A Comparison of Hydrogen Bonding and Order in a Polyurethane and Poly(urethane−urea) and Their Blends with Poly(ethylene glycol)

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ABSTRACT: The effect of hydrogen bonding on the phase behavior of a chemically similar polyurethane and polyurea and their blends with poly(ethylene glycol) is examined. The polyurethane and polyurea were synthesized from the same diisocyanate, 1,5-diisocyanato-2-methylpentane, using an aromatic diol and aromatic diamine, respectively. Fourier transform infrared spectroscopy was used to characterize the distribution of hydrogen bonds in these polymers and their blends. The distribution of hydrogen bonds in the polyurethane homopolymer was found to be quite similar to that found in an amorphous polyurethane studied previously in this laboratory. However, upon annealing, some sort of ordered structure was detected spectroscopically. The polyurea formed an equivalent ordered structure much more readily at room temperature. Ordered hydrogen-bonded domains were also detected in the spectra of the blends, either after an extended time at room temperature or after annealing at an elevated temperature. The formation of ordered structures occurred at temperatures well below the thermally measured glass transition. Melting endotherms could not be detected in most of these samples. It is suggested that the order present in these blends might be largely two-dimensional. The hydrogen bonds between adjacent urethane (or urea) units can align to form a sheet, with the methyl group that is part of each segment essentially laying in a plane that is perpendicular to this structure. Because the methyl group is asymmetrically placed in the diisocyanate used to synthesize these polymers, packing between sheets would be imperfect at best.

Introduction

Polyurethanes are an intriguing class of polymers whose properties are determined by the phase-separated hard and soft segments that usually define their microstructure. Although crystallization of the hard segments is a major factor in phase separation, the hard and soft segments are most often very different in their chemical structure, and even in the absence of order one would still anticipate a strong degree of phase separation. In addition, most hard segments have urethane and/or urea functional groups that hydrogen bond to each other in the form of extended chains, with N−H "donor" groups hydrogen bonded to C═O "acceptor" groups. This type of self-association would be an additional driving force for phase separation, except that the soft segments usually contain functional groups that do not self-associate but have hydrogen bond acceptor groups, such as ether oxygen or ester carbonyl functionalities. There is thus a complex competition between self-association, what we call interassociation (an N−H to ether −O− hydrogen bond, for example), dispersion forces, and other characteristics (molecular weight of the segments, mobility, etc.) that affect the ability to form ordered or phase-separated domains.

Infrared spectroscopy is very sensitive to hydrogen bonding, and this technique has been applied to the characterization of polyurethanes in a wide range of studies (see refs 1−17 and citations therein). Here we will apply this technique to a comparison of hydrogen bonding in a model polyurethane and a polyurea of similar structure, together with their blends with poly(ethylene glycol). Previous work indicates that self-association in polyureas is stronger than in polyurethanes as a result of the formation of bifurcated (as opposed to linear) hydrogen bonds (see below).[2−4] However, by the same token, hydrogen bonds between the two urea N−H groups and ether oxygen atoms are also stronger than the single N−H/oxygen hydrogen bonds formed between urethane groups and ethers. By comparing spectroscopic results obtained from a study of a model polyurethane and polyurea, together with their blends with simple polyethers, we aim to obtain some insight into the balance of hydrogen-bonding interactions that control miscibility and the ability to form ordered structures in these systems. We will initially focus on blends, as opposed to segmented block copolymers, so as to limit the types of functional groups present in the system and thus facilitate the interpretation of the spectra.

Experimental Section

Anhydrous dimethylacetamide (DMAC), 1,3-benzenediol (BD), and 1,5-diisocyanato-2-methylpentane (MPDI) were purchased from Sigma-Aldrich Chemical Co. The monomers were used as received, and the DMAC was dried over magnesium sulfate overnight, filtered, and kept under nitrogen.

Polyurethanes were synthesized in the following manner. A reaction vessel was purged under nitrogen. To the empty vessel 1,3-benzenediol was added followed by the solvent dimethylacetamide. The mixture was stirred, and the temperature was raised to 90 °C. Upon total dissolution of BD and stabilization of the reaction temperature, 1,5-diisocyanato-2-methylpentane was added in a molar ratio of 1:1 to BD. The diol was reacted with MPDI for a period of ∼10 h. After completion of the reaction, the contents were removed from the reaction vessel, and the solvent was allowed to evaporate in a fume hood.

The polyureas was synthesized in a similar manner. A reaction vessel was purged under nitrogen. The monomer, 1,3-phenylenediamine, was added to the dry vessel followed by the solvent dimethylacetamide. The mixture was stirred, and the temperature was raised to 60 °C. Upon total dissolution of PDA and stabilization of the reaction temperature, 1,5-diisocyanato-2-methypentane was added in a molar ratio of 1:1 to PDA. The diamine was reacted with MPDI for a period of ∼10 h. After completion of the reaction, the contents were removed from the reaction vessel, and the solvent was allowed to evaporate in a fume hood.

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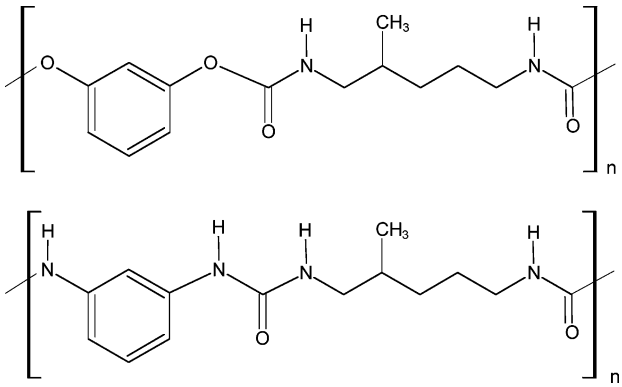

Figure 1. Chemical structures of the polyurethane (BD-MPDI), top, and polyurea (PDA-MPDI), bottom.

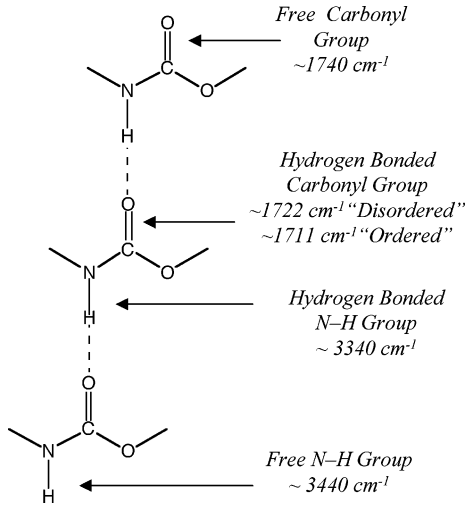

Figure 2. Band assignments for the polyurethane carbonyl and N−H stretching modes.

