below T_g have properties which depend upon sample history. In our experiments, we expect that the cooling rate must play an important role in the determining the exact magnitude of the annealing-induced changes in $\langle \tau \rangle$. These effects are probably more important in the dispersions than in the powder samples. We have not yet had an opportunity to explore the effects of cooling rate on the phenomena we report here. It is an aspect that merits examination in future experiments.

Summary

The mean fluorescence lifetime of naphthalene groups in rigid polymer matrices varies with the concentration of N groups. This lifetime is also sensitive to the environment, at high dilution being longer in PMMA (53 ns) than in saturated hydrocarbon media (43 ns).

The PIB–PMMA particles examined here contain N groups covalently bound to the PMMA chains. When the particles contain only a trace of N, the fluorescence decay curves are consistent with N being located in a PMMA phase. At higher substitution of N, the $\langle \tau \rangle$ values are much shorter than that of N in a poly(NMA-*co*-MMA) copolymer. In these samples, N groups tend to concentrate within the interphase between PIB and PMMA. We presume that the interphase is composed largely of graft copolymer formed during particle synthesis.

Annealing both sets of samples leads to changes in the fluorescence decay profile of N^*. The $\langle \tau \rangle$ values increase for dispersions of the particles in isooctane and hexadecane and decrease for the dry powder samples. We can explain both results in terms of heat-induced changes in particle morphology which lead to a net increase of the fraction of N groups located in the interphase domain. In the particles, this leads to an increase of the local concentration of N. The mean lifetimes are shortened as a consequence of an increase in self-quenching. In the dispersions, solvent swells the interphase and leads to an increase in the average separation of N groups. The lower local N group concentration leads to less self-quenching and longer values of $\langle \tau \rangle$.

Because the PMMA phase is below its T_g at the temperature of the measurements, we anticipate that the detailed expression of the phenomena we describe here depends in someway on sample history. One parameter we have not yet studied is the influence of cooling rate after sample annealing. We ascribe the behavior of the dispersions annealed above 100 °C to entrapment of solvent within the interphase. The extent of solvent entrapment may very well depend upon how rapidly the sample is cooled below T_g.

Acknowledgment. We thank NSERC Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

Registry No. PIB, 9003-27-4; MMA, 80-62-6; NMA, 28171-92-8; (NMA)(MMA) (copolymer), 110971-37-4.

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Hydrogen Bonding in Polymer Blends. 1. FTIR Studies of Urethane–Ether Blends

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ABSTRACT: The most common strong interaction in polymers, and one that is central to the properties and phase behavior of a range of important materials, is hydrogen bonding. Infrared spectroscopy is uniquely sensitive to, and considered diagnostic for, the formation of such bonds, and in recent publications we have explored the problems of using this technique to quantitatively measure the fraction of hydrogen-bonded groups in polyamides and polyurethanes. In this paper we will consider the mixing of a simple amorphous polyurethane with a polyether. This system was chosen because of its relevance to the more complicated segmented polyurethanes and in its essentials is focused upon the spectroscopic characteristics of the interaction of urethane N–H with ether functional groups.

Introduction

In previous papers we have stressed the complex nature of the N–H stretching region of the infrared spectrum of polyamides and polyurethanes.[1-4] In fact, we reluctantly concluded that this region of the infrared spectrum cannot be used in a straightforward manner to obtain accurate quantitative data concerning the fraction of "free" (non-hydrogen-bonded) and hydrogen-bonded N–H groups (and hence a measure of enthalpy of hydrogen-bond formation). On the other hand, the carbonyl stretching region of the infrared spectrum of polyamides and polyurethanes appears amenable to at least semiquantitative analysis. The infrared carbonyl band envelope is composed of separate absorptions attributed to "free" and hydrogen-bonded (ordered and disordered) carbonyl groups. A reasonable

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estimate of the fraction of "free" and hydrogen-bonded carbonyl groups can be obtained from curve fitting and by adjusting the areas to account for the difference in absorptivity coefficient ratio.[4]

To date we have only reported the results obtained from our studies of a semicrystalline polyurethane, poly(1,4-butylene hexamethylenecarbamate). Although this polymer is of little, if any, commercial significance, it was deliberately chosen for our initial studies to ensure that we had a reasonable understanding of the infrared spectrum of a "simple" polyurethane. In contrast, polyurethane–polyether block copolymers, commonly referred to as segmented polyurethanes, are important materials of industrial and academic interest but are spectroscopically much more complex.[6-15] It has long been recognized, especially in the amorphous state above the melting point of the hard urethane segments, that the ether oxygen of the polyether block competes with the urethane carbonyl group for the privilege of forming a hydrogen bond with the urethane N–H group. There appears, however, to be little agreement on the absolute or even the relative strength of this interaction. In addition, the frequency and absorptivity coefficient of the N–H stretching vibration for a N–H group hydrogen bonded to an ether oxygen is open to question.[14] Nevertheless, estimates of the concentration of urethane N–H to ether oxygen interactions have been made from the difference between the measured fraction of hydrogen-bonded N—H and C=O groups, obtained from infrared spectroscopy. These calculations were based on an oversimplified interpretation, however, and the results must now be considered to be subject to large errors.[4]

