A Spectroscopic Study of Domain Ordering in Diacetylene-Containing Model Polyurethanes

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ABSTRACT: Raman spectroscopic and visible absorption studies have been conducted to characterize the phase separation behavior of a model polyurethane containing poly(tetramethylene oxide) soft segments and reactive diacetylene units in methylenebis(*p*-phenyl isocyanate) (MDI) hard segments. Although the degree of phase separation is similar for samples cast from different solvents, perfection associated with intermolecular chain–chain packing in hard-segment domains was found to differ markedly. Crosspolymerizable diacetylene units were incorporated within the hard domains as chain extenders and used to monitor the degree of packing order, since their polymerization kinetics are strongly dependent on segmental packing. Visible absorption spectra as well as frequency shifts in Raman-active vibrations have been interpreted to be associated with different crystalline regions of poly(diacetylenes) connected to the MDI hard segments.

Introduction

Segmented polyurethanes are $-(A)_n-(B)_m-$ type multiblock copolymers which consist of hard- and soft-segment units. Due to incompatibility between the two structural units, it is generally agreed that the polymers formed undergo microphase separation, resulting in hard-segment-rich hard domains, soft-segment-rich soft domains, and an interphase.[1] An illustration of the two extremes in phase separation behavior is shown in Figure 1. Mechanical properties of phase-separated polyurethanes vary widely depending on composition ratio of the structural units as well as morphology and microstructure of a specific material. For a uniform composition ratio, mechanical properties depend on the molecular deformation mechanisms allowable, which, in turn, are related to morphological features such as degree of phase separation, size and perfection of domains, and connectivity of different domains.[2,3]

In this study Raman and visible absorption spectroscopy has been used to probe the influence of sample preparation, specifically the effects of casting solvent used on the micromorphology. Recently, Yoon and Ratner studied phase separation differences for a variety of solvents for MDI-based polyurethanes with fluorinated chain extenders.[4,5] Large effects were reported with solvents such as hexafluoro-2-propanol, being highly "structure enhancing", i.e., promoting extensive domain formation. Solvents such as THF were designated "structure perturbing", resulting in poor phase separation. Reiser and co-workers studied several diacetylene-containing block copolymers and found, among other factors, that the casting solvent significantly influences the photoreactivity of the diacetylene units, and so by implication the order associated with the hard domains.[6,7] A similar effect has been observed for these polyurethanes.[8] Due to competing intermolecular interactions between solvent/hard segment, solvent/soft segment, hard/hard segments, and hard/soft segments, an examination of the formation of phase-separated domains and degree of order in polyurethanes is of interest.

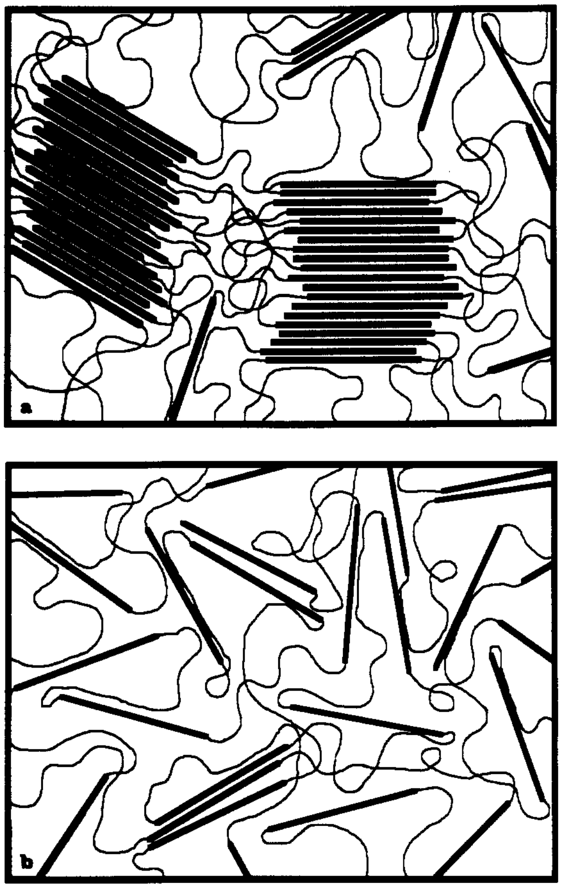

Figure 1. Schematic representation of polyurethane microstructures: (a) well-ordered, phase-separated structure attained upon annealing or slow solvent removal; (b) phase-mixed morphology.

