cross-linked to phosphorus atoms will be studied in order to better approximate point cross-links.

Acknowledgment. This work was supported in part by the Materials Research Laboratory of the University of Massachusetts.

Registry No. (PO)(TIPTP) (copolymer), 111769-80-3; (PO)(phenylene-1,4-diisocyanate) (copolymer), 111743-18-1; (PO)(toluene-2,4-diisocyanate) (copolymer), 31370-60-2.

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Hydrogen Bonding in Polymer Blends. 3. Blends Involving Polymers Containing Methacrylic Acid and Ether Groups

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ABSTRACT: Poly(ethylene-*co*-methacrylic acid) (EMAA) copolymers are strongly self-associated in the condensed state at ambient temperatures through the formation of intermolecular carboxylic acid dimers. Polyethers, in contrast, are polymers that are inherently weakly self-associated but associate strongly with EMAA by forming intermolecular hydrogen bonds between the carboxylic acid and ether oxygen groups. In this paper we present the results of Fourier transform infrared studies of EMAA copolymer blends containing poly(vinyl methyl ether) and ethylene oxide-*co*-propylene oxide copolymers. The blends studied were found to be extensively mixed at the molecular level in the amorphous state. Quantitative measurements of the fraction of EMAA carboxylic acid groups that are hydrogen bonded to ether groups have been obtained in blends of different compositions, and the results are discussed in terms of competing equilibria.

Introduction

During the past 10 years we have taken advantage of the unique sensitivity of FTIR spectroscopy to specific types of intermolecular interactions (most notably hydrogen bonds) in order to probe the molecular structure of multicomponent polymer systems, especially polymer blends. Much of this work has been summarized in a recent review.[1] More recently, we have employed conventional transmission FTIR spectroscopy to obtain a measure of the relative strength and concentration of intermolecular interactions (hydrogen bonds) in strongly self-associated polymers such as polyamides[2-4] and polyurethanes.[5] This led to studies of miscible, or partially miscible, polymer mixtures containing such polymers[6,7] and to a simple model of specific, directional interactions based upon an equilibrium theory.[8,9]

In our search for miscible or partially miscible binary polymer blends containing a strongly self-associated polymer, we have used the following simple axiom. Significant mixing at the molecular level is most likely to occur with a weakly self-associated polymer capable of forming a favorable interaction with it. In this vein, we have published the results of studies performed on amorphous polyamide–poly(2-vinyl pyridine) (P2VP)[6] and amorphous polyurethane–poly(ethylene oxide-*co*-propylene oxide) (EPO)[7] blends, both of which exhibit a high degree of molecular mixing. Here we report on our studies of a series of polymer blends in which one of the components is a polymer containing methacrylic acid (MAA) units. Unlike polyamides and polyurethanes that form a distribution of "chains" of hydrogen-bonded amide and urethane groups in the condensed state,[7,9] MAA containing polymers are strongly self-associated at ambient temperatures through characteristic intermolecular hydrogen-bonded dimers. Our guiding principles are the same, however, and significant molecular mixing of MAA polymers can be achieved with other polymers containing ether units.

Experimental Section

Ethylene–methacrylic acid copolymers (EMAA) were synthesized in the laboratories of the E. I. Du Pont de Nemours Co. Four different copolymers containing 18, 32, 44, and 55 wt % MAA (denoted EMAA[18], EMAA[32], etc.) were used in our studies.

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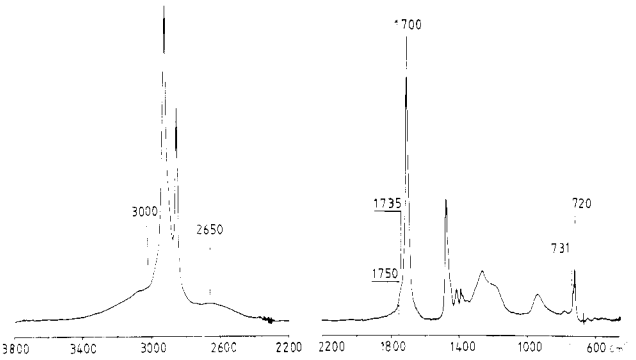

Figure 1. Infrared spectrum of EMAA[18].

On a molar basis, this corresponds to 6.5, 13.3, 20.4, and 28.5 mol % MAA, respectively. Results obtained from differential scanning calorimetry (DSC) show that the two EMAA copolymers with lowest concentration of MAA may crystallize to some extent; presumably polyethylene-type crystallinity is formed from the larger sequences of methylene units. Multiple peaks were observed in the DSC thermograms, and crystalline melting points (T_m) of 87 and 53 °C were determined at the peak maxium of the highest temperature for the EMA[18] and EMA[32] copolymers, respectively. The two copolymers containing the highest concentration of MAA, EMAA[44] and EMAA[55] did not crystallize to any measurable extent under our experimental conditions. Glass transition temperatures (T_g) of these two copolymers, as determined by thermal analysis, are in the range of 25–32 °C.

Poly(vinyl methyl ether) (PVME) and poly(ethylene oxide-*co*-propylene oxide) (EPO) containing 70 wt % ethylene oxide were purchased from Polysciences Inc. The former is an amorphous polymer with a T_g of −27 °C. The reported molecular weight (undefined) of the EPO copolymer was 12500, and thermal analysis revealed a T_g of −65 °C and a melting point (T_m) between 56 and 59 °C.

Infrared spectra were recorded on either a Digilab Model FTS-15E or FTS-60 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 by using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller. This device has a reported accuracy of ±0.1 °C. Details of the preparation of samples for FTIR analysis are given in the text. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed (<0.6 absorbance unit). 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 10–15 mg.

Results and Discussion

Infrared Spectrum of Ethylene–Methacrylic Acid (EMAA) Copolymers. Before we become immersed in the details of the infrared spectra of the polymer mixtures, it is worthwhile to briefly review the major spectral features of methacrylic acid containing polymers. The EMAA copolymers are thought to be composed of essentially random placements of ethylene and methacrylic acid units. Infrared spectra of the EMAA copolymers resemble the spectra of low molecular weight aliphatic carboxylic acids. As an example, Figure 1 shows the room-temperature infrared spectrum of a film of EMAA[18] cast from THF. The characteristic doublet at 720/731 cm^{-1} is indicative of the presence of polyethylene type crystallinity. We will be particularly interested, however, in two major frequency regions for our blend studies, the hydroxyl and carbonyl stretching regions which occur between 3800 and 2800 and 1840 and 1620 cm^{-1}; respectively. At room temperature, the large majority of the carboxylic acid groups exist as intermolecular dimers (shown schematically in Figure 2) which have a characteristic infrared band at 1700 cm^{-1}. The corresponding O–H stretching frequency for the dimer