Rather than attempting to unravel the complexity inherent in the infrared spectra of segmented polyurethanes, where factors such as crystallinity, the effect of block size (sequence distribution), different chemical structures, and phase separation etc. only serve to exacerbate uncertainty and increase the probability of errors in interpretation, we have deliberately chosen to initially study a simple(!), miscible *amorphous* polyurethane–polyether *blend*. As mentioned previously, polyurethanes are strongly self-associated through intermolecular hydrogen bonding. In order for two polymers to be intimately mixed at the molecular level, it is evident that a favorable balance must exist between the forces of self-association and association (intermolecular interactions occurring between the like and unlike polymers, respectively). A "rule of thumb", which we have employed rather successful as a scouting tool for potentially miscible polymer blends involving strong intermolecular interactions, may be simply expressed as follows. To obtain significant molecular mixing with a strongly self-associated polymer, A, we need to find a polymer, B, that is weakly self-associated but which has a site available for a relatively strong association with A (but not necessarily as strong as the self-association of A). Examples of strongly self-associated polymers A include polyamides, polyurethanes, polyphenols, epoxies, and polyacids. Polyethers and polypyridines are excellent examples of polymers B that are relatively weakly self-associated but contain sites, the oxygen or nitrogen atoms, respectively, which are capable of forming a strong interactions (hydrogen bonds in this case) with polymer A. Using the above guiding principles, we have recently reported on a miscible amorphous polyamide–poly(2-vinylpyridine) blend.[5]

Experimental Section

Ethylurethane (EU) and tetrahydrofuran (THF) were acquired from the Aldrich Chemical Co. and used as received. The amorphous polyurethane (APU) was synthesized from butanediol and a mixture of the 2,4- and 2,6-isomers of tolyl diisocyanate by Dr. T. Krizan of the E. I. du Pont de Nemours Co. The inherent viscosity of a sample in THF was 0.55, and a glass-transition temperature (T_g) of 98 °C was recorded by thermal analysis. A poly(ethylene oxide-*co*-propylene oxide) copolymer (EPO) containing 70 wt % ethylene oxide was purchased from Polysciences Inc. The reported molecular weight (undefined) of the copolymer was 12 500, and thermal analysis revealed a T_g of −65 °C and a melting point (T_m) between 56 and 59 °C.

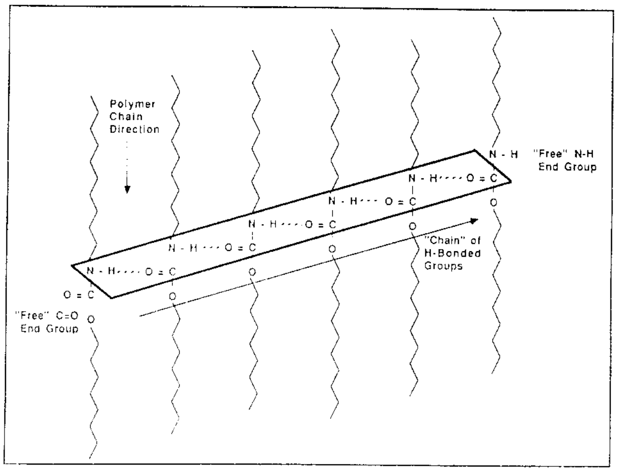


Figure 1. Schematic representation of a "chain" of hydrogen-bonded urethane groups.

Spectra were recorded on a Digilab Model FTS-15E 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 with a Micristar heat controller. This device has a reported accuracy of ±0.1 °C. Thermal analysis was performed on a Perkin-Elmer 7 Series differential scanning calorimeter. A heating rate of 20 °C/min was employed by using a sample size of approximately 15 mg. Details of the preparation of samples for FTIR and thermal analysis are given in the text.

Results and Discussion

Before we become immersed in the interpretation of the infrared spectra of polyurethane–polyether blends, we will discuss some infrared studies of low molecular weight model urethane mixtures, in order to cast some light upon the relative strength and infrared characteristics of the urethane N–H to ether oxygen intermolecular interaction. This will be crucial to an understanding of the problems associated with previous infrared studies of polyurethanes, for the reasons we will now consider.

