A Morphological Investigation of Polyurethane/Diacetylene Segmented Copolymers

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Introduction

Segmented polyurethanes functionalized with hard segments containing the reactive diacetylene group represent an exciting new class of microphase-separated materials with novel cross-linking capabilities.[1-3] Previous studies have shown that the diacetylene groups contained within the phase-separated hard domains can be converted in the solid state into conjugated polydiacetylene chains, thereby producing materials with enhanced mechanical and thermal properties and novel thermochromic and mechanochromic properties.[2,3] In order to understand the relationship between the property and structural changes brought about by hard-domain cross-linking, it is necessary to establish to what extent the original morphology has been modified by cross-linking. Of particular interest is the fact that the topochemical polymerization used to link the hard segments together is restricted to the hard domains and by its nature should not significantly modify the size, shape, or ordering of these domains. It is therefore possible to selectively and systematically alter the structure and rigidity of the hard domains without modifying the soft-segment phase or the morphology of the copolymer. This novel aspect of these materials has made it possible to directly study the influence of hard-domain cross-linking on the ultimate tensile properties of segmented copolymers.[2]

Evidence for selective cross-linking of the hard domains has previously been provided by thermal, spectroscopic, and mechanical techniques.[1-3] Such techniques, however, do not readily provide direct information about the morphological organization of the hard- and soft-segment phases and the nature of their interfaces. Thus, no direct evidence has yet been provided to confirm that the morphology of these materials is not altered by cross-linking. In order to address this issue, small-angle X-ray scattering (SAXS) techniques were used to study the effects that diacetylene cross-linking has on the morphological state of these segmented copolymers. The details of this work are provided in this paper.

Experimental Section

The segmented polyurethanes used in this study were synthesized with poly(tetramethylene oxide) soft segments (M_n = 1000 and 2000) and hard segments based on 4,4′-methylene bis(phenyl isocyanate) (MDI) or hexamethylene diisocyanate (HDI) with either 5,7-dodecadiyne-1,12-diol or 2,4-hexadiyne-1,6-diol as the chain extender. Films were cast from toluene/THF solutions and then annealed at 90 °C for 45 min using the procedures outlined in a previous publication.[2] Cross-linking was performed with electron beam radiation using a Van de Graff electron accelerator. Details concerning the synthesis, structure, and characterization of these materials can also be found in previous papers.[1]

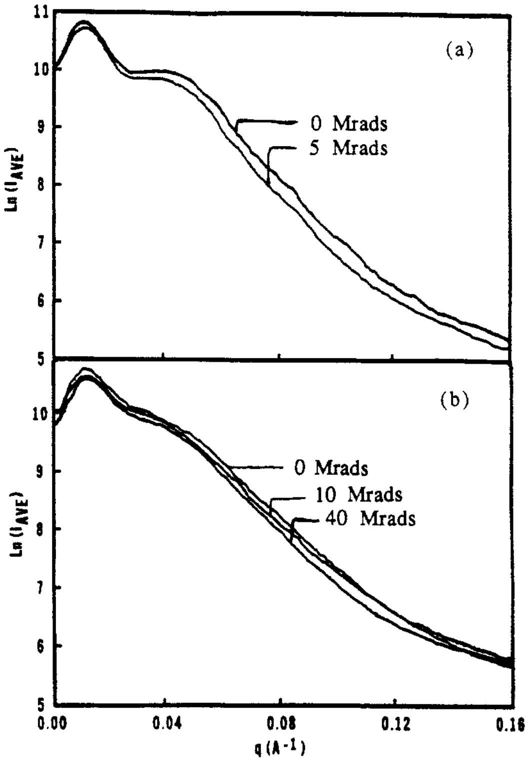

Figure 1. Intensity vs scattering vector for polyurethane films at various degrees of cross-polymerization: (a) HDI-5,7-1000; (b) MDI-5,7-2000. Numbers indicate radiation dosages.