The chemical structures of the polyurethane and polyurea are very similar and are compared in Figure 1.

Samples for Fourier transform infrared spectroscopy were prepared by solution casting onto potassium bromide (KBr) windows. The solvent was allowed to evaporate at room temperature under vacuum. Blends were prepared by dissolving poly(ethylene glycol) in DMAC and adding the appropriate amount of polyurethane or polyurea. These were also cast onto KBr windows, and the solvent was allowed to evaporate at room temperature under vacuum.

Infrared spectra were recorded on a Digilab FTS-45 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller with a reported accuracy of ±0.1 °C.

Thermal analysis was performed on a TA Instruments Q100 differential scanning calorimeter. A heating rate of 10 °C/min was used, and the mass of samples tested was approximately 3−6 mg. The reported glass transition temperatures were taken as the midpoint of the heat capacity change, and the melting points were taken at the peak maximum of the endotherm. All data were obtained from the second heating run.

Band Assignments

Before proceeding to a discussion of our experimental results, it is useful to review band assignments based on previous work in this[2−4] and other laboratories.[5,6,16] Polyurethanes self-associate in the form of linear chains, as illustrated in Figure 2. Although a number of vibrational modes are sensitive to hydrogen bonding in these systems, the most information can be obtained from the N−H and C═O stretching vibrations near 3200−3400 and 1600−1700 cm^{-1}, respectively. The carbonyl region of the spectrum can be very complicated, particularly if dilute solutions of low molecular weight model systems (e.g., ethylurethane[16]) are studied. Although one would initially expect to see just two modes, one assigned to "free" (non-hydrogen-bonded) and the other to hydrogen-bonded groups (the latter at lower frequency, due to the effect of hydrogen bonding on the distribution of electrons in the bonds), there are some subtleties. Hydrogen bonding is a cooperative phenomenon, so that in dilute solutions it is possible to distinguish between hydrogen-bonded carbonyl bands in "dimers" and those in longer chain "multimers". Because cooperativity increases the strength of the latter hydrogen bonds, the multimer band is found at a lower frequency (wavenumber) than the dimer band.[16] Similarly, the carbonyl group in very dilute solutions, where most of the molecules are "monomeric" (in hydrogen-bonding terms), has a slightly different frequency than the free group found at the end of hydrogen-bonded chains (see Figure 2). Fortunately, in the polymers studied here, the vast majority of the functional groups are present in the form of multimers, so that we observe an end-group free carbonyl and a hydrogen-bonded multimer band. There are two complications, however. In samples that crystallize, a hydrogen-bonded carbonyl band that is sharper and observed at a lower frequency than the corresponding band observed in amorphous samples is also apparent. This is a result of order in the crystalline state, where the chains are closer together and the hydrogen bonds are stronger (and shorter). For reasons we do not understand, the N−H stretching region is less complex, generally displaying just free and bonded bands (although the bandwidth of the latter narrows upon crystallization). The second complication is that the precise value of the frequencies will also depend on the chemical structure of the chain, with purely aliphatic polyurethanes having carbonyl stretching modes that are at higher frequencies than those containing aromatic groups. However, this merely shifts all the bands an (approximately) equivalent amount to higher or lower frequency. The frequencies of the modes that are observed in the polyurethane used in this study are also summarized in Figure 2. For succinctness, we will refer to these bands as "free" (non-hydrogen-bonded), "hydrogen-bonded disordered" (bands due to hydrogen-bonded groups in regions of the sample that are amorphous), and "hydrogen bonded ordered" (bands due to hydrogen-bonded groups in regions of the sample that have some degree of order or regularity).

The same considerations and arguments apply to the polyureas, although there are naturally differences in the frequencies of the modes that are observed. The urea functional group has two donor (N−H) groups and one acceptor (C═O) group. Thus, the hydrogen-bonded chains consist of 2:1 bifurcated hydrogen bonds, as illustrated in Figure 3.[4] The carbonyl stretching modes of the ureas are all found at lower frequencies than their urethane counterparts, a result of the greater delocalization of electrons in the π-bonds of the ureas relative to the urethanes. (This appears to have little effect on the N−H stretching modes, however.) The hydrogen-bonded carbonyl bands are also shifted from the position of the free band to a greater degree than in the polyurethanes, a reflection of the greater strength (enthalpy) of the bifurcated 2:1 structure. The order remains the same, however, with the free band at a higher wavenumber than the hydrogen-bonded "disordered" band, which, in turn, is at a higher wavenumber than the hydrogen-bonded "ordered" band. The frequencies of the modes that are observed in the polymers

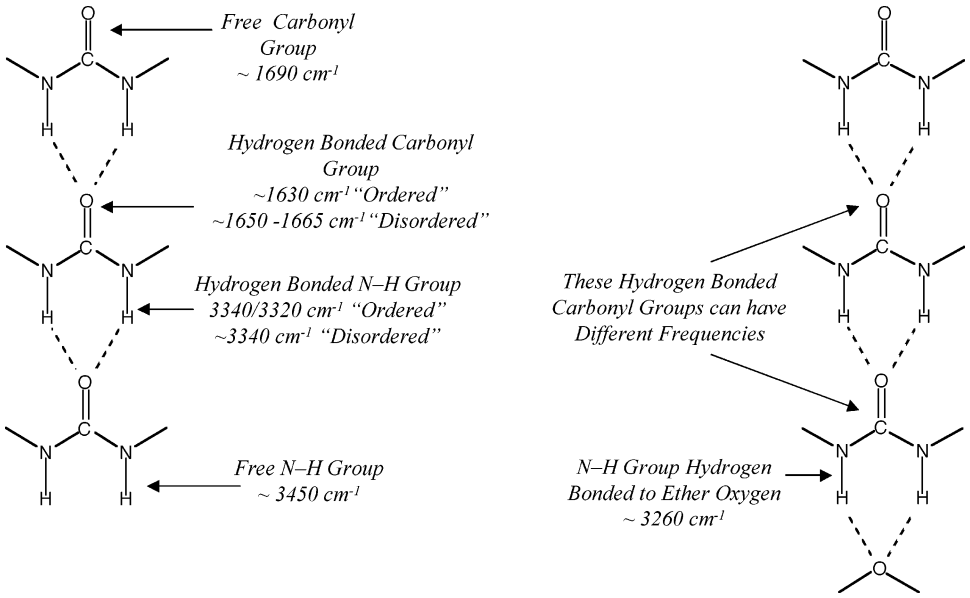

Figure 3. Band assignments for the polyurea carbonyl and N−H stretching modes. The right-hand figure shows assignments for the blends with PEG.

