Poly(ethylene-*co*-methacrylic acid)–polyether blends

Michael M. Coleman*, Joon Y. Lee, Carl J. Serman, Zhiqiang Wang and Paul C. Painter
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

(*Received 1 August 1988; revised 7 October 1988; accepted 9 November 1988*)

Theoretical equations have been developed describing the free energy changes and phase behaviour of binary polymer blends involving ether groups and carboxylic acids. The latter strongly self-associate through the formation of intermolecular dimers. Calculations have been performed for a number of poly(ethylene-*co*-methacrylic acid)–polyether blends. There is good agreement between the theoretical predictions and the experimental observations.

(Keywords: phase behaviour; polymer blends; energy changes; poly(ethylene-*co*-methacrylic acid); polyether)

INTRODUCTION

Of late we have published a series of papers that pertain to the mixing of binary polymer blends where the first polymer strongly self-associates through the formation of intermolecular chain-like hydrogen bonded structures[1–4]. Notable examples include polyurethanes, polyamides and polyphenols. The second polymer considered is weakly self-associated but capable of forming a hydrogen bond with the first. Typical examples include polyethers, polyesters, polypyridines, etc. In this paper we will turn our attention to the special case of strongly self-associated polymers where formation of intermolecular hydrogen bonded dimers occurs exclusively rather than chain-like structures. Copolymers containing methacrylic acid groups are good examples of such polymers[5].

EXPERIMENTAL

The poly(ethylene-*co*-methacrylic acid)s (EMAA) were synthesized in the laboratories of the E.I. Du Pont de Nemours Co. and have been described previously[5]. In this study, two essentially random amorphous copolymers were used that contain 44 and 55 weight % MAA (denoted EMAA[44] and EMAA[55], respectively). On a molar basis, this corresponds to 20.4 and 28.5 mole% MAA, respectively. Poly(vinyl methyl ether) (PVME), polytetrahydrofuran (PTHF) and poly(ethylene oxide-*co*-propylene oxide) (EPO) containing 70 weight % ethylene oxide, were purchased from Polysciences Inc. The former is an amorphous polymer with a T_g of −27°C and a reported molecular weight of 62 700 (undefined). Both PTHF and EPO are semi-crystalline polymers at ambient temperature. PTHF has a melting point (T_m) of 32°C and a reported molecular weight of 30 000. EPO ($MW = 12\,500$) has a T_g of −65°C and a melting point (T_m) of between 56–59°C. Poly(ethylene oxide)s (PEO) having molecular weights of 100 000, 600 000 and 5 000 000 were purchased from Scientific Polymer Products Inc. These are also semi-crystalline polymers with melting points of about 70°C. Poly(vinyl ethyl ether) (PVEE) and poly(vinyl isobutyl ether) (PVIBE) were purchased from Aldrich Chemical Co. These are amorphous polymers with T_gs of −42°C and −21°C, respectively. Poly(vinyl n-butyl ether) (PVBE) was synthesized in our laboratory[6]. Cationic polymerization was performed in methylene chloride at −78°C using boron trifluoride etherate as the catalyst. The weight average molecular weight was determined by size exclusion chromatography to be approximately 60 000 based upon polystyrene standards.

Tetrahydrofuran (THF) was used to prepare 1% (w/v) solutions of all polymer mixtures except those containing PEO. For the blends containing PEO a mixture of chloroform and THF (30:70 weight % ratio) was employed to facilitate solution. Thin films of the EMAA blends prepared for transmission *FT*i.r. spectroscopy were cast from a solution of the polymer mixture onto potassium bromide windows. After the majority of the solvent had evaporated, the films were placed under vacuum at 80°C to completely remove residual solvent. All samples were stored under vacuum in a desiccator to minimize water adsorption.

Infra-red spectra were recorded on a Digilab Model FTS-60 Fourier transform infra-red (*FT*i.r.) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disc system. Spectra recorded at elevated temperatures were obtained 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. Thermal analysis was performed on a Perkin-Elmer 7 Series differential scanning calorimeter. A heating rate of 20°C min^{-1} was employed using a sample size of approximately 10–15 mg.

The interpretation of the infra-red spectra of EMAA–polyether blends has been discussed in detail in a previous publication[5] and we will only briefly review the most salient features here. *Figure 1* shows typical examples of

---

* To whom correspondence should be addressed

0032-3861/89/071298-10$03.00

the carbonyl stretching region of the infra-red spectra of an amorphous miscible EMAA–polyether blend. Here we see scale expanded, room temperature, infra-red spectra of miscible amorphous EMAA[55]–PVEE blends of varying composition. The two bands attributed to the carboxylic acid dimer (1700 cm^{-1}) and the carboxylic acid–ether oxygen interaction (free carbonyl groups at 1731 cm^{-1}) are readily measured and a quantitative determination of the fraction of "free" carbonyls is viable after due consideration is given to the differing infra-red band absorptivities[5]. *Tables 1* and *2* summarize the results of curve fitting the carbonyl stretching region of the spectra obtained from miscible (single intermediate T_g) EMAA[55] blends with PVEE and PTHF, respectively, at 25°C. In a similar vein, *Table 3* lists the fraction of "free" carbonyls as a function of blend composition determined for EMAA[55]–PEO blends at 70°C (above the T_m of PEO) using three PEO samples of differing molecular weights.

