increasing the dosage to 20 Mrad causes a further increase in the tensile strength and modulus of the copolymer although the magnitude of these changes is still extremely small compared to those observed in the diacetylene-containing elastomers (see next section). It is clear from these results that some minor structural modification of the material does take place during electron irradiation. The effects of these structural changes on the mechanical properties of the polymer, however, are relatively small; particularly at the dosage levels found to introduce the maximum increase in tensile strength of the diacetylene-based elastomers (less than 10 Mrads for the MDI-based materials and less than 1.0 Mrad for the HDI-based materials).

The thermal properties of MDI-BD-1000 are also very insensitive to radiation treatment. For example, thermal analysis of these same samples revealed no significant changes in the DSC thermograms of this material due to electron beam exposure. As can be seen in Table I, the temperature and breadth of the glass transition were essentially unchanged by the radiation treatment. This is consistent with previously reported[1] TMA results, which demonstrated that dosages exceeding 30 Mrads of γ-radiation did not significantly alter the softening point of this material. It should also be noted that MDI-BD-1000 was found to be completely soluble in THF after the radiation treatment, implying the absence of extensive radiation-induced cross-linking.

It is to be expected that very high dosages of electron radiation will introduce either cross-linking and/or chain scission into polymers of this type. Cross-links would occur at random locations within the polymer and would be expected to increase its overall molecular weight. The weight-average molecular weight of MDI-BD-1000 was found to increase from 109 000 to 118 500 and finally to 148 500 after exposure to 10 and 20 Mrads, respectively. In general, the breadth of the molecular weight distribution increased with increasing radiation levels and a small but significant shoulder developed in the high molecular weight region of the GPC chromatogram, which was most pronounced in the sample exposed to 20 Mrads. The higher molecular weight calculated for this latter sample is a direct consequence of this shoulder, which indicates the creation of a small fraction of very high molecular weight chains. To determine if the cross-links were occurring in the soft segment phase, a sample of PTMO having an initial molecular weight of 2000 was exposed to a 30-Mrad dosage of electron radiation. The molecular weight of this material was found to increase by a factor of approximately 1.75, indicating that cross-linking does indeed occur between the soft segments at very high dosages. Thus, although the thermal and mechanical properties of MDI-BD-1000 are not significantly altered by radiation treatment, it is clear that cross-links in the soft segment phase and possibly hard segment phase are created at very high radiation dosages.

In summary, exposure of a conventional segmented polyurethane to radiation dosages representing the higher end of those employed in this study results in only modest changes in its mechanical properties and no detectable changes in its thermal properties. Thus, although random cross-links are introduced at these high dosages as indicated by changes in the molecular weight of the material, it can be safely concluded that the property changes resulting from radiation treatment of the diacetylene-
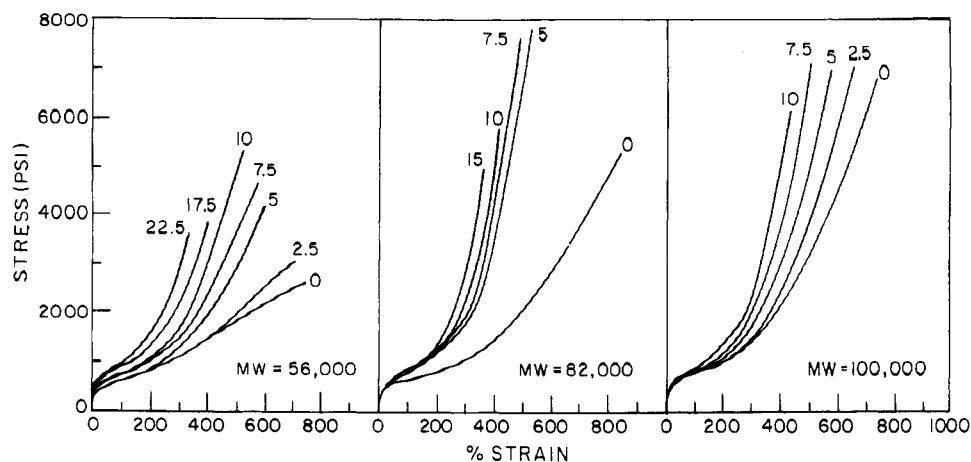
Figure 2. Stress–strain curves of samples of MDI-5,7-1000 with different molecular weights as a function of radiation dosage. Numbers indicate radiation dosage in megarads.
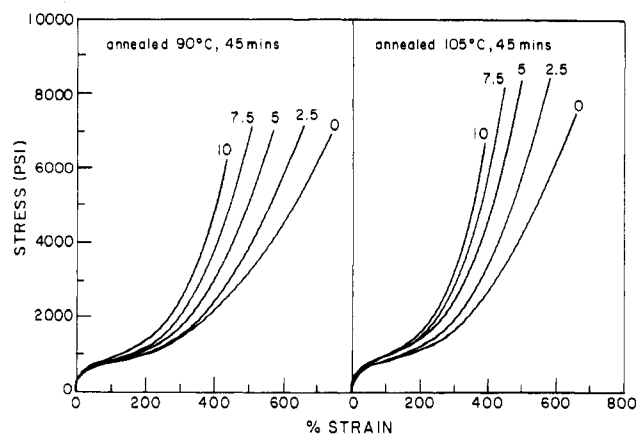

Figure 3. Stress–strain curves of MDI-5,7-1000 (M_w = 100 000), annealed for 0.75 h at either 90 or 105 °C, as a function of radiation dosage. Numbers indicate radiation dosage in megarads.

based elastomers are primarily related to cross-polymerization of the diacetylene groups residing within the hard domains. The presence of highly reactive diacetylene groups in the elastomer would also be expected to suppress some of the radiation-induced reactions that would normally occur in these materials, therefore limiting their impact on the mechanical behavior.