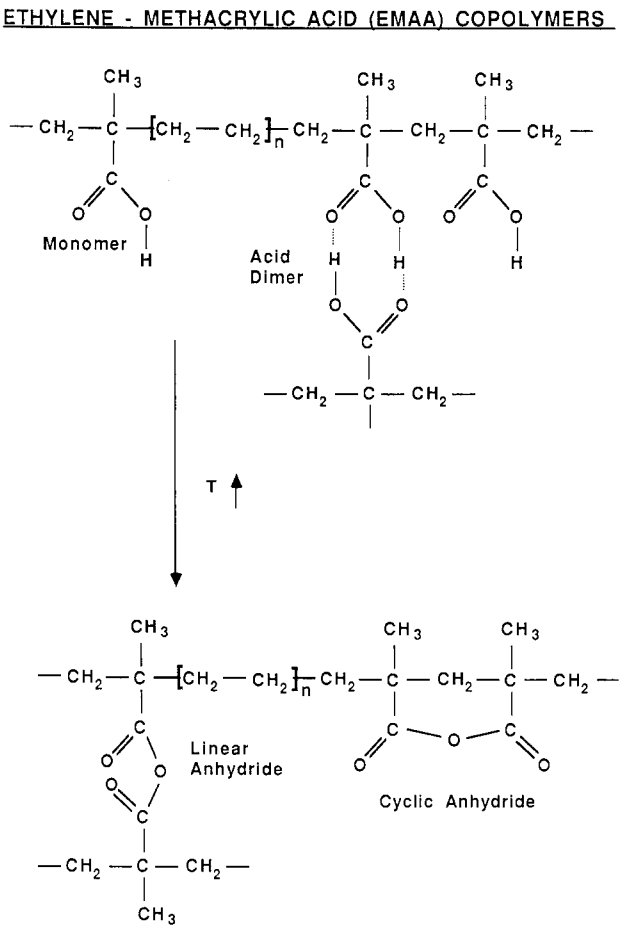

Figure 2. Schematic diagram showing the carboxylic acid monomer and dimer together with the formation of anhydrides at elevated temperatures.

is seen as a broad band at about 3000 cm^{-1} buried beneath the strong, sharp C–H stretching modes. This is indicative of a hydrogen bond of intermediate strength (i.e. greater in strength than amide or urethane self-association[2-5] but weaker than the strong carboxylic acid–pyridine interaction[10]). Satellite bands superimposed upon the broad fundemental profile are also typically observed in the spectra of carboxylic acids.[11,12] These satellite bands, seen in the spectrum of the EMAA copolymers as a broad composite band centered at 2650 cm^{-1} (Figure 1), are thought to arise from either overtones and combinations that are intensity enhanced by Fermi resonance or anharmonic coupling of the ν_s (O–H stretching) and σ_s(H···O stretching) modes. This is little evidence of any significant absorption from bands attributed to the "free" O—H or C=O of the "monomer" that have characteristic frequencies at approximately 3540 and 1750 cm^{-1}, respectively.[13,14] On unfortunate complication is the presence of a minor amount of ester groups in the EMAA copolymers that were incorporated during polymerization and are detectable by the small shoulder at 1735 cm^{-1}. It will be a source of annoyance but does not play any meaningful role in the studies presented here.

Thermal cycling experiments using three different EMAA copolymers were performed to determine the temperature at which the copolymers undergo chemical modification resulting in the formation of anhydrides. Naturally, if we are to heat polymer mixtures containing EMAA copolymers in order to remove solvents and moisture and/or to overcome phase separation via a $\Delta\chi$ effect,[1] we must be aware of any chemical reactions that can occur at elevated temperatures. It is well-known that

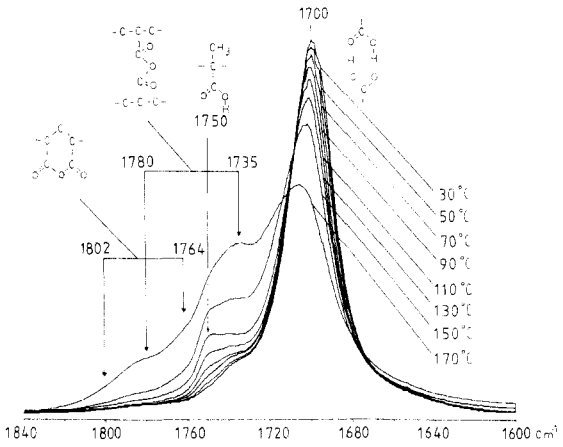

Figure 3. Infrared spectra in the carbonyl stretching region of EMAA[18] recorded as a function of temperature.

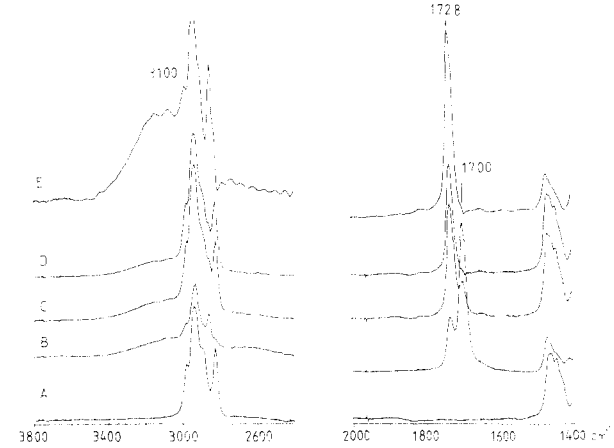

Figure 4. Scale expanded room temperature infrared spectra in the 1400–2000 and 2400–3800 cm^{-1} regions: (A) pure PVME; (B) 80:20 EMAA[44]–PVME blend; (C) 20:80 EMAA[44]–PVME blend; (D) difference spectrum, pure EMAA[44] subtracted from the 20:80 EMAA[44]–PVME blend spectrum; (E) difference spectrum, pure PVME subtracted from spectrum D.

upon raising the temperature to above about 140 °C, acid containing polymers can form both intermolecular and intramolecular anhydrides.[15-17] This is also depicted schematically in Figure 2. Figure 3 shows the effect of temperature upon the carbonyl stretching region from 1840 to 1600 cm^{-1} of the infrared spectrum of EMA[18]. Between 140 and 160 °C anhydrides are formed. For the EMAA[18] copolymer linear anhydrides (characteristic bands at 1780 and 1735 cm^{-1}) dominate over the cyclic anhydrides (bands at 1802 and 1764 cm^{-1}). The trend is reversed, however, for the EMAA[55] copolymer (not shown). The cyclic anhydride is in higher concentration; a consequence of the greater number of sequences of MAA units of two or more which are required for intramolecular cyclization. Finally, the band at 1750 cm^{-1}, attributed to the "free" carboxylic acid or monomer, is observed to increase in intensity at the expense of the dimer band at 1700 cm^{-1}. This, of course, is a manifestation of the effect of temperature upon the equilibrium between the carboxylic acid dimers and monomers. More on this later. For our purposes, as long as we do not exceed a temperature of 140 °C, we can cycle up and down in temperature without causing major changes in the chemistry and structure of the copolymers.