Phase-separated polyurethanes have been extensively studied by various techniques. Small-angle X-ray scattering (SAXS) can reveal extent of phase separation as well as average phase size and interphase thickness.[3,9–14] Wide-angle X-ray scattering (WAXS) provides information on crystalline structure, size, and degree of per-

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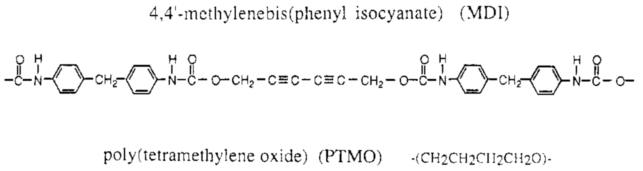

Figure 2. Hard-segment chemical structure of the poly(urethane–diacetylene) copolymer.

fection.[9,11,15–17] Infrared spectroscopy yields data on extent of phase separation along with degree of crystallinity through identification of specific bands sensitive to the molecular environment.[2,18–21] Differential scanning calorimetry (DSC) provides information on degree of phase separation by monitoring glass transition temperatures (T_g) and melting endotherms in the event of crystallinity.[3,11,12,22] The position and magnitude of these transitions in relation to the pure components are indicative of degree of segmental mixing. If a specific polyurethane sample is highly crystalline, a spherulitic structure may develop. For such conditions, small-angle light scattering (SALS) and optical microscopy can provide values of average spherulitic radius as well as an indication of organization of subunits within the spherulite.[12,14] For most polyurethanes, a combination of the techniques described above may be used to characterize the degree of hard-domain order. In this study, we present additional techniques to examine such interchain packing order, i.e., Raman and visible absorption spectroscopy.

The polymers examined are typical MDI/PTMO-based polyurethanes. The thermal and mechanical properties of these materials have been well characterized.[23,24] Instead of using a typical aliphatic diol as chain extender, however, a diacetylene diol was employed. The chemical structure of the hard segment is shown in Figure 2. Upon thermal annealing or exposure to UV light, the diacetylene units crosspolymerize, displaying optical properties similar to those observed for poly(diacetylene) single crystals.[8,25] It has previously been demonstrated that diacetylene polymerization is a topochemical reaction which is completely lattice controlled with no translational diffusion being present.[26] Therefore, even though hard-domain crystallinity is not evident, any reactivity of the diacetylenes can be correlated with orderliness of segmental packing in the hard domains. A schematic illustrating two degrees of order which could occur within the hard domains is shown in Figure 3. The domain depicted in Figure 3a would be photoreactive, while that in Figure 3b would not display significant photoreactivity. Due to the presence of diacetylene units in the hard segments, an unusual method for probing the degree of order of phase-separated hard domains is thus available. Since the poly(diacetylenes) formed have absorptions in the visible region, tremendous enhancement in the intensity of Raman-active backbone stretching vibrations can be obtained. Raman spectroscopy has already been demonstrated to be useful to characterize stress distribution in polyurethanes containing diacetylene units.[27]

Casting solvent polarity, volatility, and viscosity are factors which are expected to dominate in polyurethane structure formation. The solvents employed were chosen for polarity (solvation ability) and ability to undergo specific well-defined interactions with various polyurethane chain subunits. Tetrahydrofuran (THF), hexafluoro-2-propanol (HFP), and toluene were used. Three systems were considered. The first consisted of a 50:50 v/v mixture of THF and toluene, the second of neat THF, and the third of neat HFP. THF and HFP are highly polar and are good solvents for both the hard and soft segments in MDI/PTMO polyurethane. They do, however, differ markedly in interaction with various subunits. THF is a very good hydrogen bond acceptor and, as such, is expected to bind to a significant extent with the N–H of the urethane group. Conversely, HFP is a very good hydrogen bond donor and, in turn, is expected to bind with the carbonyl of the urethane as well as the ether oxygen of the soft segment. Toluene is a nonpolar solvent and found to be a nonsolvent for the hard segments but effective for the considerably less polar soft segments. In a 50:50 mixture by volume with THF, toluene is expected to promote phase separation/aggregation in solution to a far greater extent than either neat THF or HFP. The results of Raman, visible, and infrared spectroscopy to probe the domain structures are presented here.