In previous papers of this series[1-4] we have fastidiously enclosed the word "free" in quotation marks when describing amide and urethane N—H or C=O groups that are not *directly* hydrogen-bonded. This was, and is, a deliberate practice to emphasize that these groups are not completely isolated or truly free in the condensed state but exist in a "sea" of polar (amide or urethane) and nonpolar (aliphatic or aromatic) groups. In fact, at any given instance in time, "chains" of intermolecular hydrogen bonds exist essentially "normal" to the polymer chains as depicted schematically and in a grossly oversimplified manner, in Figure 1. The "free" N—H and C=O groups that are measured spectroscopically may actually be viewed as "end groups" of a "chain" of hydrogen-bonded urethane groups. It follows therefore that the "free" N—H or C=O "end groups" are not associated with a truly isolated urethane group but are a measure of the number of hydrogen-bonded chains in the system. The secondary interaction of adjacent C=O or N—H groups in these chains is not apparently strong enough to cause a measurable shift or

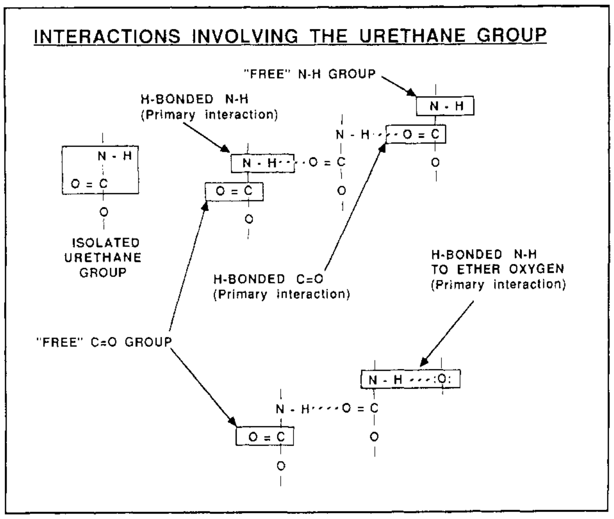


Figure 2. Intermolecular interactions involving the urethane group.

splitting of the infrared frequency of the stretching modes, but it probably contributes to the overall breadth of the "free" bands.

There is a pleasing correspondence in an equilibrium description of the formation of such hydrogen-bonded chains to the statistics of linear polycondensation, which characteristically did not escape the attention of Flory.[16] If we designate the urethane group A–B, where A and B represent the N—H and C=O groups, respectively, the hydrogen bonds formed between the N—H and C=O groups may be considered analogous to the "condensation" of A with B to yield a distribution of *n*-mers, $A\text{-}(BA)_n\text{-}B$, which depend upon an "extent of reaction", p; defined, in our case, as the fraction of A or B groups that are hydrogen-bonded. At any moment of time, the infrared bands attributed to "free" N—H and C=O stretching vibrations reflect the fraction of N—H and C=O groups that are present as end groups of the *n*-mers. We will return to this interesting analogy later in the text.

The *major* intermolecular interactions involving the urethane group with itself (self-association) and with the ether oxygen group (association) are depicted in Figure 2. An isolated (or truly free) urethane group is one in which neither the C=O or N—H moieties of the same urethane group are hydrogen-bonded to other urethane groups. (It is in fact a "monomer", using the polycondensation analogy.) The *primary* intermolecular interaction occurring in pure urethane is a hydrogen bond between the urethane C=O group of one unit with the urethane N—H group of another. As mentioned above, "chains" of hydrogen-bonded urethane groups are formed, and at the ends of these chains are two "free" (non-hydrogen-bonded) groups: one C=O and one N—H group. This one-to-one correspondence of "free" C=O and N—H groups in the pure polyurethane will be featured prominently in our future arguments. The addition of an ether to the pure urethane provides a further site (the ether oxygen atom) which is capable of forming a primary interaction (a hydrogen bond) with the urethane N—H group (see Figure 2). (Once again, it is tempting to use the analogy to polycondensation with the ether playing the role of a "chain stopper".) Each time a urethane N—H to ether oxygen intermolecular interaction is formed, a "free" C=O group is liberated. Accordingly, the one-to-one correspondence of "free" C=O to N—H groups in pure urethanes is no longer applicable in urethane/ether mixtures. The ratio of "free" C=O to N—H groups will exceed unity and will depend upon the relative strengths of the N—H to C=O interaction compared to the N—H to ether interaction, as well as the concentration of the two components.

If it were possible to directly measure the concentration "free" N—H and C=O groups in urethane–ether mixtures, it would be a rather straightforward task to determine the fraction of N—H to ether oxygen interactions present by difference. Unfortunately, as we stressed in the Introduction, we do not believe that the concentration of "free" N—H groups in polymer films can be measured accurately by infrared spectroscopy.[4] First, the initial concentration of "free" N—H groups in the pure urethane is considerably less than the hydrogen-bonded groups (<20% at room temperature), and the infrared band attributed to the "free" N—H stretching vibration has an absorption coefficient that is much smaller than that of the hydrogen-bonded N—H stretching band (to reiterate, this is not a simple relationship as the absorption coefficient is a strong function of the strength of the hydrogen bond[1,4]). These two factors combine to give an envelope in the N—H stretching region of the infrared spectrum in which the small area contribution from the "free" N—H groups is largely buried beneath the broad hydrogen bonded contribution. Curve-fitting procedures applied to this envelope must inevitably be subjected to large errors. To compound the problem, in urethane–ether mixtures, the concentration of "free" N—H groups will *decrease* with increasing ether concentration, making their quantitative measurement by infrared spectroscopy even more difficult.