2. Effects of Cross-Polymerization—General Comments. As anticipated, the mechanical properties of all of the diacetylene-containing segmented copolymers are dramatically modified by diacetylene cross-polymerization. Figures 2–6 display the stress–strain curves of the various elastomers evaluated in this work whereas Table II lists the values of various mechanical properties of the lower molecular weight samples of the elastomers. In all cases, the ultimate strain of the copolymers was found to decrease as a function of increasing radiation exposure while the response of the ultimate tensile strength to radiation is more varied and is dependent on the specific elastomer, its molecular weight, and its thermal history. The inset in select figures magnifies the region between 0 and 100% strain and illustrates that the increase in rigidity and cohesion of the hard domains due to cross-polymerization also has a significant effect on the small strain properties of the segmented copolymers. It should also be mentioned that cross-polymerized samples, even after very low radiation dosages, become completely insoluble in solvents that would normally readily dissolve them. In fact, it is possible to control the degree of solvent swelling of these materials by simply controlling their degree of cross-polymerization.

The numbers displayed in the figures indicate the total radiation dosage for a given sample and are related to the amount of cross-polymerization that has occurred within the hard domains. The range of radiation exposures required to generate a complete set of curves is highly dependent upon the type of elastomer under consideration with the MDI-based materials typically reaching their maximum tensile strengths after a 5–10-Mrad dosage compared to only a 0.5–1.0-Mrad dosage for the HDI-based materials. This later observation is a direct consequence of the higher degree of hard segment crystalline order present in the HDI-based materials, which results in larger stacks of well-correlated diacetylene groups that are better organized for the lattice-controlled polymerization. In effect, the resultant polydiacetylene chains will link together more hard segments per conjugated chain in a crystalline environment than in a paracrystalline or weakly ordered environment. Thus, both the extent of cross-polymerization and its effectiveness at rendering the hard domains more cohesive and rigid will be increased when diacetylene groups are polymerized in segmented polyurethanes with crystalline hard domains. As a result of this, higher radiation dosages are required to effect similar changes in the mechanical properties of materials with less ordered hard domains than for materials with more ordered hard domains. In the less ordered systems, there will also be a larger fraction of isolated diacetylene groups that are not capable of undergoing cross-polymerization.

3. Effects of Cross-Polymerization on the MDI-5,7-Based Materials. It was noted in the preceding paper that the mechanical properties of the diacetylene-containing segmented copolymers are highly dependent on molecular weight and thermal history. These two parameters were also found to influence the effect that diacetylene cross-polymerization has on mechanical behavior. Figures 2 and 3 display the stress–strain curves of samples of MDI-5,7-1000 with different molecular weights and annealing treatments.