EMAA Blends with Poly(vinyl methyl ether). Poly(vinyl methyl ether) (PVME), a rubbery amorphous polymer with a T_g of −27 °C, occupies a special place in the world of miscible polymer blends. PVME is miscible with polystyrene, and blends of these two polymers exhibit accessible lower critical solution temperatures.[18] This and the ready availability of well-characterized, monodispersed, protonated, and deuteriated polystyrenes have made these blends favorites amongst both theoretical and experimental scientists, including infrared spectroscopists.[19,20] PVME admirably fits our description of a polymer that is weakly self-associated but contains a chemical group, in this case the ether oxygen, that can potentially form a hydrogen bond with another chemical group of a dissimilar polymer. It is not surprising, therefore, to find that PVME is also miscible with PVPh[21] and the poly(hydroxy ether of bisphenol A),[22] both these latter polymers being strongly self-associated. Perhaps what is more surprising is that the amorphous polyurethane used in previous polymer blend studies appears immiscible with PVME but is miscible with another ether containing polymer, EPO.[7] The question to be addressed here is, "will PVME and the EMAA copolymers mix at the molecular level?"

All the EMAA copolymers form clear dilute solutions with PVME in THF at room temperature and coherent film samples can be prepared over the whole composition

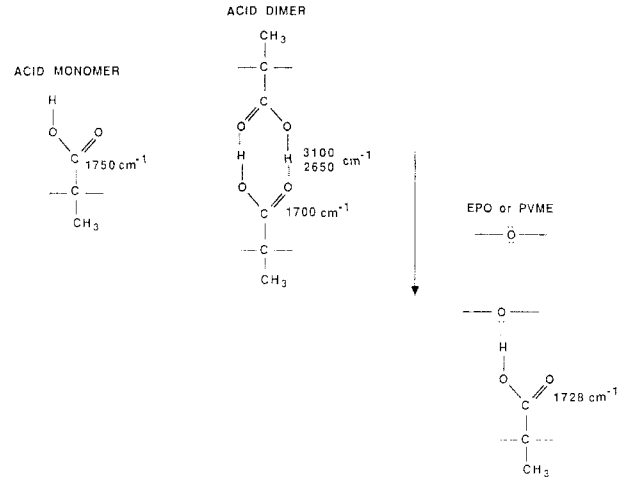

Figure 5. Schematic diagram illustrating the carboxylic acid–ether oxygen interaction.

range. We will emphasize, however, blend samples prepared from the completely amorphous EMAA[55] and EMAA[44] copolymers. This avoids complications arising from possible crystallization occurring in the blends, especially in the case of EMAA[18]. Numerous infrared spectra have been obtained as a function of copolymer composition, blend composition, and temperature. We will not show or discuss all of these. Rather, we will highlight the significant infrared spectral features that are common to all these blends.

Figure 4 shows the infrared spectra of pure PVME (denoted A) and blends of EMAA[44] and PVME containing 80:20 (B) and 20:80 (C) wt %, respectively. The only feature of the spectrum of PVME that is of interest to our studies is the lack of any significant absorptions in the carbonyl stretching region (1600–1800 cm^{-1}) and the region between 3000 and 3800 cm^{-1}. Infrared temperature studies on films of the pure PVME used in this study indicated that the onset of significant oxidative degradation occurs at 160 °C.

A salient feature of the spectrum of the 80:20 blend is the presence of infrared bands characteristic of the carboxylic acid dimer; the O–H stretching vibration at about 3000 cm^{-1}, the broad "satellite" band at 2650 cm^{-1}, and the C=O stretching vibration at 1700 cm^{-1}. The band at 1728 cm^{-1} is assigned to "free" C=O groups that occur when an intermolecular interaction (hydrogen bond) is formed

Table I
Curve-Fitting Results of the EMAA-PVME Blends

wt %	mol fractn EMAA	"free" C=O band freq,[a] cm^{-1}	width[b]	area	carboxylic acid dimer C=O band freq,[a] cm^{-1}	width[b]	area	fractn "free" C=O[c]
EMAA[32]:PVME								
80:20	0.46	1730	17	263	1698	18	892	0.32
60:40	0.24	1729	18	430	1698	18	631	0.52
40:60	0.13	1729	19	638	1698	19	502	0.67
30:70	0.08	1729	20	1299	1698	19	874	0.70
20:80	0.05	1728	18	886	1697	20	386	0.79
EMAA[44]:PVME								
80:20	0.54	1731	18	292	1697	20	1067	0.30
60:40	0.31	1729	19	425	1698	19	575	0.54
40:60	0.17	1729	19	1085	1697	21	682	0.72
20:80	0.07	1728	19	772	1698	22	231	0.84
10:90	0.03	1729	21	2603	1698	23	566	0.88
EMAA[55]:PVME								
80:20	0.6	1730	18	308	1698	21	1026	0.32
60:40	0.36	1729	19	978	1698	20	1229	0.56
40:60	0.2	1729	20	1014	1698	21	609	0.73
20:80	0.08	1728	20	1268	1698	23	344	0.86
10:90	0.04	1729	21	1365	1698	21	237	0.90

[a] Wavenumber. [b] Width at half-height, cm^{-1}. [c] Absorptivity ratio = 1.6.