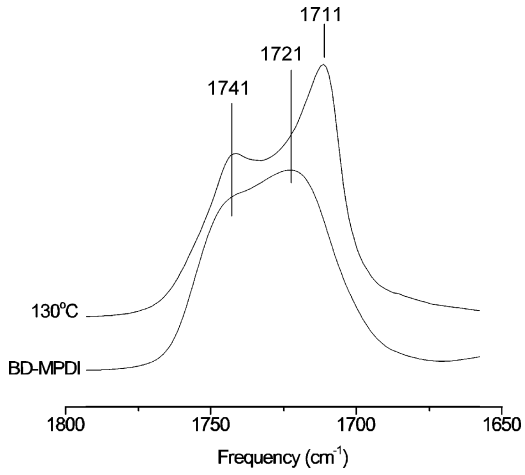

Figure 4. Carbonyl stretching region of the BD-MPDI polyurethane. Bottom, as cast, film; top, film held at 130 °C for 20 min.

used in this study are summarized in Figure 3. There is an additional band observed in the spectra of blends with polyethers, a point we will discuss in more detail later but also illustrate in this figure.

Results

Studies of a Model Polyurethane and Its Blends with Poly(ethylene glycol). In previous work in this laboratory, an amorphous polyurethane (APU), synthesized from a mixture of 2,4- and 2,6-tolyl diisocyanate and butanediol, was studied.[3] In this APU, the nitrogen atom of the urethane group is directly attached to the aromatic ring. In contrast, for the BD/MPDI polyurethane studied here, the single-bonded oxygen of the urethane group is attached to an aromatic ring. This results in a shift of the carbonyl stretching mode to higher wavenumbers. This region of the spectrum of the as-cast film of this polymer, obtained at room temperature, is shown in Figure 4. It can be seen that there are two overlapping bands, apparently centered near 1741 and 1721 cm^{-1}, due to free and hydrogen-bonded groups, respectively. (The true positions of the bands are actually centered near 1747 and 1722 cm^{-1}; see below.) Following procedures we have described at great length in previous publications and summarized in a recent review article,[18] this profile can be curve-fit to two (Gaussian) bands. (This curve-fitting procedure will be reviewed later, when we discuss the spectra of the blends.) Using the areas of these bands and a value for the ratio of the hydrogen-bonded to non-hydrogen-bonded absorption coefficients of 1.71, determined in our previous study of the APU, mentioned above,[3] we determined that the fraction of free carbonyl bands is about 0.20. This is close to the value of 0.16 determined for the APU at a temperature of 110 °C. Some differences would be expected, in that it is likely that in the as-cast film of the BD/MPDI polyurethane there will be a nonequilibrium distribution of contacts that become "frozen in" during solvent evaporation, as the T_g of the polymer/residual solvent mixture rises above ambient temperature. For reasons that will shortly be apparent, we could not compare the spectra of the APU and the BD/MPDI polyurethane at temperatures above the T_g. However, the correspondence in frequency shifts and in the proportions of hydrogen-bonded and free groups in these polymers suggests that the free energy of hydrogen bond formation, and hence the degree of self-association in these two polymers, is very similar.

We initially expected that the BD/MPDI polyurethane would be amorphous because the asymmetric MPDI should introduce disorder into the chain. Much to our surprise, we found that the polymer appeared to crystallize to some degree, or at least form some sort of ordered structure, at temperatures close to the T_g. The change in heat capacity of polyurethane hard segments is often small, making them difficult to observe,[19] but we detected what appeared to be a T_g near 130 °C in DSC measurements. A melting temperature could not be unambiguously observed, however. It is possible that it coincides with the onset of interchange and/or degradation reactions near 165 °C. Figure 4 compares the spectrum of the as-cast film to that of the same sample after annealing at 130 °C for 20 min. A sharp band near 1711 cm^{-1}, characteristic of hydrogen bonds in ordered domains, is clearly visible in the latter spectrum, so that there are now three contributions to this region of the spectrum: a free carbonyl band, a band characteristic of hydrogen bonds in disordered regions, and a band characteristic of hydrogen bonds in regions that have some degree of order. In the N−H stretching region (not shown), the hydrogen-bonded

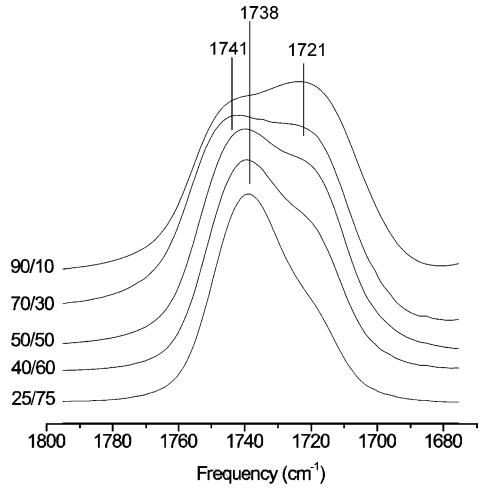

Figure 5. Carbonyl stretching region of the polyurethane/PEG blends. The composition of each blend (polyurethane/PEG) is shown in the figure.

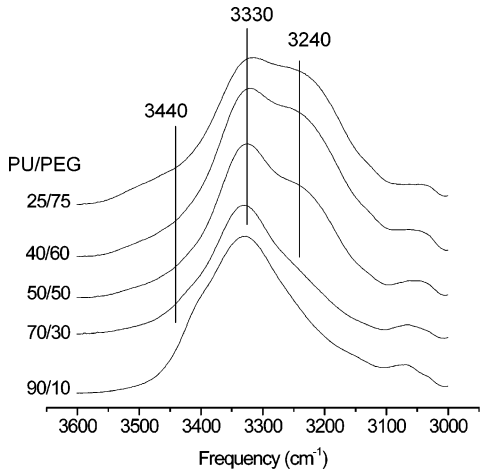

Figure 6. N−H stretching region of the polyurethane/PEG blends. The composition of each blend (polyurethane/PEG) is shown in the figure.

band near 3325 cm^{-1} becomes sharper, although it remains centered at the same frequency as the band observed in the amorphous film. (This is consistent with observations made in studies of other crystallizable polyurethanes and polyamides.[2,17])