It can be seen in Figure 2 that variations in molecular weight have a significant effect on the magnitude of the increase in tensile strength that accompanies cross-polymerization. Samples with lower molecular weights show a greater improvement in tensile strength than the higher molecular weight samples. For example, the ultimate tensile strength of a sample with a molecular weight of 56K increases by a factor of 2 whereas a sample with a molecular weight of 82K only increases by a factor of 1.5 and a sample with a molecular weight of 100K shows
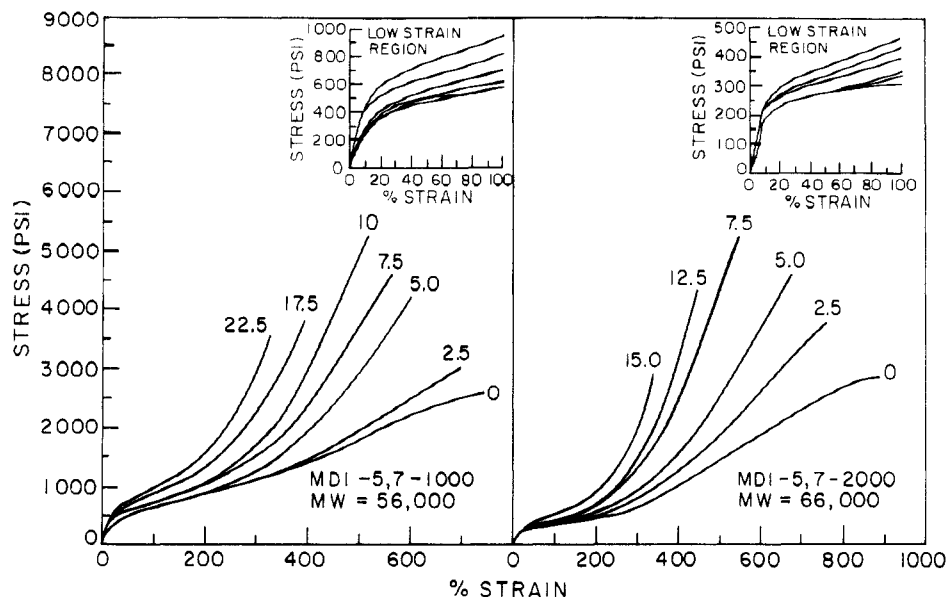
Figure 4. Stress–strain curves of MDI-5,7-1000 and MDI-5,7-2000 as a function of radiation dosage. Numbers indicate radiation dosage in megarads.
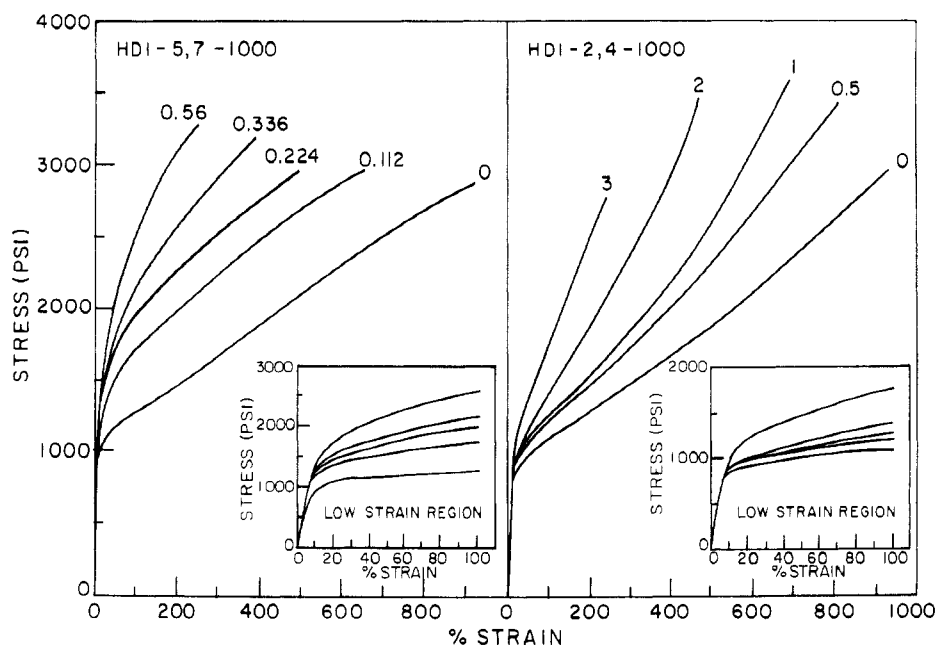

Figure 5. Stress–strain curves of HDI-5,7-1000 and HDI-2,4-1000 as a function of radiation dosage. Numbers indicate radiation dosage in megarads.

only a minor increase in tensile strength. In all cases, the ultimate strain decreases with increasing levels of cross-polymerization, while the ultimate tensile strength increases, passes through a maximum, and then begins to decrease. The lower molecular weight materials also require a higher radiation dosage to reach their maximum tensile strength as compared to the higher molecular weight materials.

Annealing also influences the way that MDI-5,7-1000 responds to cross-polymerization although in a less significant way than molecular weight. In general it was found that, for the lower molecular weight samples, the most dramatic changes in ultimate tensile strength after cross-polymerization occurred in materials with less ordered hard domains. For example, annealing the MDI-5,7-1000 sample (M_w = 82K) shown in Figure 2 for 2 h (the sample in the figure was annealed for 0.75 h) at 90 °C causes its nonirradiated curve to shift to a higher ultimate tensile strength and lower ultimate tensile strain.

After optimum irradiation treatment, however, the material exhibits tensile properties very similar to those of the material annealed for the shorter time and subsequently irradiated. As a result of this, the samples annealed for 2 h display a less dramatic improvement in tensile properties than the samples annealed for 0.75 h. This essentially reflects the fact that the samples annealed for longer times display a higher starting tensile strength (nonirradiated material) than those annealed for shorter times.

For the higher molecular weight materials, the changes observed in tensile strength as a result of cross-polymerization were less significant and only weakly dependent upon annealing treatment. The stress–strain curves of MDI-5,7-1000 (M_w = 100 K) obtained from samples annealed at either 90 or 105 °C for 0.75 h and subsequently irradiated with an electron beam are compared in Figure 3. In both cases, the tensile strength increases only slightly relative to that of the nonirradiated sam-
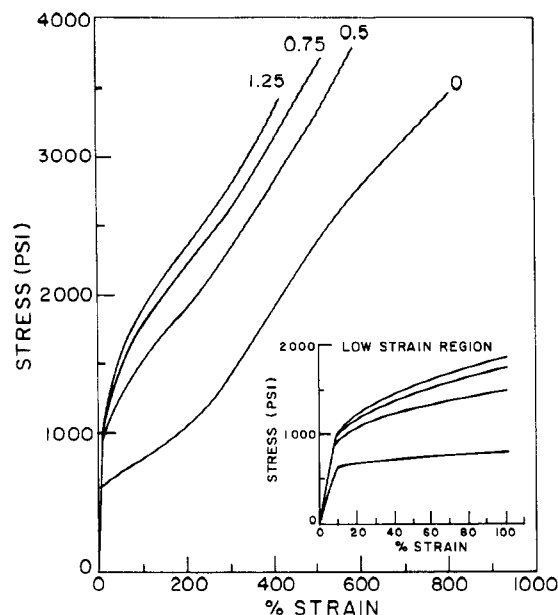
Figure 6. Stress–strain curves of HDI-5,7-2000 (M_w = 79 000) as a function of radiation dosage. Numbers indicate radiation dosage in megarads.