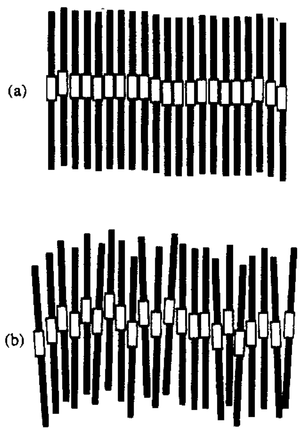

Figure 3. Schematic representation of different hard-segment domains. The perfection of intermolecular chain packing influences significantly the photoreactivity of the diacetylene units incorporated in the MDI hard segments: (a) highly ordered segmental–segmental packing; (b) disordered domain with poor segmental–segmental packing.

Experimental Section

The synthesis procedure for these model polyurethanes has been reported previously.[25] These model polyurethanes were synthesized using a multistep method which entails endcapping PTMO macrodiols (MW ~ 1000) with MDI in the first step, followed by addition of diacetylene diol chain extender in the second step. This experimental procedure, combined with the molar ratio of the reactants (2:1:1 diisocyanate, PTMO, and diacetylene chain extender), favors incorporation of a single diacetylene unit per hard segment. Thus the elastomer is expected to contain a significant amount of either isolated MDI units or hard segments consisting of a single diacetylene unit flanked by MDI units. This type of microstructural organization has been found to suppress highly ordered hard domains.[2,3] No crystallinity is detectable in the uncrosspolymerized materials by either wide-angle X-ray scattering or DSC.[25] Although the volume fraction of hard segments is approximately 30%, its glass transition was not observed, typical for MDI-based segmented copolymers.[22]

All films used were cast and dried in the dark from 0.5% solutions by weight at ambient temperature. Since both THF and HFP are highly volatile at room temperature, kinetic effects can be expected to perturb the resultant morphology. The film was cast by introducing the solution onto a glass slide placed in a Petri dish which was then immediately covered, and the solvent was allowed to evaporate. To minimize volatility, a small amount of the neat solvent was also placed in the Petri dish to provide a solvent-saturated environment. Typically 2–5 days, depending on the solvent used, is required for the films to dry. The films are then further dried in the dark under vacuum for several additional days at ambient temperature, after which they are stored at −10 °C in the absence of light. Dried film thickness is approximately 10 μm.

Diacetylene crosspolymerization is facilitated either thermally by annealing the cast films at 90 °C or by exposure to UV light

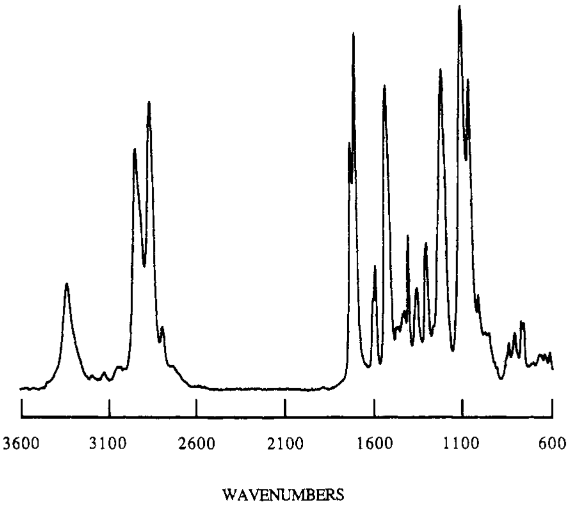

Figure 4. Infrared spectra obtained for the polyurethane-containing diacetylene.