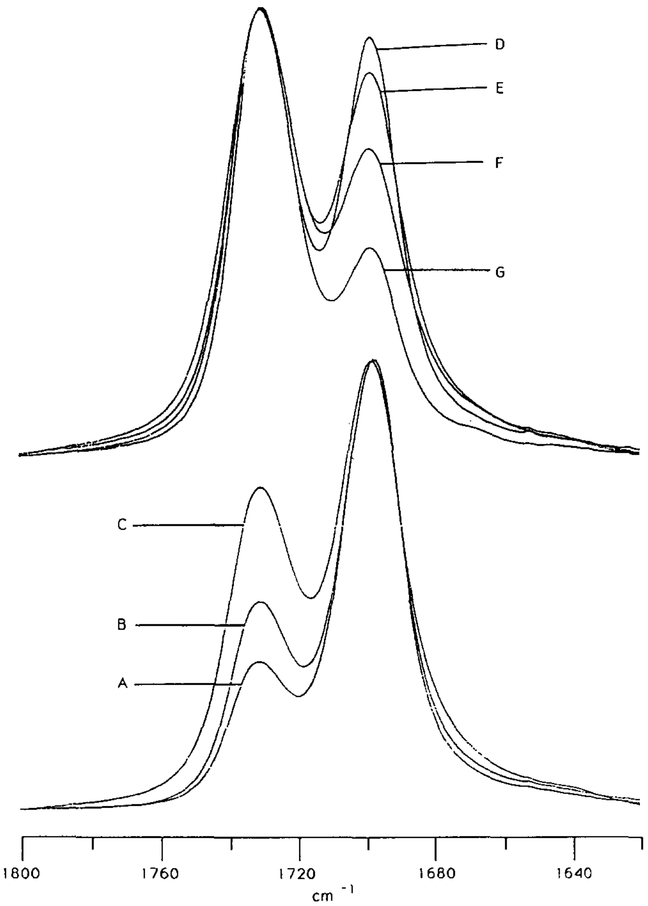

Figure 1 Carbonyl stretching region of the infra-red spectra of EMAA[55]–PVEE mixtures containing A 20, B 30, C 40, D 50, E 60, F 70 and G 80 weight % PVEE recorded at 25°C

In marked contrast, *Figure 2* shows the carbonyl stretching region of the infra-red spectra of samples of an amorphous EMAA–PVIBE blend. The band attributed to the carboxylic acid dimer (1700 cm^{-1}) dominates the spectrum and there is only a very weak contribution from the band at 1731 cm^{-1}, from which one may conclude that only very few intermolecular interactions have occurred between the component polymers. This, in turn, suggests that the blend is multiphased (immiscible), a conclusion substantiated by thermal analysis where two distinct T_gs are observed, corresponding to those of the essentially pure components.

THEORETICAL DEVELOPMENT

To be consistent with previous nomenclature[1–4], let **B** depict the (self-associating) methacrylic acid (MAA) groups and **A** the (non self-associating) ether groups. Thus:

$$\mathbf{B}_1 + \mathbf{B}_1 \overset{K_B}{\rightleftharpoons} \mathbf{B}_2$$

$$\mathbf{B}_1 + \mathbf{A} \overset{K_A}{\rightleftharpoons} \mathbf{BA} \qquad (1)$$

Table 1 Curve-fitting results of the EMAA[55]–PVEE blends

EMAA[55]:PVEE (wt%)	"Free" C=O band Frequency (cm^{-1})	Width[a]	Area[c]	Carboxylic acid dimer C=O band Frequency (cm^{-1})	Width[a]	Area[c]	Fraction "free" C=O[b]
80:20	1731	20	247	1699	20	886	0.31
70:30	1731	20	277	1699	21	678	0.40
60:40	1731	22	863	1699	23	1292	0.52
50:50	1731	21	843	1699	24	760	0.64
40:60	1731	20	642	1700	20	591	0.63
30:70	1731	24	1218	1699	25	805	0.71
20:80	1731	22	2742	1700	22	1156	0.79

[a] Width at half-height, cm^{-1}
[b] Absorptivity ratio = 1.6 (reference 5)
[c] Arbitrary units

Table 2 Curve-fitting results of the EMAA[55]–PTHF blends

EMAA[55]:PTHF (wt%)	"Free" C=O band Frequency (cm^{-1})	Width[a]	Area[c]	Carboxylic acid dimer C=O band Frequency (cm^{-1})	Width[a]	Area[c]	Fraction "free" C=O[b]
80:20	1732	21	482	1698	21	2547	0.23
70:30	1732	22	423	1698	22	1609	0.30
50:50	1731	19	583	1698	20	1410	0.40
40:60	1732	22	569	1699	23	888	0.51
20:80	1730	19	1900	1699	19	1582	0.66