Table II
Stress–Strain Properties

elastomer	radiation dosage, Mrad	% strain at failure	UTS, psi	10% modulus, psi	100% modulus, psi
MDI-5,7-1000	0.0	740	2580	2500	570
(M_w = 56 000)	2.5	700	2990	2500	570
	5.0	600	4160	2800	590
	7.5	570	4580	2800	610
	10.0	520	5270	3000	690
	17.5	400	3850	4100	820
	22.5	330	3560	4600	940
MDI-5,7-2000	0.0	880	2880	1820	310
(M_w = 62 000)	2.5	760	3780	1820	340
	5.0	680	4620	1850	340
	7.5	550	5280	2250	400
	12.5	450	4360	2310	430
	15.0	340	2810	2500	460
HDI-5,7-1000	0.0	910	2840	9820	1290
(M_w = 98 000)	0.112	650	2950	12130	1730
	0.224	480	2970	13430	1960
	0.336	380	3160	12990	2150
	0.560	240	3260	14570	2560
HDI-5,7-2000	0.0	850	3780	6140	810
(M_w = 79 000)	0.50	590	3770	9490	1500
	0.75	520	3700	10220	1760
	1.25	420	3410	10120	1860
HDI-2,4-1000	0.0	930	2960	8710	1100
(M_w = 61 000)	0.5	810	3430	9140	1210
	1.0	690	3580	9140	1300
	2.0	460	3450	8610	1400
	3.0	230	2740	10290	1790

ples, although the samples annealed at the higher temperature display a more noticeable increase in tensile strength as a result of cross-polymerization and exhibit a larger ultimate tensile strength. These latter samples also develop a very sharp endotherm at about 130 °C in their DSC curves characteristic of well-ordered hard domains, whereas all of the samples annealed at 90 °C still exhibit relatively broad endothermic transitions after annealing treatment.

It is clear from these last two figures that as the ultimate tensile properties of MDI-5,7-1000 improve by either increases in molecular weight or via suitable annealing treatments, the effect that cross-polymerization has on

increasing the tensile strength generally becomes less significant. In other words, the most dramatic enhancement of ultimate tensile strength by cross-polymerization occurs in the lower molecular weight materials and, to a lesser extent, in the materials with less ordered hard domains. To understand the overall response of the mechanical properties of MDI-5,7-1000 to cross-polymerization it is necessary to consider the primary mechanism of deformation active in this material. Before examining the impact of deformation mode on MDI-5,7-1000's response to cross-polymerization, however, it is worth briefly reviewing the basic strengthening mechanisms believed to be active in two-phase materials.

Smith[2,3] claims that the hard domains contribute to the strengthening process in two ways: first by acting as virtual cross-links that restrict viscous flow and mechanically reinforce the elastomer and second by dissipating strain energy by undergoing plastic deformation and cavitation. They also prevent failure by deflecting and bifurcating propagating cracks. The nature of the tasks facing the hard domains therefore requires opposing characteristics: their task of mechanical reinforcement demands rigidity and a high level of cohesiveness, whereas to be able to effectively dissipate strain energy they must undergo molecular reorganization and plastic deformation at some point. Optimization of these two conflicting roles would be expected to produce materials with the best overall mechanical properties.

In the preceding paper, it was noted that the less phase separated MDI-based elastomers respond to tensile elongation primarily by extension and alignment of the soft segment phase, which, in turn, is best facilitated when the hard domains remain intact during stretching. For a given molecular weight, the largest tensile strengths were realized when annealing treatments created better ordered, more cohesive hard segment domains that could resist breakup at low strains and allow the soft segments to reach higher levels of extension at lower strains. This is analogous to a strain amplification effect[4] since the presence of less deformable hard domains results in local strains in the soft segment phase that significantly exceed the macroscopic strain. The development of aligned and possibly crystalline regions of the soft segments during elongation increases the strength of the material, as these domains are very effective at inhibiting catastrophic crack growth.[2,3] Thus, for MDI-5,7-1000, structural modifications that enhance hard domain cohesion would be expected to increase the ultimate tensile strength and decrease the ultimate tensile strain of this material. The full potential of the system, however, can only be realized if the hard domains can still plastically deform when very high stress levels are reached within the material.