The carbonyl stretching region of the infrared spectrum, on the other hand, is very different. The "free" C=O stretching band is well-separated from that of the disordered hydrogen-bonded C=O stretching band, and although the absorption coefficients for the bands differ, they are not widely disparate.[4] Furthermore, in urethane–ether mixtures the concentration of "free" C=O is expected to *increase* with increasing ether concentration which serves to aid quantitative analysis. Consequently, we will spend most of our time studying the carbonyl stretching region of urethane–ether mixtures, but first we will address the question, "what is the relative strength of the urethane N—H to ether oxygen interaction compared to the urethane N—H to urethane C=O interaction?"

The Model System: Ethylurethane (EU)–Tetrahydrofuran (THF). Figure 3 shows representative room-temperature infrared spectra in the N—H stretching region of pure EU and 10% (v/v) of mixtures of EU in THF and benzene. The spectrum of pure EU is characterized by a rather broad band centered at approximately 3340 cm^{-1}, which is assigned to urethane N—H groups that are hydrogen bonded to urethane C=O groups. The "free" (non-hydrogen-bonded) N—H stretching band is barely detectible as a weak shoulder at about 3440 cm^{-1}. Contrast this with the infrared spectrum of pure EU in the carbonyl stretching region, shown at the bottom of Figure 4. The "free" carbonyl band, which appears as a shoulder at 1725 cm^{-1}, is much more definitive. This is a reflection of the different absorption coefficient ratios in the two spectral regions, because the fractions of "free" N—H and C=O groups are equivalent.

Returning to Figure 3, when EU is mixed with benzene or a hydrocarbon, where there are little or no significant specific interactions involving the urethane group with the solvent, the fraction of both "free" N—H and C=O groups increases due to a dilution effect. Thus in a 10% (v/v) solution of EU in benzene, the infrared spectrum shows a large contribution from the "free" N—H band at 3440 cm^{-1} and a relatively small contribution from the urethane

Table I
Infrared Data from Model System EU-THF

	"free" C=O band		H-bonded C=O band		
EU mol fractn	freq, cm^{-1}	width,[a] cm^{-1}	freq, cm^{-1}	width,[a] cm^{-1}	fractn, "free" C=O[b]
1.00	1725	15	1694	39	0.14
0.83	1725	15	1696	37	0.18
0.71	1724	15	1698	35	0.21
0.63	1724	15	1699	33	0.25
0.50	1724	15	1700	30	0.32
0.42	1723	15	1702	28	0.40
0.33	1723	15	1703	26	0.48
0.25	1723	14	1704	23	0.60

[a] Width at half-height. [b] Calculated based upon an absorptivity ratio of 1.71—see text.

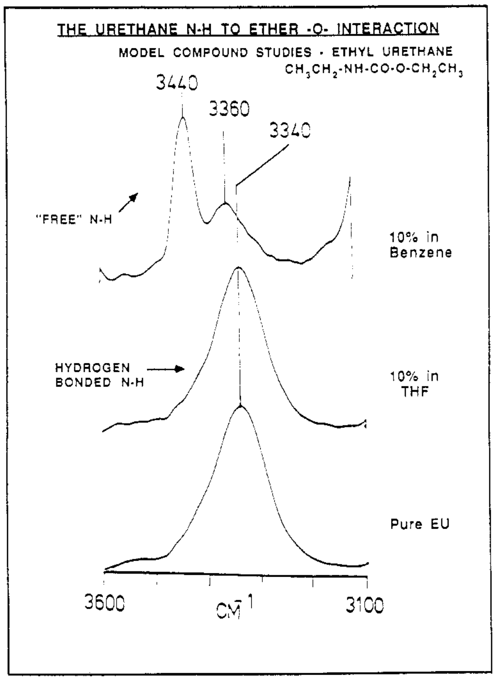


Figure 3. The N–H stretching region of the infrared spectrum of ethylurethane (EU): bottom, pure EU; middle, 10% EU in THF; top, 10% EU in benzene.

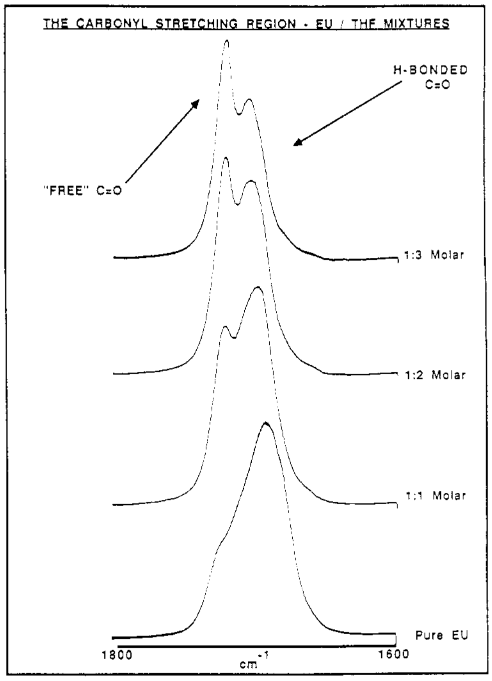


Figure 4. The carbonyl stretching region of the infrared spectrum of ethylurethane–tetrahydrofuran mixtures.