[a] Width at half-height, cm^{-1}
[b] Absorptivity ratio = 1.6 (reference 5)
[c] Arbitrary units

Table 3 Curve-fitting results of the EMAA[55]–PEO blends

EMAA[55]:PEO (wt%)	"Free" C=O band Frequency (cm^{-1})	 Width[a]	 Area[c]	Carboxylic acid dimer C=O band Frequency (cm^{-1})	 Width[a]	 Area[c]	Fraction "free" C=O[b]
PEO MW$=1\times10^5$							
80:20	1731	23	549	1699	22	1338	0.40
60:40	1730	22	850	1698	24	930	0.59
50:50	1729	23	990	1698	26	954	0.63
40:60	1729	25	883	1698	25	669	0.68
20:80	1728	21	1038	1699	24	353	0.82
PEO MW$=6\times10^5$							
80:20	1731	22	478	1699	23	1382	0.36
60:40	1730	22	864	1699	22	1188	0.54
50:50	1729	22	1069	1699	22	1090	0.62
40:60	1729	23	1979	1699	24	1614	0.67
20:80	1729	24	1691	1698	24	731	0.79
PEO MW$=5\times10^6$							
80:20	1731	23	437	1699	23	1207	0.37
60:40	1730	24	637	1698	25	921	0.53
50:50	1730	24	1680	1698	25	1664	0.62
40:60	1729	24	858	1698	25	738	0.66
20:80	1729	24	895	1698	26	500	0.75

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

[b] Absorptivity ratio = 1.6 (reference 5)

[c] Arbitrary units

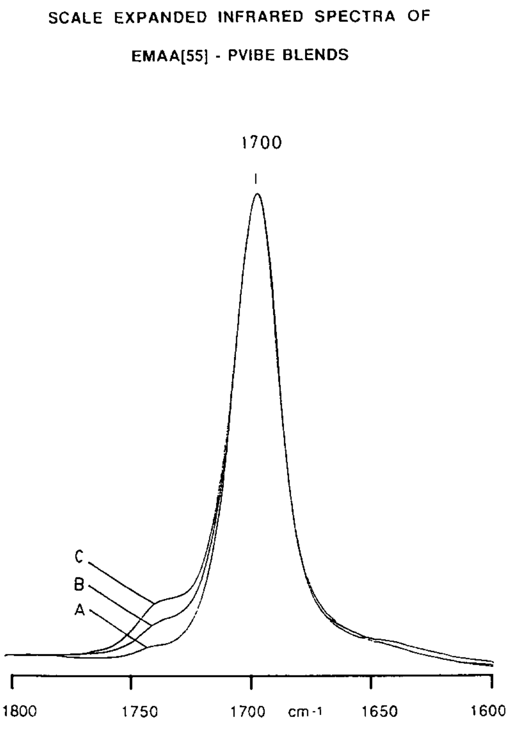

Figure 2 Carbonyl stretching region of the infra-red spectra of EMAA[55]–PVIBE mixtures containing A 0, B 50 and C 70 weight % PVIBE recorded at 25°C

The equilibrium constants, K_A and K_B, are defined in terms of volume fractions as[1]:

$$K_B = \frac{\Phi_{B_2}}{[\Phi_{B_1}]^2} \cdot [\tfrac{1}{2}]$$

$$K_A = \frac{\Phi_{BA}}{\Phi_{B_1}\Phi_{A_1}} \cdot \left[\frac{r}{1+r}\right] \qquad (2)$$

where Φ_{B_1}, Φ_{B_2}, Φ_{A_1} and Φ_{BA} are the volume fractions of the carboxylic acid monomers, carboxylic acid dimers, unassociated ethers and associated carboxylic acid–ether groups, respectively. The parameter, r, is the ratio of the molar volumes of the polymer repeat units, V_A/V_B. Using the expression describing the mass balance,

$$\Phi_{B_1} + \Phi_{B_2} + \Phi_{A_1} + \Phi_{BA} = 1 \qquad (3)$$

we arrive at the following equations describing the stoichiometry of the system:

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{K_A \Phi_{A_1}}{r}\right] + 2K_B[\Phi_{B_1}]^2 \qquad (4)$$

$$\Phi_A = \Phi_{A_1}[1 + K_A \Phi_{B_1}] \qquad (5)$$

where Φ_A and Φ_B are the volume fractions of non self-associating species **A** and self-associating species **B**, respectively. These equations describe the stoichiometry of associating species and are equally valid when expressed in terms of interacting units or chemical repeat units[2].