In light of the previous comments, we now attempt to explain the behavior of MDI-5,7-1000 in terms of its varied responses to cross-polymerization. Cross-polymerization increases the structural integrity of the hard domains by creating permanent cross-links between the hard segments. This, in turn, prevents extensive disruption and reorganization of the hard domains from taking place during tensile elongation. At low levels of cross-polymerization, the effect is equivalent to improving hard segment cohesion by suitable annealing treatments; namely, the hard domains can resist deformation at low strains, thereby increasing the local strains existing in the soft segment phase. Since only a limited number of cross-links have been introduced at this point, the hard domains can still deform at high stress levels, ensuring that this additional strengthening mechanism is still operating. At

higher levels of cross-polymerization, however, the hard domains have been cross-linked to the point that hard domain disruption and plastic deformation are severely limited. Without this latter mechanism to fend off catastrophic crack propagation, the material becomes weaker and its ultimate tensile strength decreases. This is in contrast to the annealed materials, which, due to the virtual nature of their cross-links, can still deform at high stresses. The decrease in ultimate strain that accompanies cross-polymerization is a natural consequence of the fact that the permanent cross-links created between the hard segments allow less slippage and elongation of the hard domains, giving rise to a more pronounced strain amplification effect in the material.

Preliminary visible optical studies indicate that the hard domains in MDI-5,7-1000 begin to undergo a major breakup and reorganization above about a 450% strain. This conclusion was based on the observation of a dramatic color change in lightly cross-polymerized samples near this strain level indicative of changes in the molecular environment and order of the small number of polydiacetylene chains present in the hard domains. Interestingly, this is also the strain level at which MDI-5,7-1000 begins to show decreases in its ultimate strength after optimum irradiation treatment. Thus, the best overall tensile properties are obtained when the hard domains have been lightly cross-linked to improve hard segment cohesion and yet still can undergo reorganization and breakup at high strain levels.

In low molecular weight samples, particularly those with weakly associated hard domains, the network established by the virtual cross-linking of hard segments is easily disrupted during elongation. The existence of fewer hard segments per chain in the low molecular weight samples weakens the network, as a larger fraction of the tie molecules that link the various hard segment aggregates (and possibly spherulites) together will be rendered ineffective when their limited number of hard segments within each hard domain are pulled free from the hard domains. In this case, the formation of covalent cross-links via diacetylene cross-polymerization results in hard segments that are now permanently anchored within the hard domains. Consequently, there is less opportunity for stress relaxation via slippage and pulling out of chains from the hard domains when the material is stressed. Another way of looking at it is that the hard domains in these thermoplastic elastomers are essentially pseudo-cross-links that can come apart at high stress levels. Diacetylene cross-polymerization increases the integrity of these pseudo-cross-links, making them capable of bearing larger stresses. The lower molecular weight elastomers therefore benefit from the added strength associated with the previously unobtainable development of highly extended and aligned soft segments (and possibly crystalline soft segment domains), which contributes to the dramatic improvement in ultimate tensile strength of the material.

In the higher molecular weight samples, the network is more firmly established and therefore less vulnerable to the effects of chain slippage etc. In other words, the higher degree of chain entanglements and greater number of hard segments per chain anchored in hard domains ensures that the added strength associated with extension and alignment of the soft segments will be realized. Thus, as the molecular weight of the elastomer increases, the effect that cross-polymerization has on increasing its tensile strength becomes less dramatic. The effect of cross-polymerization in this case is to decrease the ultimate tensile strain without significant changes in the ultimate

tensile strength. Also note that as the molecular weight of the MDI-5,7-1000 polymers increases, the effect that diacetylene cross-polymerization has on the small strain modulus of the material also decreases, indicating that premature breakup of the hard domains at low strains is less prevalent in the higher molecular weight samples.

Annealing also improves the effectiveness of the network by improving hard domain cohesion, which, in turn, prevents premature hard domain breakup during elongation. The weaker secondary forces holding the hard domains together (particularly small hard domains) are readily overcome during elongation, making their contribution to the effective network essentially negligible. Again we find that as the hard domain network becomes more effective, in this case by improved hard domain cohesion, cross-polymerization has less of an impact on increasing tensile strength. The effects of annealing are most noticeable in the lower molecular weight samples, which are more sensitive to weakly associated hard segment domains due to their less entangled state.

A comparison of MDI-5,7 based materials with similar overall molecular weights but different soft segment molecular weights is presented in Figure 4. The nonirradiated sample of MDI-5,7-2000 displays a lower small strain modulus, is more extensible, and exhibits a more pronounced upturn in its stress–strain curve than the nonirradiated sample of MDI-5,7-1000. This is a direct result of the higher molecular weight PTMO soft segments in MDI-5,7-2000, which are more amenable to strain induced crystallization and also lower the hard domain content of this material relative to MDI-5,7-1000. The optimum ultimate tensile strength obtained via cross-polymerization for both materials is essentially twice that of the nonirradiated materials. After this dramatic enhancement, further radiation treatment results in a decrease of the ultimate tensile strength due to the creation of highly rigid and nondeformable hard domains. It is interesting to note that both materials reach about the same tensile strength after optimum radiation exposure.

The insets of Figure 4 and the data in Table II show that diacetylene cross-polymerization has an effect on the stress–strain behavior of low molecular weight samples of MDI-5,7-1000 and MDI-5,7-2000 even at very low strains. The 100% modulus of MDI-5,7-1000 increases upon radiation from its initial value of 570 psi to value of 940 psi at 22.5 Mrads, while that of MDI-5,7-2000 increases from 310 psi to 460 psi upon radiation with 15 Mrads. The larger change in small strain modulus for MDI-5,7-1000 simply reflects its larger hard segment content compared to MDI-5,7-2000. For the MDI-based elastomers, it is possible that at the higher radiation dosages a part of the increase in the low strain modulus may be due to random cross-linking induced in the soft phase, although the changes observed in these materials are significantly greater than those observed in conventional segmented polyurethanes with similar hard segment contents after equivalent radiation dosages.