N—H to urethane C=O hydrogen-bonded band at about 3340 cm^{-1}. At lower concentrations, <1% EU in benzene, no contribution from the hydrogen-bonded band is seen. In the carbonyl stretching region (not shown) at 10% EU in benzene, the "free" C=O band at 1725 cm^{-1} dominates over the hydrogen bonded band at about 1700 cm^{-1}. At 1% EU it is difficult to detect a contribution from the hydrogen-bonded band.

The infrared spectra of the EU–THF mixtures are very interesting for several reasons. First, the spectrum of a 10% (v/v) EU in THF mixture in the N—H stretching region (Figure 3) is almost identical with that of the pure EU spectrum. Reducing the concentration to 1% EU results in a somewhat more noisy spectrum, but one of identical character. There is little, if any, evidence of "free" N—H groups (however, one must keep in mind the disparity in the absorption coefficients, which makes detection difficult at best). More importantly, the frequency of the hydrogen-bonded band remains *essentially constant* with dilution with THF. This implies that the strength of the urethane N—H to ether oxygen interaction, as characterized by the difference between the frequency of the "free" N—H band and the peak maximum of the hydrogen-bonded N—H stretching band, is *comparable* to that of urethane N—H to urethane C=O interaction. This is one reason for the debate about the relative strength of the urethane N—H to ether oxygen interaction; previous workers have been looking for a separate band in the infrared spectrum of segmented polyurethanes attributable to this interaction and as a result have misassigned two photon bands (see discussion in ref 15). The effect of dilution of EU with THF in the carbonyl stretching region is shown in Figure 4. As expected the "free" carbonyl band at 1725 cm^{-1} increases at the expense of the hydrogen-bonded carbonyl band. Although the change in this band is qualitatively the same as that obtained upon dilution with a solvent such as benzene, the extent of the effect is due to the additional concentration of ether oxygen groups that compete with the urethane carbonyl groups for the N—H proton.

As an aside, and returning to the analogy of polycondensation, the comparable strength of the interaction between the urethane N—H to the urethane C=O or the ether oxygen might lead one to assume that the "reactivity" of the "chain stopper", B– (ether oxygen) is identical with that of the monomer A–B (urethane). We must caution, however, that the enthalpy of hydrogen bond formation may be identical, but the entropy and hence the equilibrium constant could be very different.

Infrared data similar to that shown in Figure 4 may be resolved into two contributions using a curve fitting procedure described previously;[4] a "free" carbonyl band at approximately 1725 cm^{-1} and a hydrogen-bonded carbonyl band located between 1694 and 1704 cm^{-1}. The results are presented in Table I. The overall breadth of the hydro-

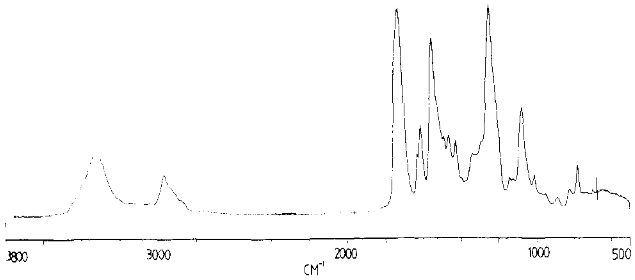
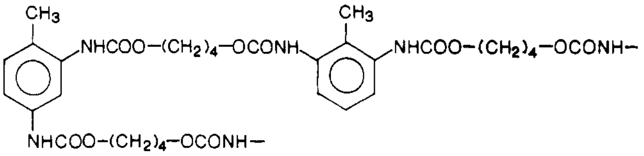


Figure 5. The infrared spectrum of the amorphous polyurethane (APU) recorded at room temperature.

gen-bonded carbonyl band decreases quite significantly as the EU is diluted with THF ($w_{1/2}$ almost halves at a mole fraction of 0.25 compared to pure EU). Presumably, this reflects the narrowing of the distribution of the hydrogen-bonded states. Assuming that the ratio of the hydrogen-bonded to non-hydrogen-bonded urethane carbonyl band absorption coefficients is similar to that determined for poly(1,4-butylene hexamethylenecarbamate)[4] at 1.71, the percent "free" carbonyl groups can be estimated from the measured areas. It is estimated that the percent "free" carbonyl groups in pure EU at room temperature is about 14.2 and rises to approximately 60.1 at a mole fraction of 0.25 EU in THF. Frankly, the absolute values must not be taken as necessarily being quantitatively well-defined, although we believe they are reasonable. There are many factors that can introduce errors into the above procedure, not the least being a change in absorption coefficient of the hydrogen-bonded carbonyl band with dilution (note that the frequency of this band increases by 10 cm^{-1}, suggesting a decreasing average strength of the hydrogen bond).