For the pure acid copolymer (superscript 0), $\Phi_B = 1$ and equations (4) and (5) reduce to:

$$1 = \Phi^0_{B_1} + 2K_B[\Phi^0_{B_1}]^2 \qquad (6)$$

Accordingly, since the negative root has no meaning:

$$\Phi^0_{B_1} = \frac{-1 + \sqrt{1 + 8K_B}}{4K_B} \qquad (7)$$

In principle, the equilibrium constants, K_A and K_B, may be determined directly from infra-red spectroscopic measurements of the fraction of "free" (non-hydrogen bonded) carboxylic acid carbonyl groups, f_F (reference 5). In order to do this, however, we need to express f_F in terms of the equilibrium constants defined above. The fraction of "free" carbonyl groups in the pure acid, assuming no volume change on forming an acid dimer, is simply given by:

$$f^0_F = \frac{\Phi^0_{B_1}}{\Phi^0_{B_1} + \Phi^0_{B_2}} \qquad (8)$$

Since, $\Phi^0_{B_1}+\Phi^0_{B_2}=1$, the fraction of "free" carbonyls is given by $f^0_F=\Phi^0_{B_1}$ and:

$$K_B=\frac{[1-f^0_F]}{2[f^0_F]^2} \tag{9}$$

K_B may therefore be determined from the quantitative measurement of the fraction of "free" carbonyls obtained from the infra-red temperature studies previously performed for the pure EMAA[44] (see table IV of reference 5). The equilibrium constants for EMAA copolymers containing different amounts (x) of MAA may be readily obtained by scaling according to the ratio of the molar volumes of the different average repeat units[1]:

$$K_B^{[x]}=K_B^{[44]}\cdot\frac{V_B^{[44]}}{V_B^{[x]}} \tag{10}$$

The equilibrium constant describing the association of carboxylic acid and ether units, K_A, may also be determined directly from infra-red measurements[3–5]. Employing the value obtained for K_B and selecting an initial value for K_A together with the appropriate value of r, the roots (Φ_{B_1}) may be calculated iteratively using Newton's method between the limits of zero and the value of $\Phi^0_{B_1}$ (equation (7)), for given values of Φ_B (equations (4) and (5)). The fraction of "free" acid carbonyl groups, f_F, in the EMAA–polyether blends as a function of the volume fraction of EMAA is given by:

$$f_F=\frac{\left[1+\dfrac{K_A\Phi_{A_1}}{r}\right]}{\left[1+2K_B\Phi_{B_1}+\left[1+\dfrac{K_A\Phi_{A_1}}{r}\right]\right]} \tag{11}$$

a relationship that is readily derived by substitution from an expression for the mole fractions of bonded and non-bonded groups, X_{A_1}, X_{B_1}, X_{AB} and X_{B_2}:

$$f_F=\frac{X_{AB}+X_{B_1}}{2X_{B_2}+X_{AB}+X_{B_1}}$$

The value of K_A may be systematically varied and a least squares method employed to determine the best fit of the experimental data. It is important to recognize that the magnitude of K_B varies with the MAA content of the copolymer but that the ratio of the two equilibrium constants $Z=K_A/K_B$ is theoretically predicted to be constant. This is because both K_B and K_A, the equilibrium constants in terms of chemical repeat units, are related to the equivalent constants in terms of interacting units, K_β and K_α, by $K_B=K_\beta/s_B$ and $K_A=K_\alpha/s_B$, where s_B is the number of segments in the self-associating polymer. In other words, the self-associating interacting unit is used to define the lattice cell size. The adjustment for the different size of the chemical repeat units enters through the factor $r=V_A/V_B$. Accordingly, having determined the values of K_B and K_A for a particular EMAA copolymer–polyether blend, it is a straightforward matter to calculate the new values of the equilibrium constants for a blend involving the same polyether with an EMAA copolymer containing a different concentration of methacrylic acid, using equation (10).

A theory describing the free energy of mixing of polymer blends, based upon a simple association model, has been developed in our laboratories and applied to systems involving strongly self-associated polymers such as those containing hydroxyl, amide and urethane groups which form distributions of chain-like hydrogen bonded structures[1,2]. EMAA copolymers are a special case, however, as we assume that dimer formation occurs exclusively. This modifies the equations somewhat but the underlying principles are the same. We start, therefore, with the following familiar relationship:

$$\frac{\Delta G^M}{RT}=\frac{\Phi_A}{N_A}\ln\Phi_A+\frac{\Phi_B}{N_B}\ln\Phi_B+\Phi_A\Phi_B\chi+\frac{\Delta G_H}{RT} \tag{12}$$