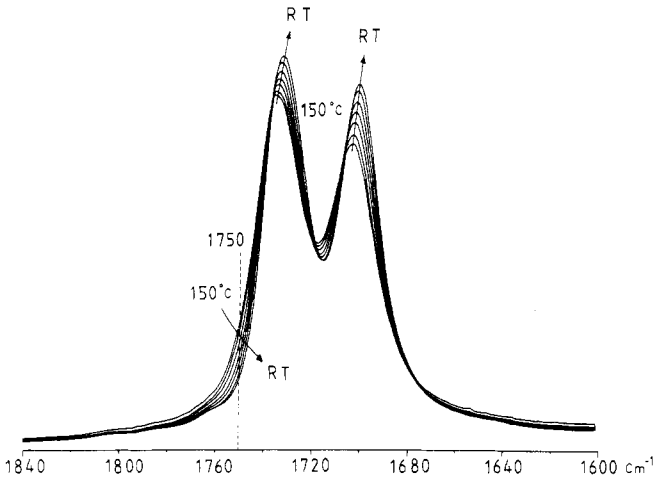

Figure 6. Infrared spectra of a 50:50 EMAA[44]–PVME blend sample recorded as a function of temperature in the carbonyl stretching region, displayed on an absolute absorbance scale.

between the carboxylic acid group of MAA and the ether oxygen atom of VME as depicted in Figure 5. There is no obvious band or set of bands that might be attributed to the O–H stretching vibration associated with this intermolecular interaction, which is perhaps not too surprising since the blend is rich in EMAA[44]. At the other extreme, the 20:80 EMAA–PVME blend is rich in PVME. This is immediately reflected in the carbonyl stretching region of the spectrum of this blend (Figure 4C), where the "free" C=O stretching band is now dominant over the band attributed to the acid dimer. As the concentration of the "free" carbonyl groups has grown at the expense of the acid dimers, a corresponding change should be apparent in the O–H stretching region of the spectrum. In other words, the infrared band associated with the O–H stretching vibration perturbed by the presence of a hydrogen bond to an ether oxygen should now be obvious. It is not. The most likely candidate is buried beneath the dominant CH stretching modes around 2800–3000 cm^{-1}. Using difference spectroscopy, however, we can accentuate this band. First, we subtract from the spectrum of the blend the contribution due to carboxylic acid dimers including the hydrogen bonded O–H stretching bands. This is achieved by using the room-temperature spectrum of pure EMAA[44] where the MAA units have been shown to be almost exclusively in the form of acid dimers. This is illustrated in Figure 4D—elimination of the 1700 cm^{-1} band is used as the criterion for correct subtraction. Second, a large fraction of the infrared absorption in the region above 2600 cm^{-1} is due to the strong CH stretching modes of the PVME. Much of this can be removed by judicious subtraction of the spectrum of PVME (A). As Figure 4E shows, this now reveals the broad band centered at approximately 3100 cm^{-1} which is assigned to the O–H stretching frequency of carboxylic acid groups that are hydrogen bonded to ether oxygens of PVME. This hydrogen bond is of intermediate strength. Furthermore, judging by the frequency shift of the hydrogen bonded compared to the "free" (non-hydrogen-bonded) O–H stretching mode at 3530 cm^{-1}, the relative strength of the hydrogen bond in the carboxylic acid dimer and the carboxylic acid–ether oxygen interaction is not dissimilar (the acid dimer being somewhat stronger). The intermediate strength of this hydrogen bond is reflected in the temperature dependence of the bands in the carbonyl stretching region of the spectrum. For example, Figure 6 shows spectra plotted on an absolute absorbance scale that were recorded as a sample of a 50:50 EMAA[44]–PVME blend is cooled from 150 °C to room temperature. Both of the carbonyl bands attributed to the carboxylic acid dimer (AA at ~1700 cm^{-1}) and the carboxylic acid–ether oxygen interaction ("free" C=O, AB at ~1728 cm^{-1}) shift slightly, but significantly, to lower frequency and increase in absolute intensity. Concurrently, a contribution to the band envelope at ~1750 cm^{-1}, attributed to the carbonyl stretching vibration of monomeric or free acid groups (A), diminishes. In simple terms, these changes in intensity with temperature primarily reflect the equilibrium distribution of the three species which we will discuss in greater depth later.

Figure 7 shows the carbonyl stretching region of *scale-expanded*, room-temperature, infrared spectra of EMAA[44]–PVME blends of varying composition. The superb resolution and striking difference between the relative intensities of the two bands attributed to the carboxylic acid dimer and the carboxylic acid–ether oxygen interaction begs for quantification. Table I summarizes the results of curve fitting[3,5] the carbonyl stretching region of the spectra obtained from three sets of blends: EMAA[32], EMAA[44], and EMAA[55] with PVME. Since at room temperature there is no detectable contribution from free or monomeric carboxylic acid groups (1750 cm^{-1}), the

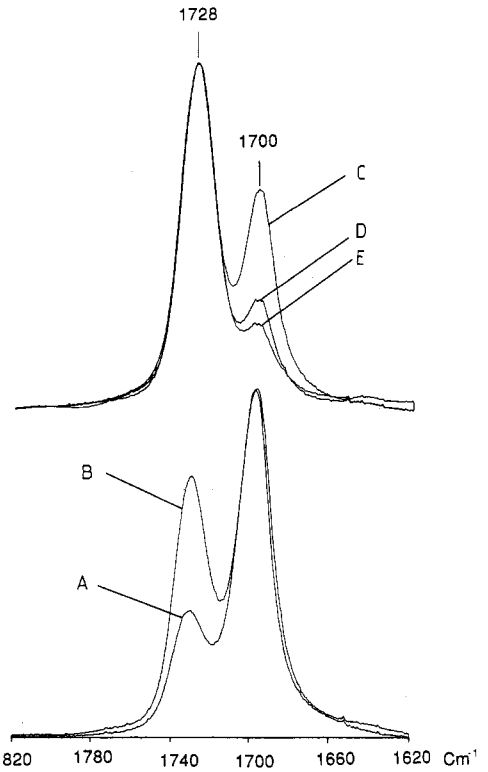

Figure 7. Scale expanded infrared spectra recorded at room temperature in the carbonyl stretching region of EMAA[44]–PVME blend samples: (A) 80:20, (B) 60:40:, (C) 40:60; (D) 20:80, and (E) 10:90 wt % EMAA[44]:PVME.

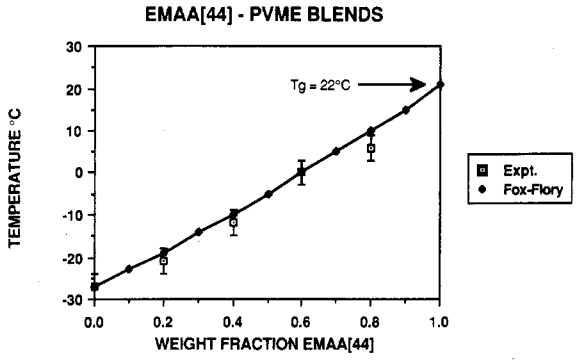

Figure 8. Graph of T_g versus EMAA[44]–PVME blend composition. The solid line was calculated from the Fox–Flory relationship.

fraction of carboxylic acid groups that are involved in intermolecular hydrogen bonding with the ether oxygen groups of PVME is given by

$$f_F = \frac{A_F}{\left[A_F + \frac{A_D}{ar}\right]}$$

where A_F and A_D are the areas of the 1729 and 1698 cm^{-1} bands, respectively (see Table I) and ar is the absorptivity ratio of the two bands, a_D/a_F. We have assumed an absorptivity ratio of 1.6—a value experimentally determined for the analogous EMAA–EPO blends discussed later in this paper. This is a potential source of error that might effect the absolute numbers, but not the overall trends.