Small-angle X-ray scattering (SAXS) was performed using the facility at the National Institute of Standards and Technology (NIST). The polymer film samples were layered to enhance scattering and ranged in thickness from 0.84 to 1.83 mm. The 10-m evacuated SAXS system includes a digital camera that utilizes a 12-kW Rigaku-Denki rotating-anode X-ray generator producing Cu Kα (λ = 1.5418 Å) radiation which was passed through a graphite monochromator. The data were collected using a two-dimensional position-sensitive gas-filled detector manufactured by TEC. The data were then corrected for parasitic scattering, sample thickness, and transmission and normalized to a constant monitor count. A circularly averaged value was used for the intensity, and a thermal background correction was applied using the slope of a line tangent to a plot of $I(q)\,q^4$ versus q^4 at the high-angle limit where q is the scattering vector defined as $q = 4\pi \sin(\theta/\lambda)$.[4,5] The data were then Lorentz corrected, as is usually performed for lamellar systems to determine an "effective" d-spacing.[6]

Transmission electron microscopy (TEM) was used to examine the HDI-5,7-2000 film. Samples from 0.125-mm cast films were first exposed to OsO_4 vapor for 24 h. The films were then cast in epoxy and microtomed; the films were cut along the thickness direction to expose the cross section of the samples. A Reichert–Jung ultracryomicrotome with a dry diamond knife at −80 °C was used. After microtoming, sections were exposed to OsO_4 vapor for 4 h to ensure uniform staining. Sections were then placed on copper grids and carbon coated. A Jeol 200 CX transmission electron microscope was operated at 200 kV.

Results and Discussion

Parts a and b of Figure 1 display the small-angle X-ray results of select polyurethane/diacetylene copolymers before and after solid-state cross-linking via irradiation. The radiation dosages used to cross-link the samples were all sufficient to produce large changes in the mechanical properties of each polymer (see ref 2 for details). As can be seen, this extensive hard-domain diacetylene cross-polymerization did not significantly alter the small-angle X-ray scattering patterns of any of these materials (the

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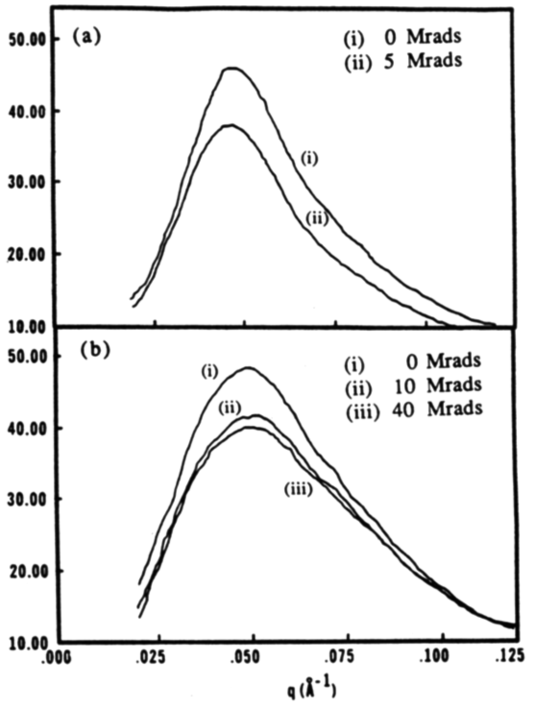

Figure 2. Lorentz plots for (a) HDI-5,7-1000 and (b) MDI-5,7-2000.

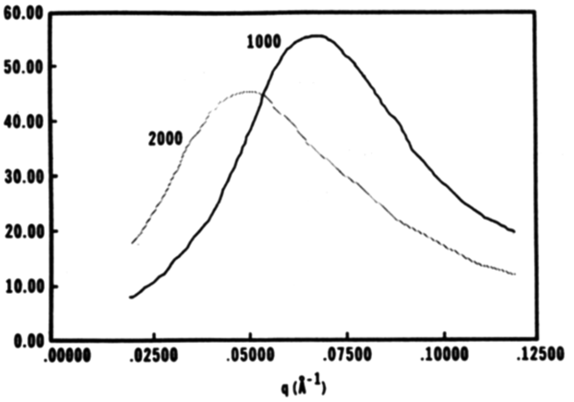

Figure 3. Lorentz plots for MDI-5,7 (1000 vs 2000).