Although crystallization complicates an interpretation of the infrared spectra, many segmented polyurethanes crystallize and thus have interesting and useful properties as a result of the resulting phase separation of hard and soft segments. Accordingly, we proceeded with a study of blends of this polyurethane with a poly(ethylene glycol) (PEG, molecular weight ∼1000). This polymer was chosen so as to facilitate a future comparison to behavior observed in segmented copolymers. The carbonyl stretching region of the spectrum of these blends is shown in Figure 5, while the N−H stretching region is shown in Figure 6. The as-cast films all appeared to be amorphous, with just two carbonyl bands, characteristic of free and disordered hydrogen bonds. As would be expected, the free carbonyl band increases in intensity as the amount of PEG in the blend increases and a larger fraction of urethane N−H groups hydrogen bond to the ether oxygen group, thus leaving the carbonyls with fewer potential partners. However, these bands, near 1741 and 1721 cm^{-1} in the spectrum of the pure BD/MPDI polyurethane, also appear to shift with increasing concentration of PEG. We will return to this point shortly, when we consider the results of curve fitting. The N−H stretching region of the

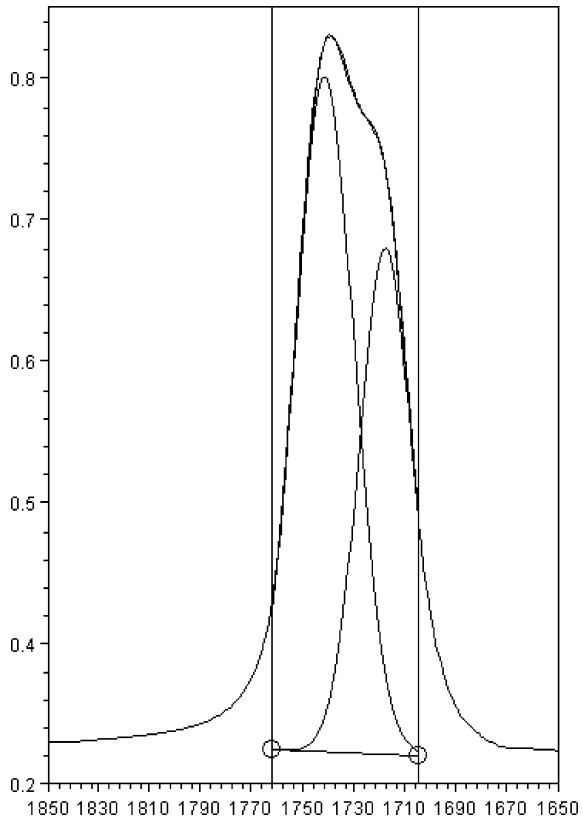

Figure 7. Curve-fitting the carbonyl region in 50/50 polyurethane/PEG blend.

spectrum has the usual free and hydrogen-bonded bands near 3330 and 3440 cm^{-1}, respectively, in the spectrum of the BD/MPDI, while an additional band near 3240 cm^{-1} becomes increasingly prominent as the concentration of PEG is increased. It is well-established that this band is due to N−H/ether oxygen hydrogen-bonded N−H groups, as these hydrogen bonds are "stronger" than the N−H/urethane C═O hydrogen bonds.[3,5]

As mentioned above, the carbonyl stretching region of the spectrum of the amorphous as-cast films can be curve-fit to two bands, characteristic of free and (disordered) hydrogen-bonded groups. We have discussed appropriate curve-resolving procedures in great detail in a recent review article[18] and will only present a brief outline here. To illustrate our methodology, the spectrum of the 50:50 (wt %) blend is shown in Figure 7. A baseline is first established using a broad region of the spectrum (outside the limited frequency range shown in the figure). This baseline is then fixed during the course of the curve-fitting process. There are sometimes weak combination, overtone, or other modes that overlap carbonyl stretching fundamentals, and we suspected that a weak mode near 1775 cm^{-1} was present in these samples. This can be accounted for by adding additional bands to the fitting process, but such weak overlapping modes are poorly defined (in terms of the number of data points) and their inclusion can lead to errors. Accordingly, unless such modes are clearly defined, we usually use a truncated region of the spectrum, as illustrated in the figure. We also usually fix the band shape to be Gaussian, partly on the basis of experience, partly to reduce the number of variables and increase precision, but mostly because if we are to determine the fraction of free and bonded groups, we must use a methodology (including band-shape assumptions) identical to that used in previous work where we obtained the value of the ratio of the absorption coefficients of the free and bonded infrared bands.

Table 1. Characteristics of the Free and Hydrogen-Bonded Carbonyl Bands in the Infrared Spectra of the BD/MPDI Polyurethane and Its Blends with PEG

		free C═O band		H-bonded C═O band		
wt ratio BD-MPDI/PEG	vol fract	freq (cm^{-1})	width (cm^{-1})	freq (cm^{-1})	width (cm^{-1})	fraction free
100:0	1.0	1747	22.5	1722	32.9	0.19
90:10	0.89	1746	26.1	1719	32.3	0.26
70:30	0.68	1743	21.2	1721	31.4	0.24
50:50	0.47	1742	26.9	1719	24.8	0.42
40:60	0.37	1742	23.4	1720	24.9	0.39
25:75	0.23	1740	22.9	1720	21.4	0.55

The results of curve-fitting the carbonyl stretching region of the BD/MPDI polyurethane and its blends with PEG are shown in Table 1. The width (full width measured at half-height) of the free band near 1747 cm^{-1} in the pure polyurethane lies in the range 22−27 cm^{-1}, comparable to values obtained in previous studies of these types of polymers. The width of the hydrogen-bonded band is significantly narrower than the value obtained in a previous study of an amorphous polyurethane (APU), however, about 33 cm^{-1} compared to 48 cm^{-1} in the pure polymers. This indicates that there is a more homogeneous local environment, presumably a narrower distribution of hydrogen bonds (in terms of hydrogen bond lengths and angles) in the BD/MPDI polyurethane relative to APU.