The Polymer Blend System: Amorphous Polyurethane (APU)–Poly(ethylene oxide-*co*-propylene oxide) (EPO). The polyurethane employed in these studies may appear somewhat complicated, especially as we have emphasized the need to keep the system as simple as possible. However, this amorphous polyurethane (APU), a copolymer synthesized from a mixture of 2,4- and 2,6-tolyl diisocyanate and butanediol, depicted schematically below,



was chosen deliberately to avoid possible complications arising from crystallization and is analogous to the amorphous polyamide used in our previous studies.[1] The APU has a glass-transition temperature, T_g, of 98 °C.

A typical infrared spectrum of APU is shown in Figure 5. In overall form it closely resembles the spectrum of the above-mentioned amorphous polyamide. Although there are significant differences between the infrared spectra of these two polymers in the form of specific normal modes and their frequencies and intensities, the gross characteristics of the two spectra are remarkably similar. Moreover, infrared temperature studies performed on the APU indicate that the general conclusions reached in the analogous studies of the amorphous polyamide are also applicable to APU. We do not believe it is necessary to rehash this subject, as the underlying principles have been detailed in our previous papers.[1-4] In this work we will restrict ourselves to two regions of the infrared spectrum; the N–H stretching between 3100 and 3500 cm^{-1} and the carbonyl stretching between 1650 and 1800 cm^{-1}.

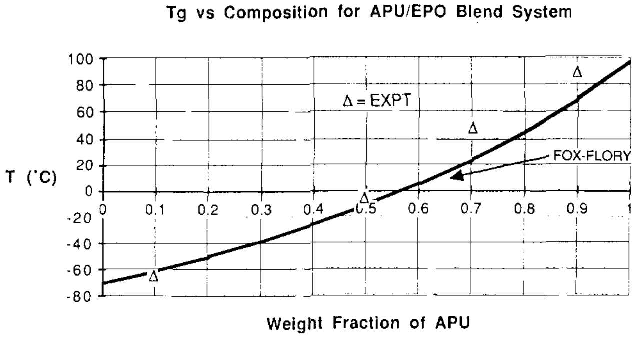
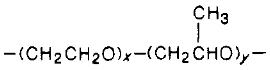


Figure 6. Graph of T_g determined by thermal analysis against blend composition. The solid line was calculated from the Fox–Flory relationship.

The polyether chosen for this study, a poly(ethylene oxide-*co*-propylene oxide) (70:30 wt %) copolymer (EPO)



$$-(CH_2CH_2O)_x-(CH_2\overset{\overset{CH_3}{|}}{C}HO)_y-$$

may also appear at first glance to be inordinately and unnecessarily complex. The choice of this polymer, however, was predicted upon its solubility in a common solvent with APU and its relatively low melting point (presumably the comonomers are not distributed entirely at random). The T_g and T_m of EPO are -65 and 56–59 °C, respectively, and the polymer is soluble in THF. The infrared spectrum of EPO is typical of any aliphatic polyether,[13] and suffice it to say that there are no significant absorptions in the N—H and C=O stretching regions of the infrared spectrum. A critical note of caution is necessary, however, concerning oxidation and degradation. EPO is not a very stable polymer. Presumably, the increased concentration of α-hydrogens from the propylene units enhances autoxidation as compared to poly(ethylene oxide). We determined from infrared temperature studies of pure EPO that in the time scale of our measurements the maximum temperature at which we can safely use the polymer without measurable oxidation (formation of carbonyl groups) is 150 °C. Significant weight loss was detected at about 200 °C using thermal gravimetric analysis (TGA).

Thin film samples for thermal and infrared analysis of polymer blends of varying composition were cast from dilute solutions of APU and EPO in the common solvent, THF. Samples for thermal analysis were prepared in conventional aluminum pans. Following the evaporation of the solvent in a vacuum oven at 100 °C the sample was sealed. A thermogram was recorded upon the second heating cycle after the blend sample had been heated to 150 °C and quenched to room temperature. The results of T_g plotted against composition (weight fraction APU) are displayed in Figure 6. Also included in this figure is a plot of the theoretical Fox–Flory equation based upon the assumption that the blend is miscible. The agreement between experiment and theory is acceptable and strongly suggests that the blend is well-mixed at the molecular level.

Infrared samples were prepared on KBr windows. After evaporation of the solvent in a vacuum oven at 80 °C for 12 h, the samples were sandwiched and sealed by using another KBr window and then transferred to the spectrometer, and heated to 110 °C and the infrared spectrum was recorded. A temperature of 110 °C was chosen for these studies for the following reasons. First, it is above the T_g's of either pure component and also above the T_m of EPO, which should facilitate mixing and minimize effects due to nonequilibrium conditions and/or phase

Table II
Infrared Data from the APU-EPO Blend System

		"free" C=O band		H-bonded C=O band		
wt ratio	vol fractn	freq, cm^{-1}	width,[a] cm^{-1}	freq, cm^{-1}	width,[a] cm^{-1}	fractn "free" C=O[b]
100:00	1.00	1737	21	1711	48	0.16
80:20	0.75	1736	21	1712	45	0.22
70:30	0.64	1735	22	1712	45	0.25
60:40	0.53	1734	23	1714	47	0.28
50:50	0.43	1733	23	1714	42	0.40
40:60	0.33	1733	25	1713	42	0.44
30:70	0.24	1733	24	1715	43	0.48
20:80	0.16	1733	24	1715	41	0.59

[a] Width at half-height. [b] Calculated based upon an absorptivity ratio of 1.71—see text.