Finally, corroborating evidence from thermal analysis strongly suggests that the EMAA–PVME blends are miscible systems. Broad single T_g's were observed at temperatures intermediate between those of the pure components of the blends. As an example, Figure 8 shows a Fox–Flory plot of T_g versus blend composition for the EMAA[44]–PVME system together with the experimental data obtained from thermal analysis. In summary, the EMAA–PVME blends can be categorized as miscible elastomeric materials that are extensively hydrogen bonded.

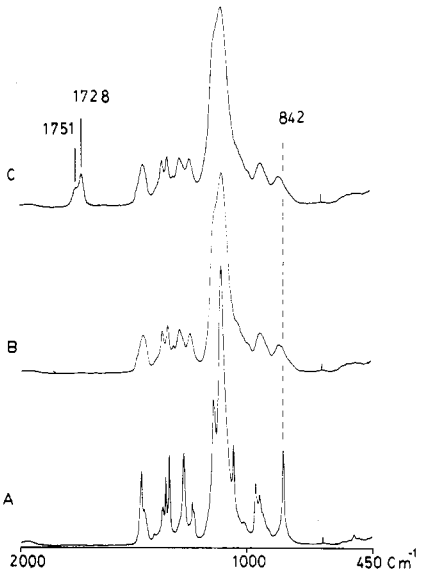

Figure 9. Infrared spectra of pure EPO in the range from 2000 to 450 cm^{-1} recorded at (A) room temperature, (B) 60 °C, and (C) 130 °C.

EMAA Blends with Poly(ethylene oxide-*co*-propylene oxide). We have used the 70:30 poly(ethylene oxide-*co*-propylene oxide) copolymer (EPO) in previous polymer blend studies with an amorphous polyurethane.[7] The choice of EPO rather than the more obvious poly(ethylene oxide) was predicated upon its enhanced solubility in the relatively low boiling solvent THF (a necessary requirement for MAA copolymers because of their limited solubility and temperature range for solvent removal), its decreased propensity to crystallize, and its lower crystallization temperature. EPO has its disadvantages, however, not the least being its predilection toward oxidative degradation at temperatures above 130 °C.

Figure 9 shows infrared spectra between 450 and 2000 cm^{-1} of EPO film samples recorded at three different temperatures. At 30 °C, an annealed EPO sample is semicrystalline, and this is reflected in the infrared spectrum (denoted A) by the presence of the very sharp bands characteristic of the preferred ordered conformation. For our purposes, the sharp isolated band at 842 cm^{-1} (predominantly a CH_2 rocking mode) will be useful in monitoring the presence of EPO crystallinity in the blends. At 60 °C, above the melting point of EPO, gone are the very sharp bands, and the infrared spectrum (B) is characterized by relatively broad bands typical of the amorphous state. Finally, at 130 °C after approximately 10–15 min, oxidation of EPO is seen is evidenced by the presence of carbonyl bands at 1728 and 1750 cm^{-1}. Accordingly, any heat treatment of the EMAA–EPO blend samples was kept to below 120 °C.

Up to this point we have emphasized studies of essentially amorphous blends. The EPO copolymer, on the other hand, crystallizes to a significant extent at ambient temperatures, and we now enter the realm of the so-called "crystalline–compatible" polymer blends.[1] One may envisage a sample of such a blend in terms of EPO crystallites buried in a miscible matrix of the two polymers. In very simple terms, given favorable chain mobility and kinetics, a fraction of a crystallizable polymer may crystallize, effectively reducing the concentration of this polymer that

Table II
Determination of Absorptivity Ratio

		"free" C=O band			carboxylic acid dimer C=O band			
sample	temp, °C	freq,[a] cm^{-1}	width[b]	area	freq,[a] cm^{-1}	width[b]	area	abs ratio
1	60	1729	21	1035	1699	23	328	1.7
	30	1729	21	863	1698	21	620	
2	60	1729	20	1172	1699	23	387	1.7
	30	1729	21	942	1698	21	771	
3	60	1729	21	1350	1699	23	461	1.5
	30	1729	21	1075	1698	21	883	
4	60	1729	21	1332	1699	24	453	1.7
	30	1729	22	1081	1698	21	888	
5	60	1729	22	1358	1698	23	469	1.5
	30	1729	22	1098	1698	22	852	
6	60	1729	20	1030	1699	23	341	1.7
	30	1729	21	773	1698	21	779	
								1.6 ± 0.1 (av)

[a] Wavenumber. [b] Width at half-height, cm^{-1}.

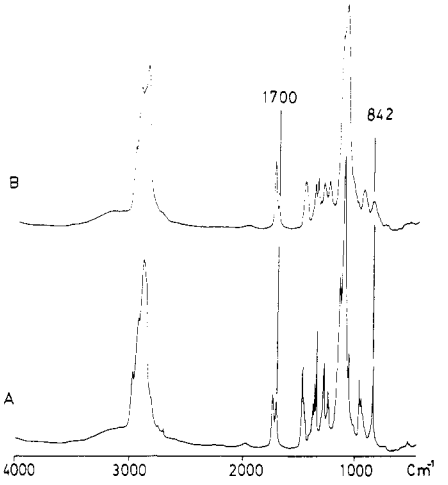

Figure 10. Infrared spectra of a 20:80 wt % EMAA[44]–EPO blend sample recorded at (A) room temperature and (B) 60 °C.

is available to mix with the noncrystallizable component. This is an important concept and relevant to our infrared studies of the EMAA–EPO blends since the fraction of intermolecular hydrogen-bonding interactions between the two polymers is dependent upon the concentration of the available interaction sites.

Figure 10 illustrates this point. Spectrum A is that of a film of a 20:80 wt % EMAA[44]–EPO blend sample recorded at room temperature. Two important spectral features immediately stand out. First, the very sharp bands characteristic of conformational order are obvious and substantiate that a fraction of the EPO copolymer has indeed crystallized. Second, the all but equal contribution of the carbonyl stretching bands associated with the carboxylic acid dimer (1700 cm^{-1}) and the carboxylic acid–ether oxygen interaction (depicted in Figure 5; "free" C=O at ~1728 cm^{-1}) belies a single phase system given the excess concentration of EPO in the blend. A fraction (say x) of the EPO copolymer having crystallized implies that only $(80 - x)$ wt % remains to mix with the 20% EMAA[44]. Accordingly, the ratio of EMAA[44] to available EPO is $20:(80 - x)$ and is richer in EMAA[44] than the primary composition. This leads to a reduction of the fraction of carboxylic acid–ether oxygen interactions at equilibrium.