The first three terms of this equation correspond to the well known Flory-Huggins equation. This may be viewed as the change in free energy of mixing the two polymers assuming that there are no significant intermolecular interactions (hydrogen bonds) involved. The combinatorial entropy expressed by the two log terms is always negative, but for high molecular weight polymers the overall contribution to the free energy of mixing is very small indeed. The $\Phi_A\Phi_B\chi$ term is usually unfavourable to mixing since, in our scheme, it cannot assume negative values, reflecting only the contribution of 'repulsive' dispersion forces. The favourable contribution to the change in the free energy of mixing arising from the presence of the intermolecular interactions (hydrogen bonds) is expressed in the fourth term of equation (12). Using identical arguments to those explicitly described in our previous publications[1,2] we derive the following expression:

$$\frac{\Delta G_H}{RT}=\Phi_B\ln\left[\frac{\Phi_{B_1}}{\Phi^0_{B_1}\Phi_B^{[1/n^0_H]}}\right]+\frac{\Phi_A}{r}\ln\left[\frac{\Phi_{A_1}}{\Phi_A}\right]$$
$$+\Phi_B[\Phi^0_{B_1}(1+K_B\Phi^0_{B_1})]-\Phi_{B_1}(1+K_B\Phi_{B_1}) \tag{13}$$

where the number average hydrogen bonded chain length, which in this case must lie between one and two, is given by:

$$\bar{n}^0_H=\frac{1+2K_B\Phi^0_{B_1}}{1+K_B\Phi^0_{B_1}}=\frac{2}{1-f^0_F} \tag{14}$$

Although it may appear that we are simply adding the effect of non-random hydrogen bonding contacts to a random mixing theory, with all the problems that might imply, the theory is a little more subtle[1]. In effect, we treat the complexes as distinguishable species and allow these to randomly mix. The change in the distribution of these species with concentration can be accounted for by the correct choice of reference state and provides the origin of the above expression for ΔG_H; the equilibrium constants being a measure of the change in free energy per hydrogen bond. For low molecular weight materials this approach involves no additional assumptions to those inherent in a Flory-Huggins lattice model. For polymers we must make the additional assumption that there is sufficient segmental flexibility for the functional groups to follow their intrinsic proclivities in forming hydrogen bonds. For the copolymers considered here, where the acid groups are separated by a number of flexible methylene linkages, that would seem to be a reasonable assumption.

In order to calculate a spinodal phase diagram we need to derive the second derivatives of the free energy with respect to Φ_B. Following the procedure employed previously[2] this can be shown to be given by:

$$\frac{\partial^2(\Delta G_M/RT)}{\partial\Phi_B^2}=\frac{1}{N_A\Phi_A}+\frac{1}{N_B\Phi_B}-2\chi$$
$$-\left[\left[\frac{1}{\bar{n}_H^0\Phi_B}+\frac{1}{r\Phi_A}\right]-\left[\frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B}-\frac{1}{r\Phi_{A_1}}\frac{\partial\Phi_{A_1}}{\partial\Phi_B}\right]\right] \qquad (15)$$

where:

$$\frac{\partial\Phi_{B_1}}{\partial\Phi_B}=\frac{1+[K_A\Phi_{A_1}\Phi_{B_1}/r\Phi_A]}{1+4K_B\Phi_{B_1}+[K_A\Phi_{A_1}^2/r\Phi_A]} \qquad (16)$$

and:

$$\frac{\partial\Phi_{A_1}}{\partial\Phi_B}=\frac{\Phi_{A_1}(1+K_A\Phi_{A_1})\cdot\left[\dfrac{\partial\Phi_{B_1}}{\partial\Phi_B}\right]}{\Phi_A} \qquad (17)$$

CALCULATIONS

Stoichiometry and the estimation of equilibrium constants

As mentioned above K_B may be determined (equation (9)) from the quantitative results of the fraction of "free" carbonyls obtained from infra-red temperature studies previously performed for the pure EMAA[44] (see table IV of reference 5). A van't Hoff plot, very similar to that shown in figure 14 of reference 5, yields the following relationship:

$$\ln K_B^{[44]}=-13.11+\frac{7217}{T} \qquad (18)$$

Thus at 25°C, the value of $K_B^{[44]}$ is calculated to be approximately 6.7×10^4. The equilibrium constants at 25°C for EMAA copolymers containing different concentrations of MAA units which are listed in *Table 4* were calculated using equation (10).

The equilibrium constant describing the association of carboxylic acid and ether units, K_A, may also be determined directly from infra-red measurements[3,4]. *Figure 3* shows the experimental values of the fraction of "free" (non-hydrogen bonded) acid carbonyl groups as a function of the volume fraction of EMAA[44] in blends of this polymer with PVME (table I of reference 5). This blend system has been shown to be miscible over the entire composition range at ambient temperature[5]. Employing the value for $K_B^{[44]}$ at 25°C determined above (6.7×10^4) together with an appropriate value of r ($=V_A/V_B=0.27$), the iterative procedure described above was employed to determine the roots (Φ_{B_1}) for a particular value of K_A over the entire composition range. The fraction of "free" acid carbonyl groups (equation (11)) was then calculated. K_A was then changed systematically and a least squares method employed to determine the best fit of the experimental data for the EMAA[44] blends with PVME. A theoretical curve was calculated using the best estimate of $K_A=173$ and is also presented in *Figure 3*. A good correspondence exists between the