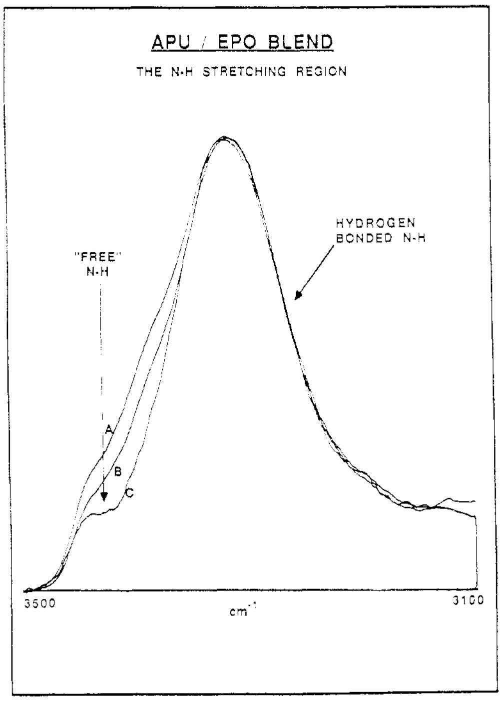


Figure 7. The N-H stretching region of APU-EPO blends recorded at 110 °C: A, pure APU; B and C, 80:20 and 20:80 wt % blends of APU and EPO, respectively.

separation due to the solvent (the so-called $\Delta\chi$ effect). Second, it is below the oxidation and/or degradation temperature of either polymer.

We will not dwell long on the N—H stretching region (3100–3500 cm^{-1}) of the infrared spectra of the APU-EPO blends, because of the inherent difficulties in quantifying the data. From our studies of the low molecular weight model compounds, however, we might anticipate that upon molecular mixing of APU with EPO the relative fraction of "free" N—H groups should decrease as the concentration of ether oxygens increases (since both C=O and ether oxygens compete for the same N—H groups and mole ratio of [C=O + O] to [N—H] has increased). Qualitatively, this is precisely what we observe, as shown in Figure 7. The "free" N—H band at 3440 cm^{-1} obviously decreases in relation to the hydrogen-bonded band centered at approximately 3340 cm^{-1}, as we progress from pure APO to an 80:20 and 20:80 APO-EPO wt % blend. Note also that there is no obvious new band in this spectral region that can be attributed to the N—H to ether oxygen interaction. The frequency of the hydrogen-bonded band occurs in the same place regardless of the concentration of EPO. This is in keeping with the conclusion drawn from the model compound study described above and strongly suggests that the two competing interactions for the N—H proton are of comparable strength.

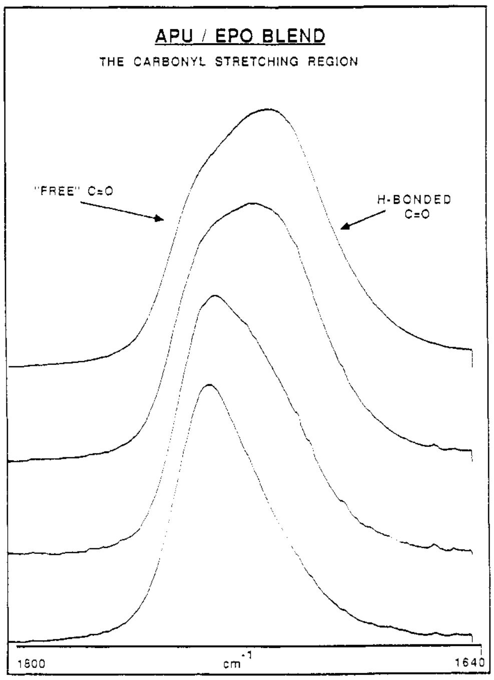


Figure 8. The carbonyl stretching region of APU-EPO blends recorded at 110 °C. From top to bottom: pure APU, 80:20, 50:50, and 20:80 wt % blends of APU and EPO, respectively.