Heating the same sample above the T_m of EPO yields the top spectrum denoted B. The very sharp bands characteristic of conformational order are now absent. Concomitant with the disappearance of order, the contribution from the carbonyl band associated with the carboxylic acid–ether oxygen interaction (1728 cm^{-1}) increases significantly at the expense of that of the carboxylic acid dimer (1700 cm^{-1}). The relative ratio of the two carbonyl bands is now more in line with that observed in the miscible EMAA[44]–PVME blend of the same composition (Figure 7). Now that the carbonyl band attributed to the carboxylic acid–ether oxygen interaction is dominant, the corresponding infrared band assigned to the O–H stretching vibration perturbed by hydrogen bonding to ether oxygen is accentuated and is readily observed at 3150 cm^{-1}.

At this point a digression is warranted. The spectral results displayed in Figure 10 immediately suggest a method, similar in principle to that previously described for poly(vinyl phenol)–poly(ethylene-*co*-vinyl acetate) blends,[23] to determine the absorptivity ratio of the respective carbonyl stretching vibrations associated with the carboxylic acid dimer and the "free" carbonyl groups (i.e. the carboxylic acid–ether oxygen interaction). By comparing the spectra of a sample of a 20:80 EMAA[44]–EPO blend recorded at 60 °C (above the T_m of EPO) to that of the same sample recorded at 30 °C (after a portion of the EPO has crystallized) leads to a direct measure of the absorptivity ratio. This is possible because a fraction of "free" carbonyls transform to carboxylic acid dimers upon reducing the temperature after partial crystallization of the EPO occurs. In mathematical terms

$$a_D/a_F = (A^*_D - A_D)/(A_F - A^*_F)$$

where a_D and a_F are the absorptivities of the carbonyl stretching vibrations of the carboxylic acid dimer and "free" carbonyl groups, respectively. A^*_D and A_D are the respective areas of the carboxylic acid dimer band recorded at 30 and 60 °C. The areas of the "free" bands are similarly defined as A^*_F and A_F. Six such samples were examined, and the results are given in Table II. The average value of the absorptivity ratio was found to be 1.6 ± 0.1. The success of this method necessitates: 1, the amount of sample in the infrared beam must remain constant; 2, there must be a large transformation of "free" to hydrogen bonded carbonyl groups in order to minimize errors; 3, the change in absorption coefficient with *temperature* must be insignificant (a fair assumption in this case). The estimation of polymer infrared absorptivities or ratios is not a trivial task, and this simple method, where applicable, permits facile quantification of the fraction of the specific interactions occurring in polymer blends of the type described in this paper.

To return to the main thrust, Figure 11 shows scale expanded room-temperature infrared spectra obtained from a series of EMAA[55]–EPO blends of varying com-

Table III
Curve-Fitting Results of the EMAA[55]–EPO Blends

wt % EMAA[55]:EPO	mol fractn EMAA	"free" C=O band			carboxylic acid dimer C=O band			fractn "free" C=O[c]
		freq,[a] cm^{-1}	width[b]	area	freq,[a] cm^{-1}	width[b]	area	
room temp								
80:20	0.55	1731	20	560	1698	21	2300	0.28
70:30	0.41	1729	20	757	1698	20	1474	0.45
60:40	0.31	1728	20	688	1698	21	892	0.55
50:50	0.23	1728	20	971	1698	22	1194	0.57
40:60	0.17	1728	21	1024	1698	22	971	0.63
30:70	0.12	1728	21	1286	1698	21	1229	0.63
20:80	0.07	1728	21	1396	1698	24	1274	0.64
60 °C								
80:20	0.55	1731	22	632	1699	21	1939	0.34
70:30	0.41	1731	22	1286	1699	22	2749	0.43
60:40	0.31	1730	22	708	1699	22	826	0.58
50:50	0.23	1729	22	995	1699	22	991	0.62
40:60	0.17	1729	21	1076	1699	22	792	0.68
30:70	0.12	1729	21	1401	1699	23	593	0.79
20:80	0.07	1729	22	1800	1698	24	679	0.81

[a] Wavenumber. [b] Width at half-height, cm^{-1}. [c] Absorptivity ratio = 1.6.

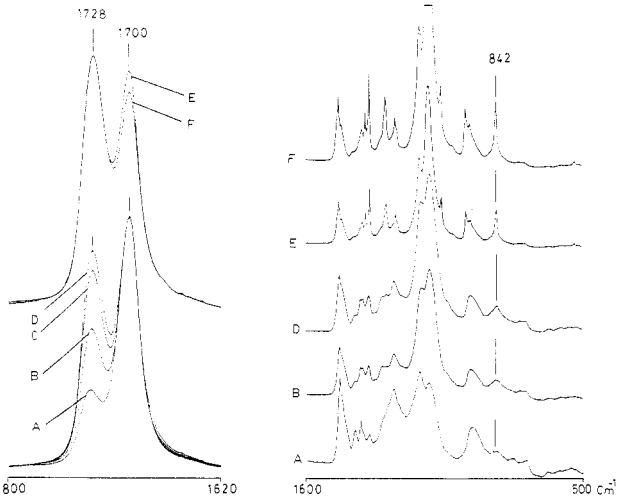

Figure 11. Scale expanded infrared spectra recorded at room temperature in the ranges 500–1600 and 1620–1800 cm^{-1} of EMAA[55]–EPO blends of varying composition: (A) 80:20, (B) 70:30, (C) 60:40, (D) 50:50, (E) 40:60, and (F) 20:80 wt % EMAA[55]–EPO.

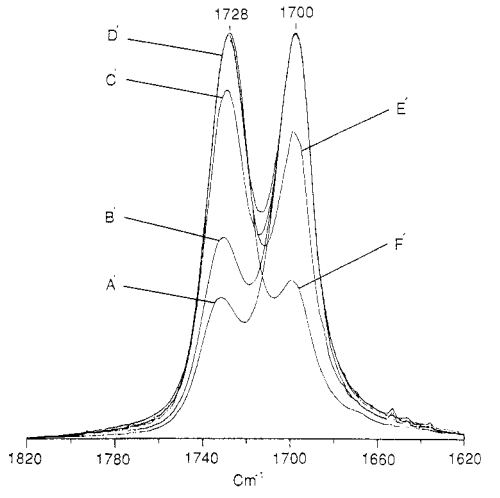

Figure 12. As in Figure 11 but recorded at 60 °C.

position. The now familiar increase of the "free" carbonyl stretching band at 1728 cm^{-1} relative to that attributed to the carboxylic dimer (1700 cm^{-1}) is again seen with increasing EPO concentration in the blend. Comparison with the analogous EMAA–PVME blends (Figure 7 and Table I), however, leads one to suspect that at EPO concentrations of greater than about 50% the blends are multiphased; the fraction of carboxylic acid–ether oxygen interactions just does not appear to be large enough. Indeed, if one now examines the 500–1600 cm^{-1} region of the blends (RHS of Figure 11), it is immediately obvious from the appearance of the very sharp bands characteristic of conformational order (e.g. the 842 cm^{-1} band) that crystallization of a fraction of the EPO has occurred in the blend samples containing >50% EPO. Repeating the experiment at 60 °C, however, eliminates crystalline order, and the fraction of "free" carbonyl groups now increases systematically throughout the range of blend composition (see Figure 12). Quantitative results of curve fitting these spectra are summarized in Table III.