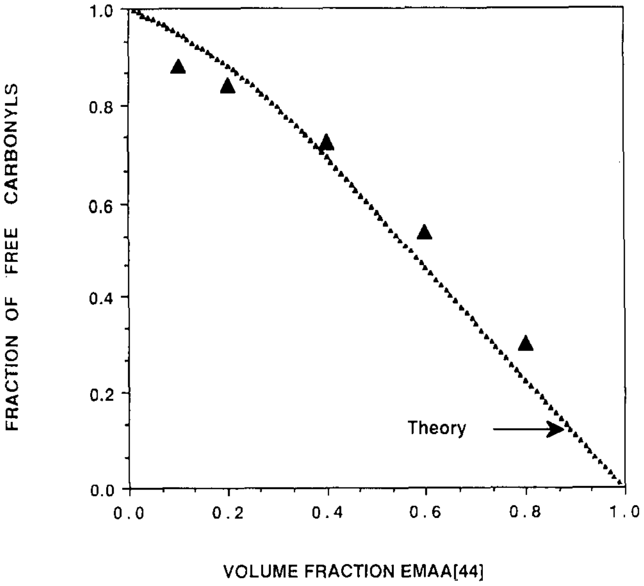

Figure 3 Comparison of the experimentally and theoretically determined fraction of "free" or non-hydrogen bonded carboxylic acid carbonyl groups at 25°C in EMAA[44]–PVME blends as a function of the volume fraction of EMAA[44] ($K_B=67\,000$, $K_A=173$)

Table 4 EMAA copolymer parameters

wt% MAA	# CH_2's	V_B (cm^3 $mole^{-1}$)	ΣF_i (cal cm^3)$^{1/2}$ $mole^{-1}$	δ_B (cal cm^{-3})$^{1/2}$	$K_B\times10^{-4}$ at 25°C
100	1.0	81.5	1058	12.98	17.3
90	1.7	93.0	1150	12.36	15.1
80	2.5	106.2	1255	11.82	13.2
70	3.6	124.3	1400	11.26	11.3
60	5.1	148.9	1597	10.72	9.44
55	6.0	163.7	1715	10.48	8.58
50	7.1	181.8	1860	10.23	7.73
45	8.5	204.5	2044	9.98	6.86
44	8.8	209.7	2083	9.93	6.70
40	10.2	232.8	2268	9.74	6.04
35	12.4	269.0	2557	9.50	5.23
30	15.3	316.7	2938	9.28	4.44
25	19.4	384.2	3477	9.05	3.66
20	25.6	486.2	4293	8.83	2.89
15	35.8	653.9	5634	8.62	2.15
10	56.3	991.2	8330	8.40	1.42
8	71.6	1242.8	10342	8.32	1.13
6	97.2	1664.0	13708	8.24	0.85
5	117.7	2001.2	16404	8.20	0.70
4	148.4	2506.2	20441	8.16	0.56
3	199.6	3348.5	27174	8.12	0.42

theoretical curve and the experimental data for the EMAA[44]–PVME blends at 25°C. Thus, for this blend system we calculate a value for Z ($=K_A/K_B$) of 2.6×10^{-3}. As we mentioned above, the magnitude of K_B varies with the MAA content of the copolymer (equation (10)) but the ratio of the two equilibrium constants, Z, is theoretically predicted to be constant. Accordingly, K_A values for blends of PVME with EMAA copolymers of different MAA contents may be calculated.

A similar procedure was performed using the data listed in *Table 1* for the miscible EMAA[55]–PVEE system at 25°C. Employing equation (10), $K_B^{[55]}$ was calculated to be 8.6×10^4. The ratio of the molar volumes, r, was determined to be 0.45 and, following the least squares fitting procedure of the experimental data, a value of $K_A=278$ was established. Z in this case is 3.2×10^{-3} and in reasonable agreement with that determined for the EMAA[44]–PVME blend system. Assuming no major changes in chemistry, steric hindrance, etc., comparable values of Z for EMAA–poly(vinyl alkyl ether)s are anticipated.

There is reason to suspect that we may have to consider at least two distinct categories of alkyl ether groups: those present in the main chain of the polymer, poly(alkylene oxide)s, (PEO, EPO and PTHF) as distinct from those present in the side chains, poly(vinyl alkyl ether)s (PVME, PVEE, PVIBE, etc.). Certainly, the frequency shifts of the fundamental O–H stretching modes observed in the infra-red spectra of poly(vinyl phenol) (PVPh)–polyether blends, suggest significant differences in the enthalpies of formation of O–H to ether interactions[7]. With this in mind, we might anticipate a meaningful distinction in the magnitude of the Z for the two categories of polyethers. The crystalline melting point of PTHF is close to room temperature and we have established[8] that amorphous polymer blends of PTHF and EMAA[55] are miscible at 25°C. The fraction of "free" carbonyls has been measured and the results are given in *Table 2*. In this case ($r=0.45$), K_A was determined to be 166 and the value of Z is 1.9×10^{-3}.