(254 nm), produced by a Hg lamp. No differences were observed between the two methods of polymerization. A dramatic color change accompanies the polymerization process. Before crosspolymerization, the films are totally transparent. After polymerization, the films are typically either deep blue or red, depending, as shown below, on hard-domain order. Although a quantitative description of the extent of crosspolymerization is difficult to obtain, it is possible to estimate the conjugation length distribution of the poly(diacetylene) chains formed. Visible absorption spectra were recorded on a Beckman DU-40 spectrometer operating at 2-nm resolution at a scan rate of 500 nm/min. Film thickness was chosen to keep the maximum absorbance below 2, well within the range of linear response as determined by a Beer's law calibration.

Because poly(diacetylenes) formed have strong absorptions in the visible region, all completely symmetric Raman-active vibrations coupled to the electronic states are resonance enhanced. Resonance Raman data were collected with an ISA HG.2S grating spectrometer. A solid-state He–Ne (632.8 nm) laser operating at a power of roughly 1 mW was used as sample excitation. Spectral resolution was maintained at approximately 1 cm^{-1}. An RCA C31034 thermoelectrically cooled photomultiplier was used for detection. To avoid photoselectivity effects inherent in resonance Raman scattering, an extremely long wavelength excitation line [Nd:Yag laser (1064 nm)] in the near-infrared region was used. To alleviate the low scattering signal due to the nonresonant ω^4 scattering power dependence, we utilized a Fourier transform Raman for multiple signal averaging. Fourier transform Raman data were collected on a Bruker 88 bench. Incident laser power was maintained at 300 mW. Typically 512 scans were coadded to achieve an acceptable signal-to-noise ratio. The excitation/collection geometry was 180°, and spectral resolution was maintained at 4 cm^{-1}. Because of the long wavelength used in the FT-Raman instrument, we also have obtained fluorescence-free spectra. Transmission infrared spectra were obtained on an IBM Model 98 vacuum Fourier transform infrared spectrometer (Bruker IFS 113v FTIR). Typically 256 scans were coadded, with spectral resolution maintained at 2 cm^{-1}. All spectroscopic data were subsequently transferred to other computers for further analysis. A typical infrared spectrum of these polyurethanes is plotted in Figure 4.

Results and Discussion

Polyurethane phase separation may be determined most conveniently by DSC or infrared spectroscopy. The glass transition temperature of the soft phase is raised when intersegmental mixing occurs. Ideally, observation of a melting point depression for crystalline hard segments can also reveal the extent of intersegmental mixing. Pure PTMO has a T_g close to −85 °C. For our PTMO samples, T_g was in the range −54 to −50 °C, depending on the casting solvent. The broad transition zone, ~20 °C, makes a precise T_g determination difficult. Importantly, no significant differences were observed by DSC for the solvents used, suggesting equal intersegmental mixing for the three systems.

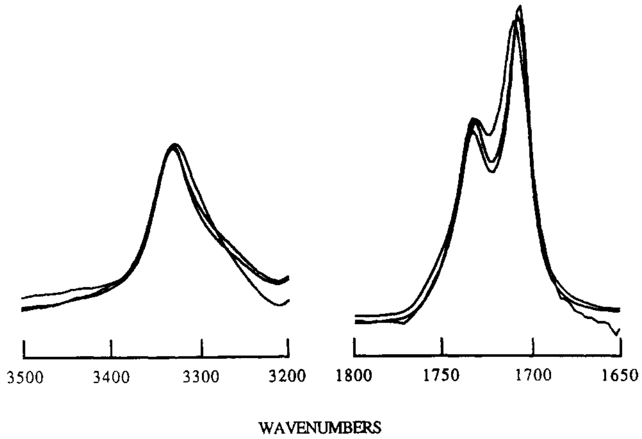

Figure 5. Infrared spectra of the NH and C=O stretching regions in the presence of hydrogen bonding.