The widths of the hydrogen-bonded bands also narrow considerably in blends of high PEG content relative to those with a higher polyurethane content. There are some fluctuations in values, no doubt partly a result of errors in curve-fitting (because of baseline problems, for example), but also possibly as a result of some samples being more homogeneous than others, in the sense of the type and distribution of hydrogen bonds present. The relative sharpness of the hydrogen-bonded band in the high PEG content blends is most likely because most of the polyurethane N−H groups in these blends are now hydrogen bonded to ether oxygens, as opposed to some distribution of carbonyl and ether oxygen "acceptor" groups. This, again, is consistent with observations made in previous studies.[2,3]

There is also the probability of heterogeneity in a broader sense. When blends are cast from solution, phase separation can occur as a result of the so-called "$\Delta\chi$" effect. In addition, as the solvent evaporates from the films, the T_g of the residual mixture at some point exceeds room temperature, "freezing in" a certain distribution of hydrogen bonds. These two effects would combine to give a sample with a nonequilibrium distribution of hydrogen-bonded groups. Because the T_g of the blends decreases with increasing PEG content, hydrogen bond distributions corresponding to that found at different temperatures should be obtained as the PEG content is varied. However, the solvent used in this study (DMAc) evaporates more slowly than the THF used in our previous work on an APU, allowing a closer approach to the equilibrium distribution found near the T_g. Accordingly, we thought a comparison of the fraction of free carbonyl groups would be interesting, particularly as the polyurethanes and polyethers used in the two studies have about the same molar volumes, so that plots of the fraction of free or bonded groups against volume fraction should coincide (within error). This comparison is shown in Figure 8. It can be seen that in the pure BD-MPDI polyurethane and those blends with a high content of this polymer the fraction of free carbonyl groups exceeds the equilibrium distribution found in the APU/polyether blends, probably as a result of a combination of the factors mentioned above. However, starting at about 70% (w/w) polyurethane content and decreasing, most of the blends have, within error, the same proportion of free and bonded groups in the two systems.

The APU/polyether blends were characterized at a temperature of 110 °C. The T_g of the BD-MPDI homopolymer could not be determined unambiguously by DSC (although there was some evidence of a transition near 130 °C). Apparently, this is not uncommon, and many polyurethane hard segments show very small or undetectable heat capacity changes in DSC experiments.[19] However, as described above, infrared studies show that crystallization or partial ordering occurs around 130 °C, suggesting that the T_g is close to this temperature. Furthermore, DSC measurements did reveal single T_gs for the 70/30 (urethane/ether) and 50/50 blends near 102 and 73 °C, respectively. Glass transition temperatures were not evident on samples containing greater than 50% PEG content (in the range 25−170 °C), but as mentioned above, the curve-fitting results revealed that those blends with greater than 30% PEG content appear to approach the equilibrium distribution of hydrogen bonds characteristic of temperatures close to or just above the T_g. This indicates that these particular blends are single phase.

In the 70/30 and 50/50 blends there appears to be a surprising degree of mobility at temperatures well below the thermally measured glass transition, leading to the formation of some ordered structures. Figure 9 compares the carbonyl stretching region of the spectrum of an as-cast film of the 70/30 blend to the same sample annealed at 90 °C for 10 min (about 12 °C below the T_g measured by DSC) and a difference spectrum obtained by subtracting until the point that negative (below the baseline) bands start to appear, essentially until the disordered hydrogen-bonded band was eliminated. Upon heating to 90 °C, a sharp band appears at 1711 cm^{-1} and the band at 1743 cm^{-1} becomes sharper. The difference spectrum clearly reveals the presence of the "ordered" hydrogen-bonded band near 1711 cm^{-1}, together with a residual free band near 1743 cm^{-1}. This residual free band is readily explained. As the sample crystallizes, the PEG content of the remaining amorphous domains

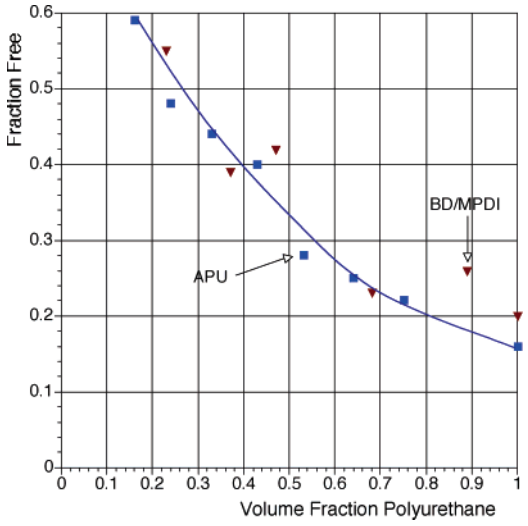

Figure 8. Fraction of free carbonyl groups vs volume fraction of APU, BD-MPDI in the blends.

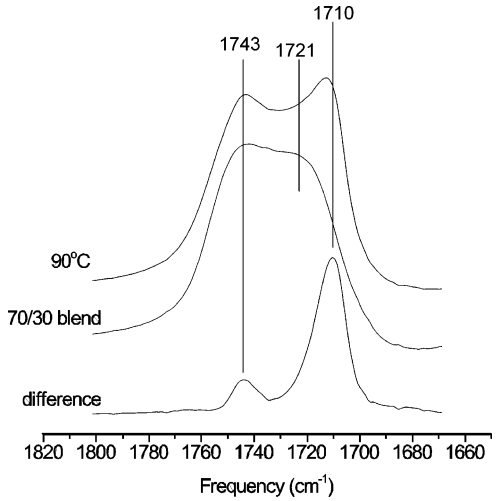

Figure 9. Infrared spectrum of the as cast film of the 70/30 (BD-MPDI:PEG) blend, the spectrum after 10 min at 90 °C, and the difference spectrum.

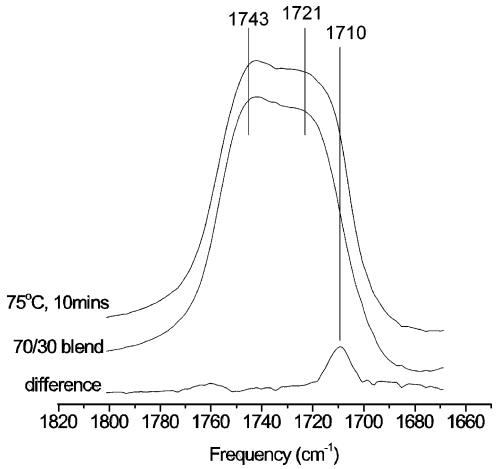

Figure 10. Infrared spectrum of the as-cast film of the 70/30 (BD-MPDI:PEG) blend, the spectrum after 10 min at 70 °C, and the difference spectrum.

increases, thus increasing the proportion of free carbonyl groups relative to the purely amorphous film.