Calculations were also performed on data obtained from the EMAA[55]–EPO system at 60°C (table III of reference 5) and the EMAA[55]–polyethylene oxide (PEO) system at 70°C (*Table 3*). At these temperatures, above the respective crystalline melting points of EPO and PEO, both blends are amorphous and miscible. Using equations (18) and (10), $K_B^{[55]}$ was estimated to be 6.7×10^3 and 3.6×10^3 at 60 and 70°C, respectively. K_A was then determined, using the appropriate values of r, by a least squares best fit of the experimental data. *Figure 4* shows the example of the EMAA[55]–EPO blend where the best fit of the experimental data yielded a value of $K_A=56$. The corresponding value for PEO at 70°C was determined to be $K_A=40$. Assuming the enthalpy of hydrogen bond formation between the carboxylic acid and ether moieties has a value of 6 kcal mole^{-1} (an estimate calculated from O–H infra-red frequency shifts and ΔH correlations[12]), values of $K_A=162$ and 151 at 25°C were calculated from the van't Hoff relationship for the EMAA[55]–EPO and EMAA[55]–PEO blends, respectively. Values of Z are thus 1.9×10^{-3} and 1.8×10^{-3}, respectively, which compare very favourably with the calculated value for the EMAA[55] blends with PTHF and is in gratifying agreement with the predictions of our model.

From the results discussed above, it seems reasonable to employ somewhat different average values of Z in subsequent calculations of EMAA–polyether blends, i.e. for poly(vinyl alkyl ether)s $Z=2.9\times10^{-3}$ while for poly(alkylene oxide)s $Z=1.9\times10^{-3}$. We should emphasize, however, that the ratios of the equilibrium constants, Z, for the different EMAA–polyether systems at the same temperature are of roughly the same order of magnitude. Given the disparity in the magnitudes of K_A and K_B, we find that even a large variation (20%) in the absolute value of K_A does not materially affect the outcome of the free energy calculations.

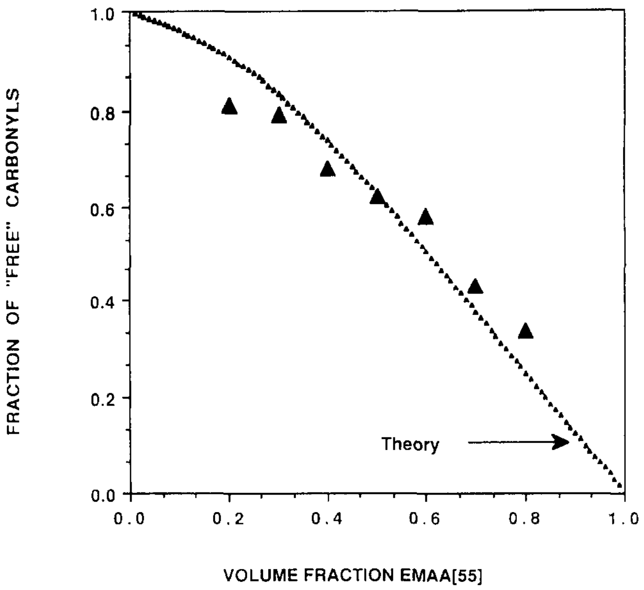

Figure 4 Comparison of the experimentally and theoretically determined fraction of "free" or non-hydrogen bonded carboxylic acid carbonyl groups at 60°C in EMAA[55]–EPO blends as a function of the volume fraction of EMAA[55] ($K_B=6700$, $K_A=56$)

The free energy of mixing

Having obtained the two equilibrium constants, K_B and K_A, we are now in a position to calculate the free energy of mixing using the equations (12) to (14). We require values for the molar volumes, V_B and V_A, the degree of polymerization, N_B and N_A, and the interaction parameter, χ.

An average repeat unit for the individual EMAA copolymers was calculated from the reported concentration (weight %) of MAA in the material. After conversion to molar concentrations, the average repeat was expressed in terms of the number of methylene groups per $-C(CH_3)COOH$ group. For example, the average repeat for EMAA[44] is $(CH_2)_{8.8}-C(CH_3)COOH$. Employing the group contributions (V_r) listed in table 4.4 of van Krevelen's book[9], molar volumes of the chemical repeat units were calculated for both experimental and hypothetical EMAA copolymers together with those of the polyethers considered in this study (*Tables 4* and *5*). The molar volume group contribution for the COOH group was estimated from raw density data[10,11] by subtracting the corresponding group contributions of the aliphatic groups from the total molar volumes of nine aliphatic acids (linear and branched ranging from propanoic through octanoic). An average value of 37.5 ± 1.8 cm^3 mole^{-1} was obtained. Unless otherwise stated, the degree of polymerization for all the polymers was assumed to be $N_A=N_B=250$.