Representative spectra in the carbonyl stretching region (1640–1800 cm^{-1}) of the blend samples recorded at 110 °C are shown in Figure 8. The pure APU is characterized by a major band centered at approximately 1710–1715 cm^{-1} which is ascribed to hydrogen-bonded urethane C=O groups and a shoulder at about 1735 cm^{-1} attributed to "free" C=O groups. As the concentration of the EPO polymer is increased in the blend, the relative proportion of "free" to hydrogen bonded carbonyls also increases. This again is in keeping with the premise that when N—H groups interact with ether oxygens they liberate additional "free" C=O groups. With use of a curve-fitting procedure described previously,[4] spectra similar to those shown in Figure 8 may be resolved into these two components and typical examples are illustrated in Figure 9. The results are summarized in Table II and presented graphically in Figure 10 (which also includes the data from the EU-THF mixtures). The percent "free" carbonyl groups is again calculated by assuming an absorptivity ratio of the hydrogen bonded to "free" carbonyl bands of 1.71. For pure APU at 110 °C the amount of "free" C=O is determined to be about 16%, a result that is remarkably similar to that measured for the pure low molecular weight urethane, EU (14%—see Table I). With increasing concentration of EPO in the blend, the fraction of "free" C=O increases and approaches about 60% for a 20:80 wt % APU-EPO blend. We wish to again emphasize that the absorptivity

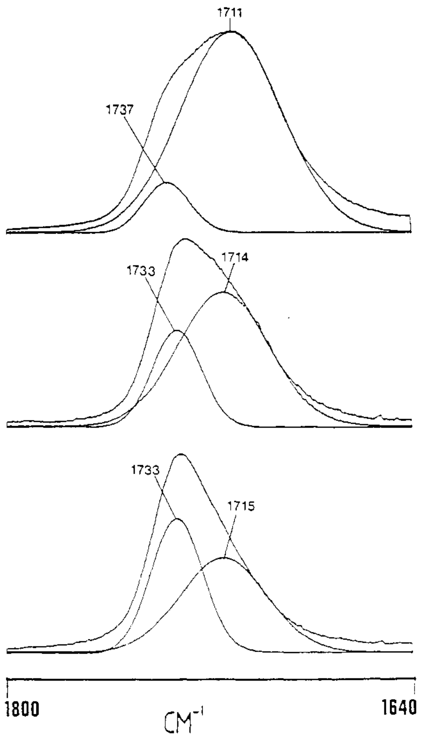


Figure 9. Examples of curve fitting the carbonyl stretching region of APU-EPO blends recorded at 110 °C: top, pure APU; middle, 50:50, and bottom, 20:80, wt % blends of APU and EPO, respectively.

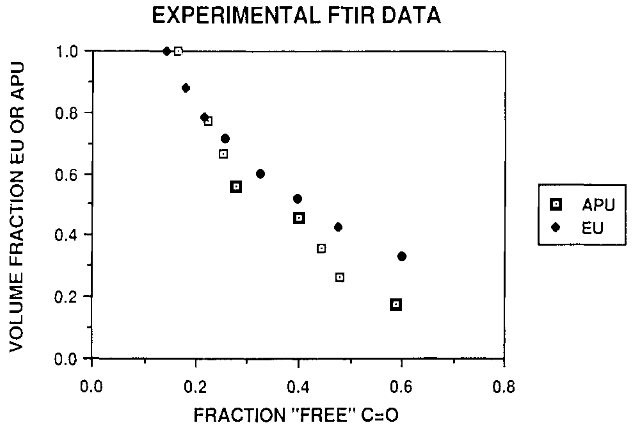


Figure 10. Graph of the percent "free" C═O groups against the volume fraction of EU or APU.

ratio is a possible source of error in the absolute numbers generated; nevertheless the overall trend is valid.

Final Words and a Preview of a Theoretical Approach. This paper is in its essentials focused upon the spectroscopic fundamentals of the interaction of urethane with ether functional groups and its relevance to the phase behavior of multicomponent polymer systems containing such groups. We believe that this is important because a misassignment of bands and a misinterpretation of the intensity changes in the N—H stretching region of the spectrum with temperature has led to an escalating series of erroneous interpretations in the literature.

This is all well and good, but it is frustrating to us and no doubt annoying to our colleagues to be constantly critical without offering an alternative scheme or theoretical framework. As a result of these studies, however, we perceive a possible approach, hinted at throughout the course of this paper in the analogy to polycondensation. Essentially, we aim to consider the statistics of forming hydrogen-bonded chains and set up an equilibrium scheme that will allow us to relate infrared measurements to the thermodynamics of polymer mixing. This approach is not novel; it has been used for more than 30 years by chemical engineers seeking to describe self-association of alcohols in hydrocarbon solvents. The polymer field, with its attachment to interaction parameters (χ's) and random mixing, has not as yet adopted this approach, however. It is our view that an equilibrium approach will prove the simplest way of describing strong, specific, directional interactions in polymers. The results described here will be used in such a scheme, the details of which are presented in the following paper.

Acknowledgment. The financial support of the National Science Foundation, Polymers Program, and the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, is greatly appreciated.

Registry No. EU, 51-79-6; THF, 109-99-9; EPO, 9003-11-6; (butanediol)(tolyl diisocyanate) (copolymer), 37338-53-7; (butanediol)(tolyl diisocyanate) (SRU), 54633-10-2.

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