The changes in 100% modulus of the MDI-5,7-based diacetylene elastomers are smaller than those observed for the HDI-5,7-based materials (see next section). This is to be expected since the less phase-separated MDI-5,7-based materials also exhibit a less interconnected hard domain morphology. The fact that radiation-induced modulus enhancement is still observed in these materials, however, demonstrates that the hard domains participate in the deformation process even at low strains. This fact emphasizes the role of the hard domains in providing

reinforcement to the soft segment phase and, in particular, how increased hard domain rigidity can increase the copolymer's resistance to deformation. Xue-Hai et al.[5] also reported an increase in Young's modulus upon increasing the rigidity of the hard domains via increases in crystallinity or ionic aggregation in PDMS–polyurethane elastomers. Part of the additional reinforcement observed after cross-polymerization in the lower molecular weight materials results from a contribution from very weakly associated domains that become effective only after they have been cross-linked. Thus, the number of effective hard domains may be increasing with increasing radiation dosage.

4. Effects of Cross-Polymerization on the HDI-Based Materials. Figure 5 displays the stress–strain curves of two HDI-based copolymers obtained from samples that were exposed to various radiation treatments. Both of these elastomers are well-phase-separated systems with highly crystalline hard segment domains. The changes in tensile strength resulting from cross-polymerization are very similar (albeit slightly smaller) to what was found when these same samples were annealed to improve hard domain cohesion. However, in contrast to the changes in mechanical properties brought about by annealing, the ultimate tensile strain of these materials continuously decreases with increasing levels of cross-polymerization. It is to be recalled from the preceding paper that annealing increased the tensile strength of these HDI-based copolymers without decreasing their ultimate tensile strains. The radiation induced changes in ultimate tensile strength of the HDI-based elastomers are noticeably less dramatic than those observed in the MDI-5,7-based elastomers. The influence of molecular weight on radiation-induced tensile strength changes in the HDI-PTMO-1000 based materials has yet to be determined, although initial results indicate that the response of these materials to cross-polymerization is less sensitive to variations in molecular weight than MDI-5,7-1000.

For HDI-5,7-1000 and HDI-2,4-1000, significant elongation (greater than 200% strain) under a tensile loading can only take place with a concomitant irreversible deformation of the hard domains (see preceding paper). Due to their highly phase-separated state and crystalline, more interconnected hard domains, stretching of these materials results in a simultaneous deformation of both the hard and soft segment phases. Cross-polymerization of the hard segments increases the resistance of the hard domains to deformation and prevents the hard segments from undergoing major structural reorganizations during elongation. The net effect of this is to significantly increase the modulus of the material and decrease its strain to failure. For example, the 100% modulus of HDI-5,7-1000 increases by a factor of about 2 when irradiated with only 0.56 Mrads. In fact HDI-5,7-1000 shows the most dramatic effect of diacetylene cross-polymerization in the low strain region when compared to all the other elastomers. The ultimate tensile strength, on the other hand, only increases modestly with cross-polymerization, as the creation of more rigid, nondeformable hard domains does not significantly alter the deformation response of the soft segments during elongation (they still cannot reach a state of full extension and alignment).

Figure 6 shows the stress–strain curves of the lower molecular weight sample of HDI-5,7-2000 (M_w = 79K) as a function of increasing levels of cross-polymerization. As was the case for the HDI materials based on PTMO-1000, only a modest increase in ultimate tensile

strength is observed to occur with cross-polymerization. This is in contrast to MDI-5,7-2000, where it was found that the tensile strength of a lower molecular weight sample dramatically increased after optimum radiation exposure. Apparently, the higher cohesion of the crystalline hard segments of the HDI-based materials is sufficient for these materials to realize the full potential of their hard domains. Cross-linking in this case produces minor increases in tensile strength and the expected decreases in ultimate tensile strain. It appears that the lower tensile strength of HDI-5,7-2000 (compared to higher molecular weight samples) is more related to a less entangled soft segment state as opposed to the existence of some weakly associated hard segment domains. In other words, weakly linked hard segment domains are not responsible for its poorer mechanical properties. It is important to note that the mechanical properties of this material are also completely insensitive to annealing treatments.

As can be seen in the inset of Figure 6, the low-strain properties of HDI-5,7-2000 are significantly altered by cross-polymerization. It is reasonable to conclude that the higher soft segment molecular weight used in this material would result in a less interconnected hard domain morphology and less hard domain reinforcement compared to HDI-5,7-1000. The higher small-strain modulus of the latter material is consistent with this conclusion. The magnitude of the increase in small-strain properties such as the 100% modulus (see Table II) and yield strength, however, is very similar to that of HDI-5,7-1000. This means that the level of hard segment interconnectivity may still be high enough in this material to influence its mechanical behavior. Alternatively, the morphology of the HDI-based materials (i.e., shapes and sizes of their hard domains) and possibly the nature of their domain interfaces and level of domain adhesion may give rise to local stress concentrations during loading that can only be relieved by plastic deformation of the hard domains. In either case, it is clear that for all of the HDI-based materials, elongation involves a simultaneous deformation of both the hard and soft segment phases starting at very low strains. Hard domain cross-linking via diacetylene cross-polymerization of the HDI-based elastomers therefore produces a dramatic enhancement of their resistance to deformation even at low strains. The highly crystalline nature of their hard domains, however, substantially moderates the changes in tensile strength resulting from cross-polymerization.