Theoretical Considerations—Competing Equilibria. The blends of the EMAA copolymers with PVME and EPO discussed above may be reasonably described in terms of two competing equilibria, not unlike the amorphous polyurethane–EPO system recently described, with one notable exception. EMAA self-associates in the form of intermolecular dimers instead of "chainlike" structures.[7] Accordingly, in the case of the EMMA–polyether blends, it will be more convenient to express equilibrium constants in terms of mole fractions rather than volume fractions. (The choice of definitions rests upon the correct description of the combinatorial entropy of mixing the true species present. In this initial exploration of the stoichiometric relationships between association units we do not believe the difference in the molar volume between a "monomer" and a "dimer" will greatly affect the general observations we wish to make.) Equilibrium constants, K_A and K_B, are then used to express the self-association of EMAA and the association of EMAA with PVME (or EPO), respectively, as depicted

$$A + A \underset{}{\overset{K_A}{\rightleftharpoons}} AA \qquad A + B \overset{K_B}{\rightleftharpoons} AB \tag{1}$$

$$K_A = \xi_{AA}/\xi_A^2 \qquad K_B = \xi_{AB}/\xi_A\xi_B \tag{2}$$

where ξ_A, ξ_B, ξ_{AA}, and ξ_{AB} are the mole fractions of A, B, AA, and AB units in the mixture at equilibrium. Now

$$\xi_A + \xi_B + \xi_{AA} + \xi_{AB} = 1 \tag{3}$$

Substitution leads to

$$\xi_B = \frac{1 - \xi_A - K_A\xi_A^2}{1 + K_B\xi_A} \tag{4}$$

Table IV
Curve-Fitting Results of the Pure EMAA[44] Copolymer

	"free" C=O band			carboxylic acid dimer C=O band			
temp, °C	freq,[a] cm^{-1}	width[b]	area	freq,[a] cm^{-1}	width[b]	area	fractn "free" C=O[c]
140	1744	15	75	1700	24	1459	0.076
130	1744	15	63	1700	23	1499	0.063
120	1744	15	47	1700	23	1522	0.047
110	1744	15	38	1698	23	1553	0.038
100	1744	15	28	1699	22	1577	0.028
90	1745	15	26	1699	22	1620	0.025

[a] Wavenumber. [b] Width at half-height, cm^{-1}. [c] Absorptivity ratio = 1.6.

Now X_A, the initial mole fraction of A units in the blend, may be expressed as

$$X_A = \frac{\xi_A + 2\xi_{AA} + \xi_{AB}}{\xi_A + \xi_B + 2\xi_{AA} + 2\xi_{AB}} \quad (5)$$

Substituting and rearranging yield

$$X_A = \frac{(1 + K_B)\xi_A + 2K_A\xi_A^2 + K_AK_B\xi_A^3}{1 + 2K_B\xi_A + (K_A - K_B)\xi_A^2} \quad (6)$$

This equation may be resolved numerically by assuming initial values of K_A and K_B. Hence, values of X_A are calculated over the range from zero to unity by using appropriate values of ξ_A. The parameters ξ_{AA}, ξ_B, and ξ_{AB} are then calculated from eq 2 and 4. The theoretical fraction of "free" C=O groups, f_F, is then defined as $\xi_{AB}/(\xi_{AB} + 2\xi_{AA})$, and this may be compared directly to the experimental data as it is equivalent to what we measure in the infrared spectra.

Implicit in our "rule of thumb" for the mixing of polymers involving moderately strong hydrogen bonding is the balance between the respective equilibrium constants, K_A and K_B. Numerous sets of similar curves of X_A versus f_F can be generated for different values of these equilibrium constants. What we require is an independent value of at least one of these constants. Fortunately, K_A can be determined from infrared temperature studies of the pure EMAA copolymers performed over a restricted temperature range.[13,14]

EMAA[44] was chosen for this study. Spectra were recorded at temperatures between 140 °C and room temperature. The spectral contribution at 1745 cm^{-1} attributed to the "free" or monomeric carboxylic acid group is relatively small, and the presence of the ester impurity at 1735 cm^{-1}, albeit weak in itself, nonetheless interferes with quantitative analysis. As luck would have it, it proved a remarkably straightforward process to synthesize a single band duplicating the ester band and to subtract from the spectra the contribution due to the ester impurity. We should perhaps emphasize that the identical amount of the synthesized spectrum was subtracted from each of the experimental spectra. The result is displayed in Figure 13. Note that the spectra are scale expanded to the 1700 cm^{-1} band for illustrative purposes. Spectra recorded between 140 and 90 °C were subsequently fitted to two curves by using a least-squares program, and the results are given in Table IV. At temperatures below 90 °C the contribution from the 1745 cm^{-1} band was too small to measure with any accuracy. We again used an absorptivity ratio of 1.6. This appears to be the best compromise given that there is a distinct similarity between the "free" nonhydrogen-bonded carbonyl groups in the carboxylic acid monomer and the carboxylic acid–ether oxygen specific interaction. We recognize, nonetheless, that this is a potential source of error, but we would argue, not a large or critical one.

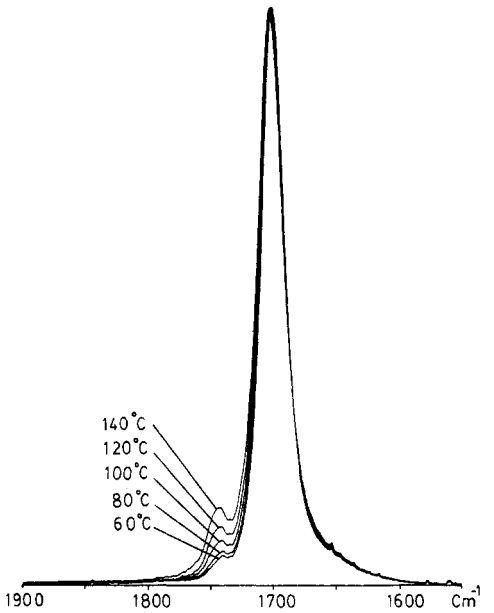

Figure 13. Scale expanded infrared spectra in the carbonyl stretching region of pure EMAA[44] recorded as a function of decreasing temperature from 140 °C.