The use of infrared spectroscopy for phase separation determination entails observation of spectroscopic features sensitive to intermolecular aggregation. For polyurethanes, this procedure is well established, with major emphasis directed at bands sensitive to formation of various hydrogen-bonding possibilities.[2,18–21] NH and C=O stretching vibrations in the 3300- and 1700-cm^{-1} regions, respectively, are plotted in Figure 5. The hydrogen-bonded NH stretching vibration is located at 3320 cm^{-1}, with the relatively weak free NH stretching vibration located at 3450 cm^{-1}. The carbonyl stretching band occurs as a doublet with one component at 1732 cm^{-1} (free component) and the other at 1708 cm^{-1} (hydrogen-bonded component).[28,29] Since the sole hydrogen bond donor is the urethane NH group, only an interurethane hydrogen bond (hard segment–hard segment interaction) can account for the presence of the bonded carbonyl. Therefore, the amount of bonded carbonyl, manifested by intensity of the 1708-cm^{-1} band, yields a direct measure of the extent of hard-domain formation. Although oversimplified, it is generally accepted that a two-phase approximation can be used, wherein all bonded carbonyls are located in the hard domains and all free carbonyls originate from hard segments dispersed throughout the soft domains. The nature and amount of the interphase remain an active research area.[10] With the use of procedures developed earlier, the fraction of hydrogen-bonded component for the THF/toluene system was ~64%, while somewhat lower, at ~60%, for samples prepared from HFP or THF solutions.[18,19] It can then be concluded that the degree of phase separation for these materials is independent of solvent system, as determined from both infrared and DSC analyses.

Crosspolymerization of the diacetylene units either thermally by annealing at 90 °C or exposure to UV light at 254 nm was found to be equivalent. It is well-known, however, that thermal annealing strongly perturbs morphological features of polyurethanes.[22] Most of our studies were therefore completed using photopolymerization. The dried films were initially optically clear but, upon exposure to UV radiation, became deeply colored. This coloration is due to the presence of delocalized π electrons along the conjugated poly(diacetylene) backbone. The lowest energy optical transition of the π electrons has been assigned as an excitonic transition, with the exciton localized over a

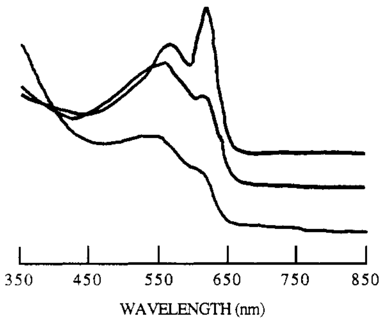

Figure 6. Visible absorption spectra for crosspolymerized solvent-cast samples: (top) THF/toluene; (middle) HFP; (bottom) THF.

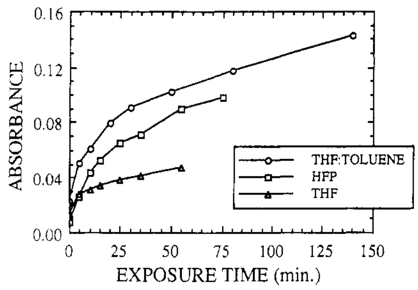

Figure 7. Plot of the height of the 620-nm band for the three samples as a function of UV exposure time.

few backbone atoms.[30,31] This optical transition was interpreted to be interband in nature, i.e., from the valence to the conduction band. Photoconductivity experiments have, however, shown that this interband transition should occur at much higher energies.[32]

We observed significantly different photoreactivity behavior, depending on casting solvent used, similar to the work of Reiser and co-workers.[6,7] The films cast from THF/toluene turned deep blue upon crosspolymerization, while both the THF and HFP films had a slightly redder appearance. Visible absorption spectra corresponding to the three solvent systems are shown in Figure 6, with the curves normalized for film thickness. All three films were exposed to UV light for approximately 60 min. When the height of the ~620-nm band is considered to be representative of planar highly conjugated poly(diacetylene) present, it is possible to conclude that photoreactivity of the various systems proceeds in the order THF/toluene > HFP > THF. This suggests that the degree of segmental packing order associated with the hard domains follows the same trend, with highest order found in the THF/toluene film. One also notes better resolved band structure for the THF/toluene film (narrow line width), indicating a more homogeneous poly(diacetylene) chain environment.[33]