Slow crystallization at temperatures close to but just below the T_g is not surprising, given the nature of this transition. Even 12 °C below the thermally measured T_g, there could still be a degree of mobility, given the broad glass transition characteristic of most blends. However, there is evidence for the formation of ordered structures at even lower temperatures, about 25 °C below the T_g. Figure 10 compares the carbonyl stretching region of the spectrum of an as-cast film of the 70:30 blend to the same sample annealed at 75 °C for 10 min. It can be seen that the intensity of the free carbonyl group (near 1743 cm^{-1}) increases slightly relative to the hydrogen-bonded band (near 1721 cm^{-1}). The bands also appear to broaden, indicating a change in the distribution of hydrogen bonds in this system, even though the sample is well below the thermally measured T_g. The difference spectrum reveals the presence of the "ordered" hydrogen-bonded band near 1711 cm^{-1}.

In order to determine how much of the blend had, in fact, formed an ordered structure, the spectrum of the sample annealed at 90 °C was curve resolved using three bands corresponding to the free, disordered hydrogen-bonded, and ordered hydrogen-bonded modes (in order of decreasing frequency) using the methodology described above. The fraction of ordered material was calculated using peak areas and was found to be 0.26 (assuming the same ratio of absorption coefficients for ordered and disordered hydrogen-bonded bands relative to free bands). It seems unusual that 26% of this polymer has formed ordered structures, but as we will see, these ordered structures may not correspond to regular crystalline domains.

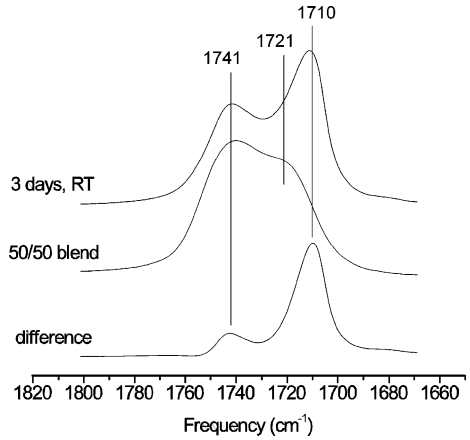

Figure 11. Infrared spectrum of the as-cast film of the 50/50 (BD-MPDI:PEG) blend, spectrum after 3 days at room temperature, and the difference spectrum.

The behavior of the 50/50 blend system is even more interesting. This blend slowly forms ordered structures over the period of a few days at room temperature, ∼45 °C below the measured glass transition temperature. Figure 11 compares the spectrum of an as-cast film of this blend to the same sample after 3 days at room temperature and a difference spectrum. The sample has clearly developed a significant degree of order of some description, as measured by the ordered hydrogen-bonded band near 1711 cm^{-1}. These results are even more surprising when considering crystallization in other polymer systems. As a point of reference, we studied the crystallization of isotactic polystyrene using FTIR, as characteristic sharp bands appear in the spectrum of this polymer upon forming ordered structures. This polymer crystallized extremely slowly at the T_g (∼100 °C). A significant degree of crystallinity was not obtained until samples were annealed at temperatures that were 10−15 °C above the glass transition temperature.

Studies of a Model Polyurea and Its Blends with Poly(ethylene glycol). The polyurea synthesized for the purposes of this study is similar in chemical structure to the BD/MPDI polyurethane, with a urea-linking group simply replacing the urethane. However, the polyurea homopolymer shows a much greater propensity to form ordered structures than the corresponding polyurethane. Figure 12 compares the carbonyl stretching region of the spectrum of the as-cast film to spectra obtained at elevated temperatures. It can be seen that the room temperature spectrum is far more complex than that obtained from the equivalent polyurethane. In addition to the free and bonded bands characteristic of the amorphous state, near 1687 and 1662 cm^{-1}, respectively,[4] there are two other prominent bands, near 1622 and 1605 cm^{-1}. On the basis of previous work, the 1622 cm^{-1} band can be assigned to hydrogen-bonded carbonyl groups in ordered domains,[4] while the 1605 cm^{-1} band is a ring stretching mode. However, the energy levels of bands that are close in frequency often mix, each taking on some of the character of the other. Indeed, in a normal coordinate analysis of substituted benzamides, Qayyum et al.[21] found that the ring modes near 1600 cm^{-1} mix with the amide I mode. It would not be surprising if an equivalent mixing of modes occurs here.

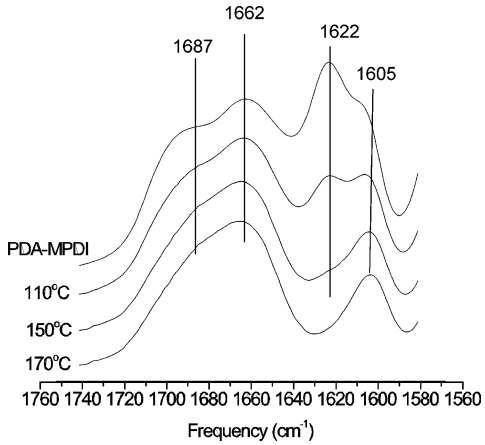

Figure 12. Carbonyl stretching region of the polyurea, PDA-MPDI, at various temperatures (top spectrum, room temperature).

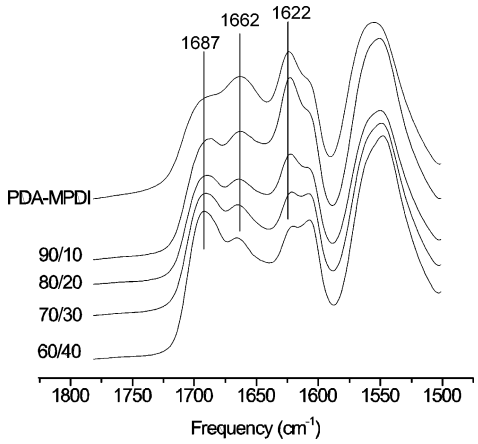

Figure 13. Carbonyl stretching region of PDA-MPDI/PEG blends. The composition of each blend (polyurea/PEG) is shown in the figure. PDA-MPDI is the pure polyurea.

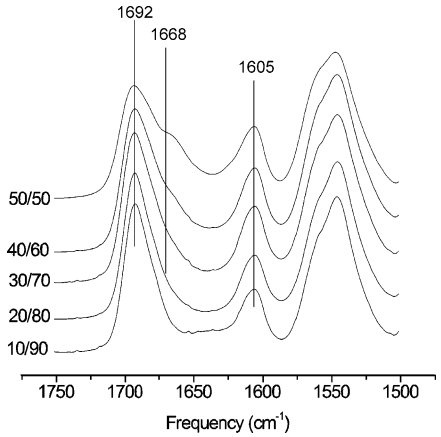

Figure 14. Carbonyl stretching region of PDA-MPDI/PEG blends (50/50−10/90). The composition of each blend (polyurea/PEG) is shown in the figure.