slight decreases in intensity most likely reflect the changes in electron density associated with the introduction of conjugated polymer chains). Similar results were obtained for all of the various diacetylene-containing segmented copolymers examined (MDI-2,4, MDI-5,7, HDI-2,4, HDI-5,7). Thus, as has been inferred by other techniques, cross-linking of the hard domains via a diffusionless topochemical polymerization process does not significantly alter the average hard-domain size or the relative spacing between the hard and soft domains. It should be noted that no color change was observed in the non-cross-polymerized samples after the X-ray exposure, indicating little, if any, cross-linking took place during the experiment.

From the X-ray data it is possible to extract a number of useful molecular parameters for these materials. For example, Lorentz-corrected data are shown in parts a and b of Figure 2 for HDI-5,7-1000 and MDI-5,7-2000 before and after cross-polymerization. The Lorentz correction is normally applied to lamellar systems and essentially provides a one-dimensional analog of the interdomain spacing.[7] The Bragg spacings based on the Lorentz-corrected intensities for HDI-5,7-1000 and HDI-5,7-2000 were found to be 12.92 and 13.96 nm, respectively. For MDI-2,4-1000, MDI-5,7-1000, and MDI-5,7-2000, these values were 8.17, 9.14, and 12.32 nm, respectively. In general, the HDI materials were found to exhibit larger spacings than their MDI counterparts (i.e., 5,7-1000 and 5,7-2000 materials) which is consistent with the more extended chain lengths of the HDI-based hard segments. As expected, materials based on the higher soft-segment molecular weight PTMO chains (2000 vs 1000) consistently exhibited larger spacings than related PTMO-1000 materials. This can be clearly seen in Figure 3, which shows that the Lorentz peak of the higher soft-segment molecular weight form of MDI-5,7 is shifted to a smaller scattering vector relative to the PTMO-1000 material.

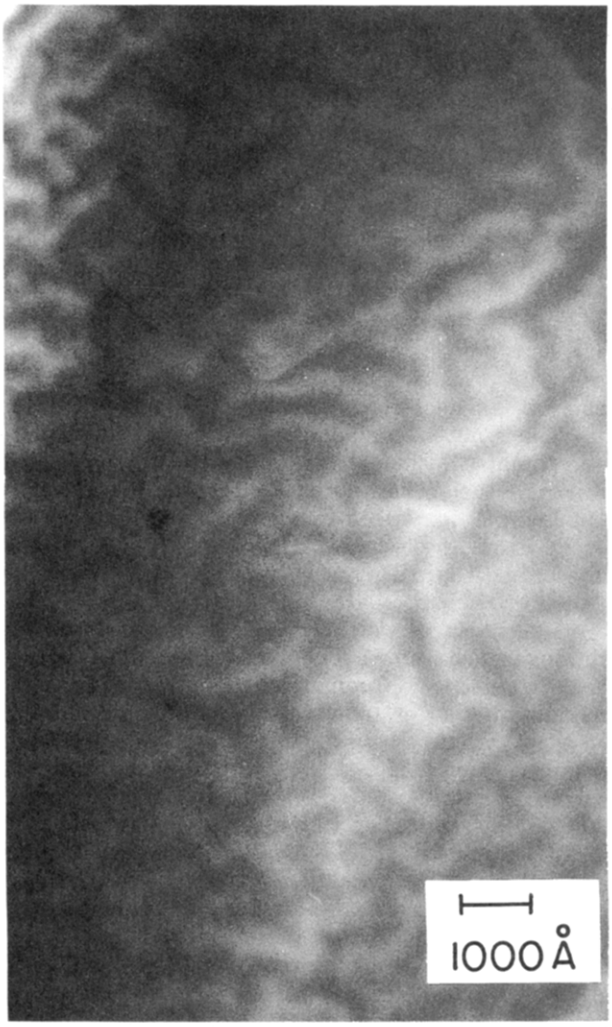

Figure 4. Transmission electron micrograph of a HDI-5,7-2000 stained section.