All the transitions observed in this region are associated with poly(diacetylenes). When overall area of the absorptions is considered, a similar functional form as a function of time are observed for all three samples. These plots are identical to the ones using only the height of the 620-nm transition. A plot of the 620-nm band absorbance as a function of exposure time is shown in Figure 7. The general trend of the curve is the same for all three systems, suggesting similar polymerization mechanisms. Therefore only differences in the extent of conversion appear important, affirming segmental–segmental packing to be the critical factor. We have unfortunately been unable to quantify the absolute extent of conversion from monomer to polymer. For the THF/toluene curve the second band, centered around ~575 nm, is generally considered a vibronic sideband to the primary electronic transition at 620 nm.[8,34] Vibronic transitions are due to the one-dimensional nature of the conjugated poly(diacetylene) (PDA) chain, which gives rise to a coupling between the valence electron levels and the backbone double- and triple-bond stretching vibrations. For the other systems, neat THF and neat HFP, the second band is located at ~540 nm. This absorption band appears more intense than the 620-nm band, even if the upturn of the baseline is considered. The upturn in the baseline with decreasing wavelength results from some combination of scattering, absorption of unreacted diacetylenes, and absorption of the aromatic phenyl group. This band may also be assigned to PDA chains with a nonplanar backbone and not a vibronic sideband. A similar transition is seen for poly(diacetylenes) in solution.[35,36] Another possible explanation for the absorption would be the presence of short absolute PDA chain lengths.

It is impossible to deduce directly the PDA length distribution from the Raman or absorption data obtained. On the basis of modified versions of Kuhn's free-electron model for conjugated polyenes, however, a relationship between the position of the electronic transition and conjugation length can be obtained.[37-39] Transitions occurring at wavelengths longer than ~600 nm correspond to chromophores of infinite conjugation length. This is supported by visible absorption data of PDA single crystals.[40] Electronic transitions centered around 540 nm are attributed to conjugation lengths approximately ~80 Å (~15 repeat units), while transitions lower than 460 nm are due to conjugation lengths of 30 Å or less (5 or fewer repeat units). These latter two conjugation lengths are typically observed for PDA's dissolved in poor/moderate and good solvents, respectively.[35,36] The 540-nm transition seen most significantly for the HFP and THF systems is most likely due to the presence of a different PDA phase consisting of chains of shortened conjugation length, rather than short absolute chain length. In support of this hypothesis is the observation that as polymerization proceeds, there is no red shift (shifting to lower energies) of primary electronic transitions (620 or 540 nm) for any of the samples, implying that the chain length of the PDA formed is constant on the time scale of the experiment. Nor is there any change in the absorption line width. These results are consistent with earlier investigations.[31]

Previous diacetylene single crystal and other diacetylene crosspolymerization studies have shown a blue or red shift as polymerization proceeds. This shift is usually interpreted as a lattice perturbation occurring as it is forced to accommodate newly formed PDA chains. Shift direction is dependent on structure of the initial lattice, i.e., whether the developing PDA chain is initially stretched or compressed to accommodate substituent groups.[7,8,41,42] There is no apparent blue or red shifting during polymerization of the primary absorption (620 nm) in the model polyurethanes studied, as shown in Figure 8 for a THF/toluene sample. We interpret this observation as suggesting that packing of MDI hard segments is not perturbed by PDA chain formation.

Raman spectroscopy has seldom been used for the characterization of polyurethanes, since almost all vibrations indicative of hard segment–hard segment interactions are strong in the infrared. Due to the incorporation of the diacetylene moieties in the hard segments, these model polyurethanes lend themselves uniquely to a Raman spectroscopic investigation.[27] Raman spectroscopy has been extensively used to characterize poly(diacetylenes).[42] Because of low-lying electronic transitions, enhancement

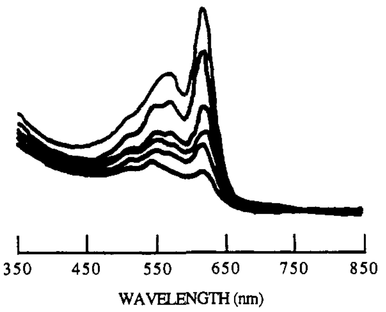

Figure 8. Visible absorption spectra of a THF/toluene-cast film as a function of increasing UV exposure time.