As the temperature of the sample is raised, the band near 1622 cm^{-1} gets less intense and is no longer apparent at a temperature of 160−170 °C, supporting the assignment of this band to some sort of ordered hydrogen-bonded structure. The intensity of the disordered hydrogen-bonded band also decreases relative to the free carbonyl band as the temperature is raised, as would be expected. At temperatures just above this, the spectrum starts to change dramatically, as a result of interchange and degradation reactions. This region of the spectrum was curve-fit (using the methodology outlined above), and using the assumption that the ratio of absorption coefficients (bonded/free) was the same as in the polyurethanes, it was estimated that the fraction of free carbonyl groups was of the order of 30%. We could not determine the fraction of free groups in the equivalent polyurethane at this temperature, because the latter sample had already started to degrade. However, as mentioned above, the polyurethane used in this study and an APU used in previous work have similar molar volumes and their hydrogen-bonding characteristics also closely correspond. In the APU sample at 170 °C, 39% of the carbonyl groups were "free". This would suggest, unsurprisingly, that the polyurea has a greater tendency to hydrogen bond than the equivalent polyurethane, no doubt because of the greater "strength" of the bifurcated hydrogen-bonded structures found in this polymer. This factor would also provide a greater enthalpic driving force for the formation of ordered structures, providing one explanation for the difference in the as-cast films of the polyurethane and polyurea. Indeed, the ordered hydrogen-bonded band in the polyurea, at 1623 cm^{-1}, is shifted 64 cm^{-1} from the free band near 1687 cm^{-1}, while in the BD/MPDI polyurethane the ordered hydrogen-bonded band is shifted 36 cm^{-1} (from 1747 to 1711 cm^{-1}). This indicates that the "strength" or enthalpy of the hydrogen bonds in the ordered regions of the polyurea are significantly greater than those found in the ordered segments of the polyurethane.

Blends of the BD/MPDI polyurea with PEG display some interesting characteristics. Figure 13 shows the carbonyl stretching region for blends 90/10, 80/20, 70/30, 60/40 (PDA-MPDI/PEG), and pure PDA-MPDI. The 90/10 blend has the usual free and hydrogen-bonded bands. The free carbonyl band is near 1687 cm^{-1}, the disordered hydrogen-bonded band is at 1662 cm^{-1}, and the ordered hydrogen-bonded band occurs at 1622 cm^{-1}. Most noticeable is the systematic decrease in the intensity of the ordered hydrogen-bonded band with increasing PEG content. Along with the decrease in the ordered band, the free band and the disordered hydrogen-bonded band shift to higher frequencies. The disordered band shifts from 1662 to 1665 cm^{-1}, and upon close inspection the spectrum appears to contain two overlapping modes near the disordered frequency (the second near 1650 cm^{-1}).

Figure 14 shows the carbonyl stretching region of the spectra of the high PEG content blends (50/50; 40/60; 30/70; 20/80; 10/90; polyurea/PEG). In the spectrum of the 50/50 blend, the "ordered" hydrogen-bonded band is no longer present, while the disordered hydrogen-bonded band is now a shoulder near 1668 cm^{-1}. The intensity of this mode decreases relative to that of the free band as the PEG content of the blend increases, while the frequency of the free band continues to increase and is observed at 1692 cm^{-1} in the spectrum of the 10/90 blend.

The frequency shift in the free band is readily understood. There is a delocalization of electrons in the π-bonds of the OCN_2 atoms of the urea group. If the N−H functionalities are hydrogen bonded to an acceptor group, in this case either the urea carbonyl group of a different polyurea segment or an ether oxygen atom of a PEG segment, there will be a shift in the distribution of electrons that depends on the strength of the hydrogen bond. A carbonyl that is directly hydrogen bonded to N−H groups apparently "weakens" and shifts to lower frequencies; the greater the strength of the hydrogen bond, the larger the shift. A carbonyl group that is "free", while the N−H groups belonging to the same urea unit are bonded, shows the opposite effect. The hydrogen bonds to ether oxygen atoms are much stronger than those to carbonyl oxygen atoms. As the concentration of PEG in the blend is increased, there is a larger number of N−H/ether oxygen hydrogen bonds and a resulting apparent shift of

the end-group free band to higher frequency. (There are probably two "free" bands present at lower concentrations, but these are close in frequency and cannot be resolved.)

The presence of two "disordered" hydrogen-bonded bands near 1650 and 1668 cm^{-1} can be similarly explained. The higher frequency mode can be assigned to a hydrogen-bonded urea/urea carbonyl where the N−H atoms of the same urea functional group are hydrogen bonded to an ether oxygen, as illustrated on the right-hand side of Figure 2. The lower frequency mode is due to hydrogen-bonded urea carbonyls with N−H groups hydrogen-bonded to other urea carbonyls.

As noted above, the ordered hydrogen-bonded band disappears in blend concentrations of 50% polyurea and lower. It is well-known that the presence of a solvent or a second polymer can depress the melting point of the crystallizable component of a miscible mixture. For polymer blends with weak interactions, this melting point depression is not large, but in hydrogen-bonded systems it can be significant. In work in this laboratory reported a number of years ago, we demonstrated how this effect can be understood using an association model.[20] Using spectroscopic data (to account for the contribution of hydrogen bonds to the free energy) and solubility parameters (to account for dispersion forces), this model was able to reproduce the experimentally observed melting point depression of poly(ethylene oxide) (PEO) in a blend with the amorphous polyurethane (APU) mentioned previously in this paper. Over the limited composition range (up to 50% APU content) possible in this study, a maximum melting point depression of about 10 °C was observed. Qualitatively, the melting point depressions we are observing here appear to be significantly larger than any we observed previously. Melting point data obtained from samples crystallized over a range of temperatures would have to be used to obtain an equilibrium melting temperature and a quantitative comparison, but the observed depression of more than 100 °C (the pure polyurea melts in the range 160−170 °C) would appear to be outside the range of any corrections for crystallite size. As one might expect, the model we developed previously predicts that the stronger the hydrogen bonds between the blend components, the larger the melting point depression,[20] but the observed depressions observed here seem unusually large.