A Porod analysis was performed on the background-corrected data to determine the extent of segmental mixing at the interface. For an ideal case of a two-phase system with sharp interfaces, the slope of a plot of $I(q)\ q^4$ versus q^2 should reach a constant value at high angles. An analysis of such data for these materials revealed only slight deviations from the ideal Porod behavior which indicates relatively sharp interfaces for a two-phase system. The MDI-based materials exhibited slightly greater negative deviations compared to the HDI systems, suggesting that these materials exhibit a more diffuse interface. In all cases, however, the slopes were found to remain relatively close to zero. This remained the case even after extensive cross-polymerization, again supporting the notion that cross-linking of the hard domains does not significantly alter morphology. An estimation of the width of interface gave numbers too small to be meaningful, i.e., less than 0.1 nm.

The relative degree of phase separation among each of the systems was determined via Porod's invariant and the electron density variance utilizing the method of Tyagi, McGrath, and Wilkes.[7] The electron density variance was calculated from the molecular weight, total number of electrons, and mass density of each component. These numbers were 0.396 (MDI-2,4), 0.381 (MDI-5,7), 0.365 (HDI-5,7), and 0.328 electrons/Å^3 (PTMO). The relative degrees of phase separation found for MDI-5,7-1000, MDI-5,7-2000, and MDI-2,4-1000 were 0.111, 0.154, and 0.140, respectively. HDI-5,7-1000 and HDI-5,7-2000 phase-separation values were 0.184 and 0.210. These values represent the degree of overall phase separation and approach unity when complete phase separation is achieved.[7] The electron density gradient across the interface is not known which suggests that this value is overestimated. The calculated value is therefore lower than the actual. This approach is therefore valid only for a qualitative comparison among the materials and is used herein to rank the systems for degree of phase separation. As indicated, the MDI systems were not as phase separated as their HDI counterparts. In addition, the higher soft-segment molecular weight yielded improved phase separation for each system. These results are consistent with those obtained from thermal and spectroscopic studies.[1,2]

To obtain a better understanding of the morphology of the polyurethanes, cross sections of these films were examined using TEM. Figure 4 shows an electron micrograph of a stained microtomed section of HDI-5,7-2000 at 50 000 magnification. Lamellar domains of varying thickness are clearly visible. The dark regions are domains rich in hard segment; these domains alternate with a white soft-segment-rich phase. The lengths of the hard domains vary from a few microns to 50 nm. Thus, these results suggest that the use of a lamellar model for the interpretation of the SAXS data is valid. It is also notable that there are clearly defined phase boundaries present in these films, which is consistent the sharp interfaces indicated in the SAXS Porod analysis. The domains shown in Figure 4 have a long repeat period of 32–40 nm, which is much larger than the 14-nm *d*-spacing obtained from SAXS. An explanation for the size discrepancy is the existence of superstructures consisting of several stacks of ordered hard segments. This is currently under investigation. In any event, the TEM studies confirm that the HDI-based materials are well phase separated and form a lamellar-like morphology.

Results obtained from MDI-based materials (not shown) also indicate lamellar regions. The domain interfaces in the MDI films appeared to be somewhat coarser than those of the HDI films, with a larger amount of undulation in lamellar thickness. The domain boundaries are also more diffuse, suggesting a lesser degree of phase separation, as confirmed by the SAXS Porod analysis discussed above.

In summary, SAXS has shown that the solid-state cross-polymerization of diacetylene groups in the hard domains does not significantly alter the morphology of polyurethane/diacetylene segmented copolymers. From a Porod analysis, it was found that these materials display relatively sharp interfaces, with those of the HDI systems being somewhat sharper than their MDI counterparts. Ranking according to degree of phase separation indicated that a higher soft-segment molecular weight improved the degree of phase separation. The HDI-based materials were also found to be more phase separated than the MDI-based systems. Higher soft-segment molecular weight systems are presently being investigated.

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