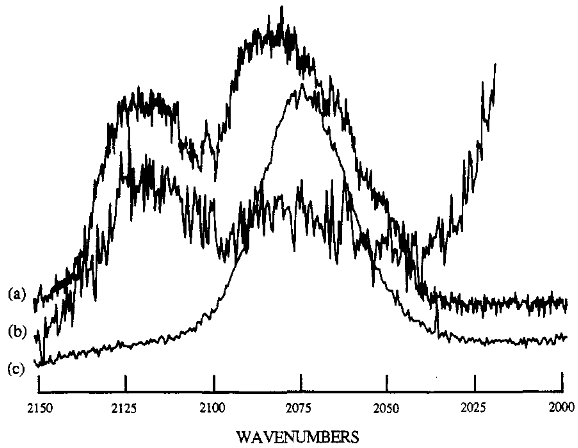

Figure 9. Raman spectra of the three systems (632.8-nm laser excitation, 1-mW laser power at the sample, 1-cm^{-1} band-pass): (a) HFP; (b) THF; (c) THF/toluene.

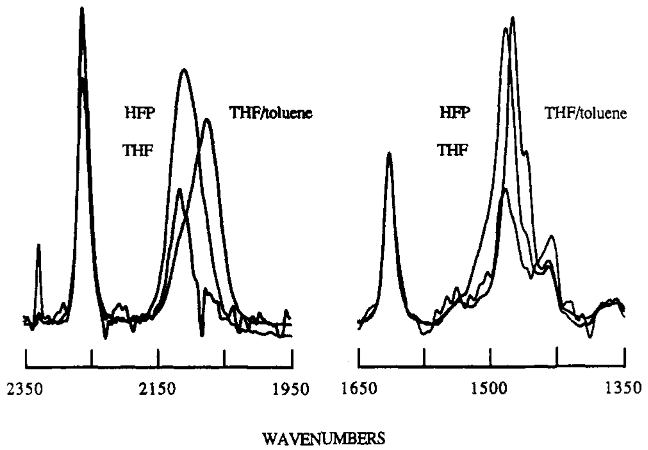

Figure 10. Fourier transform Raman spectra (C≡C and C=C stretching regions) obtained for samples prepared using three different solvents (1064-nm laser excitation, 4-cm^{-1} resolution).

of the totally symmetric backbone vibrations is considerable when lasing excitation in the visible range is used. Resonance-enhanced Raman spectra for the three casting solvent systems in the region of the PDA C≡C stretch are shown in Figure 9. For the THF/toluene sample there is a single band located at 2074 cm^{-1}, while both the HFP and THF samples exhibit a doublet. The HFP displays bands of similar intensity located at 2119 and 2082 cm^{-1} while the two bands for THF occur at 2116 and ~2078 cm^{-1}, with the latter being extremely weak. To understand the large frequency and intensity differences exhibited by the C≡C stretching bands for the three systems, we must examine each of their possible origins. There are a number of distinct ways in which the position of the Raman frequencies may vary. These include the extent of polymer conjugation (or electron delocalization), which is related to the degree of order present along the chain backbone.[33,42-45] Also, the packing environment of the poly(diacetylene) chain can be altered by either a lattice mismatch between monomer and polymer in partially polymerized crystals or by a solid-state phase transition involving some combination of backbone and side-group conformational rearrangement.[42,46,47] Finally, the state of the macroscopic stress (tensile or compressive) has also been found to exert a large influence over the position of the PDA backbone stretching vibrations.[47-51]

Shifts in the C≡C stretching vibrations have been observed for one-step bulk-polymerized polyurethanes under stress. Since Raman spectra for our samples were collected from free-standing films, it is clear that there is no macroscopic stress on the systems. Any possible residual stresses incurred from the drying processes are considered negligible. As stated previously, the hard domains are noncrystalline. They are, however, clearly not completely amorphous since there is enough order present for some crosspolymerization of the diacetylene units to occur. It is unlikely that there is a sufficient amount of order present to cause lattice mismatch between diacetylene monomer and polymer, causing a shift in the absolute position of the C≡C band. There is essentially no difference between photopolymerization and thermal polymerization procedures. If diacetylene monomer–polymer lattice mismatch were important, the annealing inherent in thermal polymerization would relieve this lattice strain to some extent. Thermal polymerization in the presence of significant lattice mismatch often proceeds heterogeneously through the nucleation of pure PDA phase, evidenced by a discontinuous shift in the C≡C frequency to that of the fully polymerized single crystal. No evidence of any shifting of the C≡C band was observed for several samples polymerized to different extents under different conditions.