As discussed earlier in this paper, the 1622 cm^{-1} ordered hydrogen-bonded band in the spectra of the polyurea samples is detectable up to temperatures of about 160−170 °C. At this point, the band disappears, and it is assumed that the ordered structures, whatever their nature, have melted. However, most of the DSC data obtained on high polyurea content samples did not show clear melting endotherms. One problem is that the homopolymer and high polyurea content blends have a tendency to degrade at higher temperatures. Nevertheless, given the FTIR results, we expected to see some evidence of melting. Accordingly, we began to suspect that the crystallite or ordered domain size is smaller than the probe size of the DSC.

To explore this possibility, the 60/40 (PDA-MPDI/PEG) blend was used in an annealing study. This blend was chosen because it had previously displayed a detectable heat capacity change that can be assigned to a T_g. The temperature of a sample was raised to 75 °C in the DSC, about 20 °C below the measured T_g, and was annealed for 80 min. The temperature was then lowered to just above room temperature and then ramped to almost the point of degradation at about 160 °C. Figure 15 shows two runs of the 60/40 blend in the DSC. The upper curve shows a run without annealing. At 96 °C a small change in heat capacity, probably the T_g, is detected. However, no clear melting

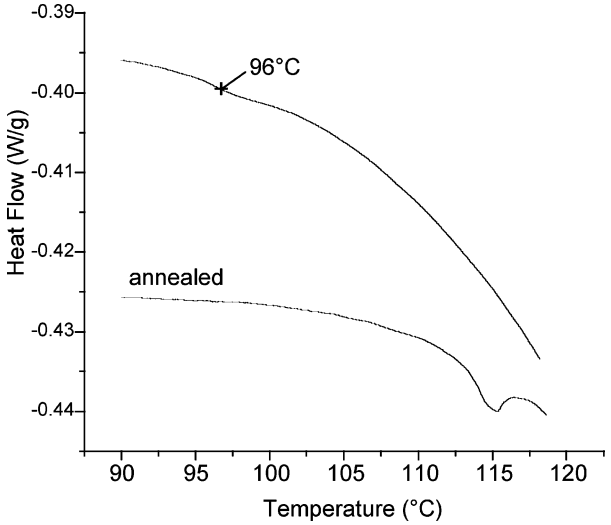

Figure 15. DSC thermograph 60/40 polyurea blend: top curve, initial DSC run; bottom curve, DSC run after annealing at 90 °C.

point is apparent, even though the ordered hydrogen-bonded band near 1622 cm^{-1} is clearly visible in the room temperature spectrum of blends of this composition (see Figure 13). The lower curve shows the subsequent heating run after the sample was annealed. As in most of the DSC work performed in this study, a T_g was not detected in this run, but a small melting endotherm is apparent. The onset of the melting occurs near 110 °C, and the total heat of melting is quite small. This result would suggest that there is only partial ordering or the size of any crystalline domains is very small.

One final point before we get to our conclusions concerning these results. Poly(ethylene glycol) with a molecular weight of 1000 was used in the these studies. PEG of this molecular weight has a glass transition temperature of about −60 °C and a melting point in the range 35−40 °C. The infrared spectrum of the pure PEG displays three sharp bands between 1060 and 1150 cm^{-1}, which broaden and shift considerably in the amorphous state. The blends reported here displayed these amorphous bands, and there was no evidence for the formation of PEG crystalline domains.

Discussion and Conclusion

On the basis of the detection of a single T_g in certain samples and the observation that the blends appeared to form the equilibrium distribution of hydrogen bonds, we conclude that the BD-MPDI polyurethane synthesized for this study formed miscible blends with a PEG sample (molecular weight ∼1000) for blends having less than 70% polyurethane. Higher polyurethane blends were probably also miscible, but the formation of ordered structures of some type prevented the samples from attaining the equilibrium distribution of hydrogen bonds normally found in the amorphous state. Miscibilty in these mixtures is not surprising, given the strong hydrogen bonds that can form between the urethane and ether groups. What is surprising is the ability of the urethane chains to form ordered structures, even though the polyurethane was synthesized from a diisocyanate that has an asymmetrically placed methyl group that should introduce disorder into the chain (see Figure 1). For the pure homopolymer, an infrared band due to ordered hydrogen-bonded groups appeared in the infrared spectra of the initially amorphous as-cast films upon annealing close to what we believe to be the T_g, near 130 °C. A melting endotherm could not be detected, but that could well be because of the onset of degradation and/or trans reactions near 160−170 °C.

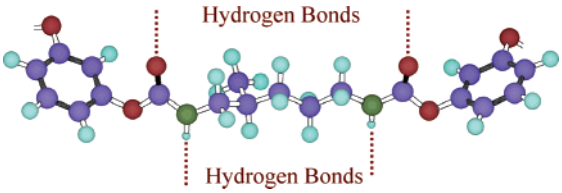

Figure 16. Schematic representation of a segment of the polyurethane chain.

The infrared spectra of the as-cast films of the polyurethane/PEG blends showed no initial evidence of order. However, after annealing at temperatures close to the T_g a band assigned to ordered structures emerged. This band appeared in the spectra of certain samples that were held at room temperature, ~45 °C below the thermally measured T_g, over a period of days. There is now considerable evidence that glassy systems are dynamically heterogeneous,[22−24] and it is well-known that the glass transition in polymer blends is broader than in their constituent homopolymers. Even so, the nucleation of normal crystals this far below the T_g would seem to be unlikely. Furthermore, in these blends a normal melting endotherm could not be detected. One would expect that any melting transition in the blend should be sufficiently depressed to lower temperature to be observed before the onset of degradation.

Similar results were obtained for the polyurea, except that the stronger hydrogen bonds in this polymer and its mixtures with PEG provided a greater driving force for the formation of ordered structures. In this case, however, a very weak endotherm was detected in a DSC study of an annealed 60/40 blend, significantly depressed from the melting point of the polyurea ordered structures, detected spectroscopically near 165 °C.

These results indicate that the ordered structures are at best small, imperfect crystals. We suggest that the order present in these blends might be largely two-dimensional. A schematic representation of a segment of the polyurethane chain is shown in Figure 16. The hydrogen bonds between adjacent urethane (or urea) units can align to form a sheet, with the methyl group that is part of each segment laying in a plane that is essentially perpendicular to this structure. Because the methyl group is asymmetrically placed in the diisocyanate used to synthesize these polymers, packing between sheets would be imperfect at best. This would explain why a band due to ordered structures is detected spectroscopically, while endotherms cannot be detected in most of the blends using DSC.

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