5. Effects of Cross-Polymerization on Thermal Properties. Figures 7 and 8 display the DSC curves for MDI-5,7 and HDI-5,7 materials with different soft segment molecular weights before radiation treatment and after radiation dosages that produce the optimum enhancement of their mechanical properties. In all cases it can be seen that the endotherms related to thermal disordering of the hard domains are still present, although they have been reduced in intensity and shifted to higher temperatures. The existence of these endotherms indicates that the hard domains still retain a sufficient number of non-cross-linked hard segments to exhibit molecular mobility at elevated temperatures. The hard domains are therefore still capable of partially deforming during tensile elongation. Samples exposed to higher dosages display no endothermic activity in their DSC thermograms and exhibit very poor mechanical properties. This again illustrates the trade-off between good hard domain cohesion and excessively rigid, nondeformable hard domains.

The elevation of the endotherms of these materials is an interesting observation. One might assume that it is
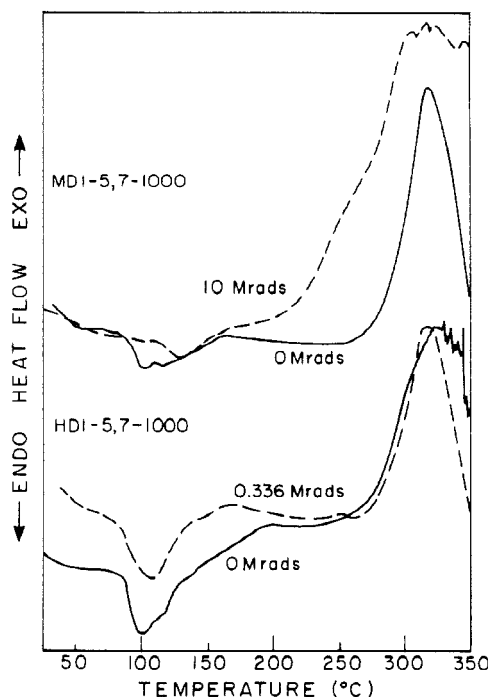
Figure 7. DSC thermograms of MDI-5,7-1000 and HDI-5,7-1000 before and after radiation treatment.
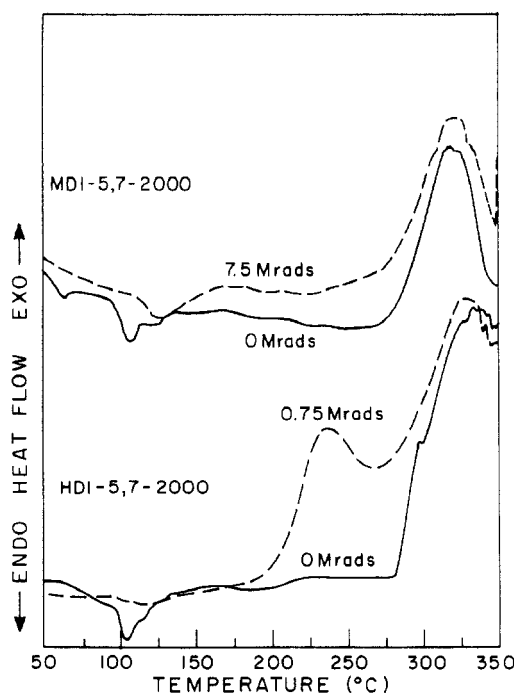

Figure 8. DSC thermograms of MDI-5,7-2000 and HDI-5,7-2000 before and after radiation treatment.

simply due to annealing effects that are introduced by thermal energy that is deposited in the sample during irradiation. However, as mentioned in the experimental section, care was taken to ensure that the temperatures of these materials did not rise above 50 °C during radiation treatments. Annealing experiments show that temperatures in this range are not sufficient to promote any changes in the DSC thermograms and, hence, mechanical behavior. This phenomenon is best explained by considering the nature of the solid state, topochemical reaction of the diacetylene groups. It is well documented in the literature[6] that the polydiacetylene chains resulting from this reaction can enter into the host matrix as isolated entities, essentially forming a solid solution of the

polydiacetylene chains in the monomer matrix. When this occurs, the melting point of the matrix is sometimes observed[7] to increase due to the change in stiffness that accompanies formation of a solid solution. Thus, the elevation of these endotherms to higher temperatures is directly related to an increase in the ridigity of the hard domains due to the homogeneous introduction of polydiacetylene chains. These results show that diacetylene cross-polymerization does much more than simply linking hard segments together at random sites throughout the hard domains, as would be the case for traditional methods of cross-linking.