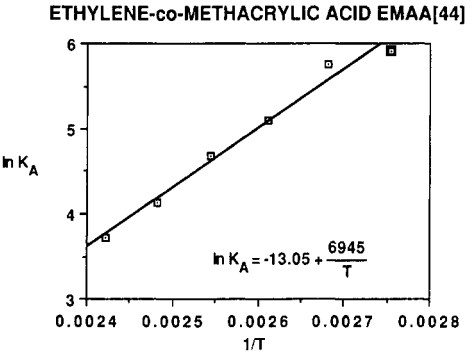

Figure 14. Plot of ln K_A versus T^{-1} for EMAA[44].

Having obtained a quantitative estimation of the fraction of "free" monomeric carboxylic acid groups as a function of temperature, a van't Hoff plot of ln K_A versus $1/T$ can be prepared by using the relationship

$$K_A = (1 - f_F^2)/4f_F^2$$

Such a plot is shown in Figure 14. We have severely criticized the use of van't Hoff plots in previous infrared studies of hydrogen bonding in polyamides[2-4] and polyurethanes[5] primarily on the grounds that ΔH varies significantly with temperature and that there is a broad distribution of interaction strengths which cannot be simply represented by a single average value of ΔH. In the case of the EMAA, however, these concerns appear unwarranted. There are no significant changes in the frequency or broadness of the two carbonyl bands with tem-

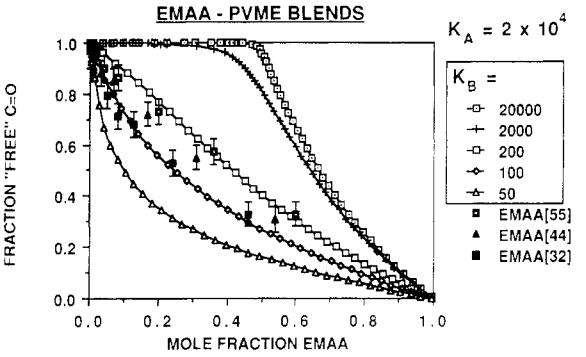

Figure 15. Plot of the fraction of "free" carbonyl groups versus the mole fraction of EMAA copolymers in blends with PVME at room temperature. The solid lines are calculated using the values of K_B indicated—see text.

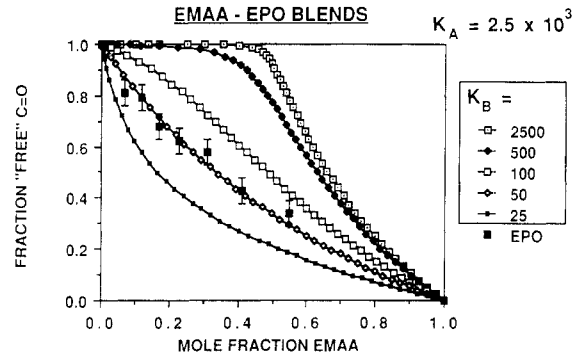

Figure 16. Plot of the fraction of "free" carbonyl groups versus the mole fraction of EMAA copolymers in blends with EPO at 60 °C. The solid lines are calculated by using the values of K_B indicated—see text.

perature (see Figure 14 and Table IV) which suggests that changes in ΔH with temperature are minimal. Furthermore, the specific conformational nature of the carboxylic acid dimer precludes a broad distribution of interaction strengths. Thus an estimation of the enthalpy and entropy of hydrogen-bonded dimer formation was determined from the slope and intercept of the van't Hoff plot yielding values of −6.95 kcal mol^{-1} and −13.1 eu mol^{-1}, respectively. Extrapolating to room temperature yields a value of the equilibrium constant of approximately $K_A = 2 \times 10^4$. This is equivalent to a fraction of "free" monomeric carboxylic acid groups of 0.35% at room temperature. At 60 C, K_A is closer to a value of 2.5×10^3.

Armed with an estimation of K_A we can now proceed to compare experimental blend data (Tables I and III) with theoretical curves of the fraction of "free" C=O groups versus mole fraction of EMAA using appropriate values of K_B in eq 6. The results are displayed graphically in Figures 15 and 16. For the room-temperature PVME blends theoretical curves were determined for K_B values of 2×10^4, 2×10^3, 200, 100, and 50. The experimental data for the EMAA[55]–PVME blends fit splendidly the theoretical curve obtained for $K_B = 200$. Thus the magnitude of K_B in this case is some 100 times less than that of K_A. (It should perhaps be recalled that the equilibrium constant is related to the enthalpy and entropy of hydrogen bond formation via the well-known relationship, $\ln K = -\Delta H/RT + \Delta S/R$. Accordingly, in these terms, $\ln K_A$ and $\ln K_B$ (9.9 and 5.3, respectively) differ only a by a factor of about 2.) The analogous EMAA[44] and EMAA[32] blends systematically match curves corresponding to somewhat smaller K_B values of approximately 150 and 100, respectively. As mentioned previously, all three of these blends appear miscible and the interesting question arises, "what is the lower limit or critical value of K_B necessary to ensure molecular mixing?" We intend to address this question by formulating free energy of mixing equations akin to those presented for the polyurethane–polyether blends.[7,9] Finally, for the EPO blends at 60 °C, where we have assumed a K_A of 2500, the experimental data match the theoretical curve generated for a K_B value of 50 (Figure 16), i.e. a ratio of 50:1.

In summary, molecular mixing of a strongly self-associated polymer A (defined in terms of an equilibrium constant, K_A) with a weakly self-associated polymer B is possible as long as there is a reasonable association of B with A (defined in terms of an equilibrium constant, K_B); i.e., K_B can be orders of magnitude less than K_A. Viewed simply, the polymer A "loses" in mixing with polymer B, but this is more than offset by the "gains" made by the polymer B in associating with polymer A—it is the balance of the free energy contributions that are paramount.

Acknowledgment. The financial support of the National Science Foundation, Polymers Program, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly appreciated. We also wish to acknowledge the many discussions with Dr. Barbara Varnell of the E. I. du Pont de Nemours Co. and the assistance of Larry Miller and Yung Park of Penn State University in performing some of the equilibrium calculations.

Registry No. EMAA, 25053-53-6; PVME, 9003-09-2; EPO, 9003-11-6.

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