As can be seen from Figure 6, the most intense 620-nm absorption was found in the THF/toluene sample. We would expect intense Raman scattering for this sample when a laser excitation of 632.8 nm is used, due to length photoselectivity effects.[42-45] This is shown for the THF/toluene sample in Figure 9 as having the highest signal to noise ratio, followed by the HFP and THF films. It is well-known that the positions of the C≡C and C=C stretching bands are dependent on the excitation wavelength when this wavelength falls within the electronic absorption envelope and that lower frequency values are associated with lower energy electronic transitions.[42-45] The spectra in Figure 9 indicate that very few PDA chains in the THF sample are of sufficiently long conjugation length to undergo significant resonance enhancement, while the HFP sample contains somewhat more chains of long conjugation length. The majority of PDA chains in both THF and HFP are of short to moderate conjugation length, as evidenced by the ~2115-cm^{-1} band, and correspond to the 540-nm absorption. For the HFP sample, two bands are observed of similar intensity. For the THF/toluene sample, only long conjugated chains (2074 cm^{-1}) are observed at an excitation of 632.8 nm.

To avoid the complications of length photoselectivity, a laser with an excitation wavelength far removed from the electronic transition is useful. A Nd:Yag laser was used, which places the excitation (1064 nm) at the extreme tail of the absorption curve and samples the entire distribution of PDA chains. The Raman spectra of the C=C and C≡C stretching regions using long-wavelength excitation are shown in Figure 10 for the differently prepared samples. The bands at ~2100 cm^{-1} are assignable to the $C{\equiv}C$ stretching in a conjugated PDA chain, while the band at 2260 cm^{-1} is assigned to the $C{\equiv}C$ stretching of unreacted diacetylenes. The $C{\equiv}C$ stretching found in the THF/toluene sample (2076 cm^{-1}) differs considerably from that found in the HFP (2107 cm^{-1}) and the THF (2116 cm^{-1}) samples, suggesting the chains reside in different crystalline environments. As the conjugation length increases (increase in electron delocalization along the backbone), the $C{\equiv}C$ bonds and the $C{=}C$ bonds weaken, with a corresponding decrease in the backbone stretching frequencies. We can conclude that based on the relative position of the $\nu_{C\equiv C}$ for the PDA chains, the chains in the THF/toluene cast system have the most planar backbone and thus are the most highly ordered, possessing the ensemble average of greatest conjugation length, followed by the PDA chains in the HFP and then the THF solvent cast systems.

Conclusions

We have demonstrated that by using different solvents it is possible to significantly influence hard-segment packing order, while having a negligible effect on the overall degree of phase separation. Through the use of visible and in particular Raman spectroscopy, it was possible to probe the amount of order associated with the hard domains. Incorporation of diacetylenes as chain extenders in the hard segments of segmented polyurethanes proved to be an effective tool for probing the order associated with phase-separated hard domains. The reactivity measured by visible absorption and Raman spectra for the diacetylenes contained in the hard segments differs for samples prepared from different solvents. Both spectroscopic techniques are sensitive to not only the presence of crosspolymerized poly(diacetylene) but also order associated with packing of PDA side groups, in this case the MDI units. THF/toluene appears to promote the highest domain order, followed by neat HFP and THF.

It seems evident that the better segmental–segmental packing exhibited by the THF/toluene system must be due, in part, to extensive phase separation/domain formation in solution. The domains formed for di- and triblock copolymers have been well characterized.[52,53] It has been suggested that similar mechanisms would apply for polyurethanes.[21] As HFP promoted significantly higher photoreactivity than THF, solvent quality of the neat solvents appears to be most influential. Exact identification with a molecular parameter is, however, not straightforward. The solvent qualities of the two solvents differ, with THF perhaps being a better solvent for the hard segments than HFP. The differences in morphological features may also impact overall mechanical properties of polyurethanes. Further studies are currently underway to elucidate these effects.

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Registry No. MDI/PTMO/HOCH$_2$C$\equiv$CC$\equiv$CCH$_2$OH (block copolymer), 107702-75-0; THF, 109-99-9; HFP, 920-66-1; MePh, 108-88-3.