In general, the primary endothermic peaks of these materials show the expected reduction in intensity and area after cross-polymerization. The reduction in endothermic peak area is most pronounced in HDI-5,7-2000. In contrast, the change in peak area of HDI-5,7-1000 is very small. This is remarkable considering the very dramatic changes in mechanical behavior that take place in this material after this particular radiation dose. This reflects the very high level of hard domain crystallinity present in this material and the enhanced effectiveness of diacetylene polymerization in crystalline environments. The high level of hard domain interconnectivity present in this material also ensures that only modest changes in hard domain cross-linking will have a significant impact on mechanical properties. For the MDI-based materials, the lower temperature endotherms around 60 °C are essentially eliminated by cross-polymerization. Interestingly, the peaks of the primary endotherms of the MDI-5,7-based materials shift to temperatures very close to the peak temperatures (around 130 °C) realized by annealing these materials under optimum conditions of temperature and time. These same annealing conditions also produced the most dramatic enhancement of ultimate tensile strength.

It is interesting to note that the higher temperature exotherms of some of these materials, which are associated with thermal diacetylene cross-polymerization and degradation, broaden and develop a low-temperature exothermic peak after radiation treatment. This is most noticeable in HDI-5,7-2000 and MDI-5,7-1000. Although the exact origin of this effect is not known, it is possible that irradiation creates active species in the hard domains that become trapped after radiation exposure and can be subsequently activated during heating. Once released, they would be free to initiate additional chemistry, possibly cross-polymerization, in the psuedoliquid state present at these temperatures.

IV. Conclusions

The ridigity and mechanical integrity of the hard segment domains of segmented polyurethanes (SPU) play an extremely important role in determining the mechanical behavior of these two-phase systems. The specific influence exerted by the hard domains is strongly dependent on sample molecular weight, the level and type of hard segment ordering, and the microstructure of the material. In this work, hard domain cohesion and rigidity were varied systematically by selectively cross-linking the hard domains of a number of structurally different SPUs via the solid-state cross-polymerization of diacetylene groups contained within the hard segments. In all cases, the effect of diacetylene cross-polymerization was to increase the modulus of the material and decrease its ultimate tensile strain. The ultimate tensile strength of the material, on the other hand, was found to initially increase, reach a maximum, and eventually decrease with increasing levels of cross-polymerization. The magnitude of these

various changes was strongly dependent on the particular material under investigation and its primary mode of deformation.

The largest increases in ultimate tensile strength (by over a factor of 2) were encountered in materials with weakly associated hard segments whose microstructures allowed significant extension and alignment of the soft segment phase during tensile elongation. Cross-polymerization of these materials, particularly samples with low molecular weights, increased the mechanical integrity of the hard domains, thereby improving the effectiveness of the elastic network established by the hard segments. In this case, cross-polymerization limits the amount of hard domain disruption that can take place at low strains and allows the soft segments to reach a higher level of extensibility at lower strains. As the molecular weight of the polymer increases, or, alternatively, as the level of hard domain order is improved by annealing, the effect that cross-polymerization has on increasing the tensile strength becomes less dramatic. Thus, optimum mechanical properties in such a system are obtained by improving the mechanical integrity of the hard domains by either annealing (see preceding paper) or diacetylene cross-polymerization. Extensive diacetylene cross-polymerization, however, can significantly compromise the mechanical properties of the copolymer. This results because, in contrast to annealing, which improves hard domain cohesion by the development of stronger nonbonded secondary forces, high levels of cross-linking via the diacetylene groups render the hard domains nondeformable under high-strain conditions, thereby eliminating one of the major strengthening mechanisms of these materials. This fact reminds us of the dual role played by the hard domains in strengthening SPUs, which requires these entities to be both mechanically sound at low strains and readily deformable at higher strains. The MDI-5,7-1000 elastomers are examples of materials that exhibit this general type of behavior.

For diacetylene-containing SPUs with microstructures that require the hard domains to deform and reorganize during nearly all stages of elongation, the effects of cross-polymerization are quite different. These materials, which are typically characterized by well-phase-separated morphologies and highly crystalline and interconnected hard domains, show a large enhancement of their small-strain modulus with increasing levels of cross-polymerization and only modest increases in their tensile strength. The response of their mechanical properties to cross-polymerization also seems to be less sensitive to the overall molecular weight of the polymer. In this case, cross-polymerization increases the rigidity of the hard domains and their resistance to deformation,

producing a much stiffer and less extensible material. The existence of reasonably cohesive crystalline hard domains in these materials limits the amount of tensile strength improvement generated by cross-polymerization. In other words, the level of stress required to produce failure in these materials remains about the same since no additional mechanisms of strengthening are activated by diacetylene cross-polymerization. Again it was found that extensive diacetylene cross-polymerization dramatically reduced the mechanical properties of these materials. Examples of materials exhibiting this type of behavior are the HDI-based copolymers.

In summary, the controlled cross-polymerization of diacetylene groups contained within the hard domains of segmented polyurethanes has been shown to be an effective way to dramatically modify and improve the mechanical properties of these materials after they have been processed (via molding or casting techniques) into suitable forms. By examining segmented copolymers with different hard segment structures, we have demonstrated that it is possible to use this chemistry to gain new insights into the factors controlling the modulus, strength, and extensibility of these complex multiphase materials. This work has also confirmed that hard domain disruption and reorganization at high stress levels is an extremely important strengthening mechanism in segmented polyurethanes.

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

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