Table 5 Polyether parameters

Polymer	V_A (cm^3 mole^{-1}) at 25°C	ΣF_i (cal cm^3)$^{1/2}$ mole^{-1}	δ_A (cal cm^{-3})$^{1/2}$
PEO	41.40	378.0	9.13
EPO	45.37	403.2	8.89
PTHF	74.30	641.0	8.63
PVME	57.60	480.8	8.35
PVEE	74.05	612.3	8.27
PVBE	106.95	875.3	8.18
PVIBE	106.70	846.6	7.93

It is entirely appropriate to consider the interaction parameter, χ, which in our theory represents a non-hydrogen bonding contribution to the free energy of mixing, as an adjustable parameter. Accordingly, in the future, when detailed experimental phase diagrams have been determined for such hydrogen bonded polymer blends systems it should be feasible to 'back out' a value of χ, since there is only this one adjustable parameter that would be included in a fit to the experimental data (unfortunately this procedure is unlikely to be applicable to the EMAA blends due to the chemical changes, i.e. anhydride formation, that occur at temperatures in excess of 140°C[5]). For the purposes of identifying potentially miscible polymer blend systems or describing useful trends, however, an initial estimation of χ can be obtained from solubility parameters. The problem therefore reduces to what scheme should one use to obtain solubility parameters. This is not a trivial problem and we have tested most of those which are based upon the addition of molar attraction constants (F)[9]. The parameters compiled by Hoy[10] appear to give the most consistent results and we have employed them successfully for PVPh blends with polyacrylates and methacrylates, polyacetates, polyesters and polyethers and amorphous polyurethane blends with polyethers. Lamentably, there is a snag in calculating the analogous solubility parameters for the EMAA copolymers because the molar attraction constant for the acid group determined by Hoy was corrected for carboxylic acid dimer formation. To be candid, we cannot duplicate the experimental results and trends for the EMAA blends described in this study if we employ the 'corrected' molar attraction constant for the carboxylic acid suggested by Hoy. Returning to the raw data[10,11] we decided to use the same procedure outlined above to obtain the molar volume of the COOH group for the determination of the corresponding molar attraction constant. Using the experimentally determined solubility parameters and molar volumes of the same nine aliphatic carboxylic acids, we obtained the total group contribution to F ($=\delta^* V$) and then subtracted the contribution of the aliphatic groups (Hoy) to yield the contribution from the COOH group. A value of 750 ± 100 (cal cm^3)$^{0.5}$ was obtained, which obviously contains a wide margin for error. This is the value we employed in our calculations of the solubility parameters for the EMAA copolymers. One final point; although the absolute value of the solubility parameter for a particular EMAA copolymer may be subject to significant error, the trend of the values of solubility parameters as a function of the number of methylene groups in the polymer repeat unit is basically sound (*Table 4*). Estimates of the value of χ may now be determined for a given polymer pair (*Table 6*) using the well known relationship[12]:

$$\chi = \frac{V_B}{RT}[\delta_A - \delta_B]^2$$

where the molar volume of the EMAA repeat is the reference volume, V_B.

Employing the parameters listed in *Tables 4* and *5* in equations (12) to (17), the free energy of mixing at 25°C was calculated as a function of the volume fraction of EMAA[44] in blends with PVME, PVEE, PVBE and PVIBE. The results are displayed in *Figure 5*, which also displays the second derivative of the free energy of mixing with respect to EMAA[44] volume fraction. The calculated results predict that at 25°C the EMAA[44] blend with PVME is miscible, which is in agreement with experimental observations. The free energy of mixing is negative and the second derivative is positive throughout the whole composition range. The calculations suggest that the EMAA[44] blend with PVEE is nearly miscible. There is an inflection in the free energy curve and the second derivative curve dips below zero at high concentrations of EMAA[44]. Experimentally, this system appears miscible. Conversely, the EMAA[44] blends with PVnBE and PVIBE are predicted to be multiphased, again in agreement with experiment. The free energy is not negative throughout the entire composition range and the second derivative assumes negative values over a significant composition range.

Similar calculations were performed for EMAA[55] blends with PEO, EPO and PTHF at 70°C (above the crystalline melting points of each of these polymers) using the parameters listed in *Tables 4* and *5*. To accomplish this, however, we need to calculate the free energy as a function of temperature, which in turn requires us to make two further assumptions. A simple van't Hoff temperature dependence of the equilibrium constants K_B and K_A is assumed, implying a constant ΔH over the entire temperature range considered (−100–500°C). The enthalpy of hydrogen bond formation for self-association, corresponding to the equilibrium constant K_B, has been determined experimentally (equation (18)) as

Table 6 EMAA–PEO blend parameters

EMAA wt % MAA	K_A at 25°C	χ_{PEO}
100	322	2.04
90	282	1.64
80	247	1.30
70	211	0.956
60	176	0.638
55	160	0.501
50	144	0.371
45	128	0.248
44	125	0.227
40	113	0.146
35	97.4	0.064
30	82.7	0.012
25	68.2	0.004
20	53.9	0.074
15	40.1	0.293
10	26.4	0.883
8	21.1	1.37
6	15.7	2.23
5	13.1	2.94
4	10.5	4.02
3	7.8	5.82

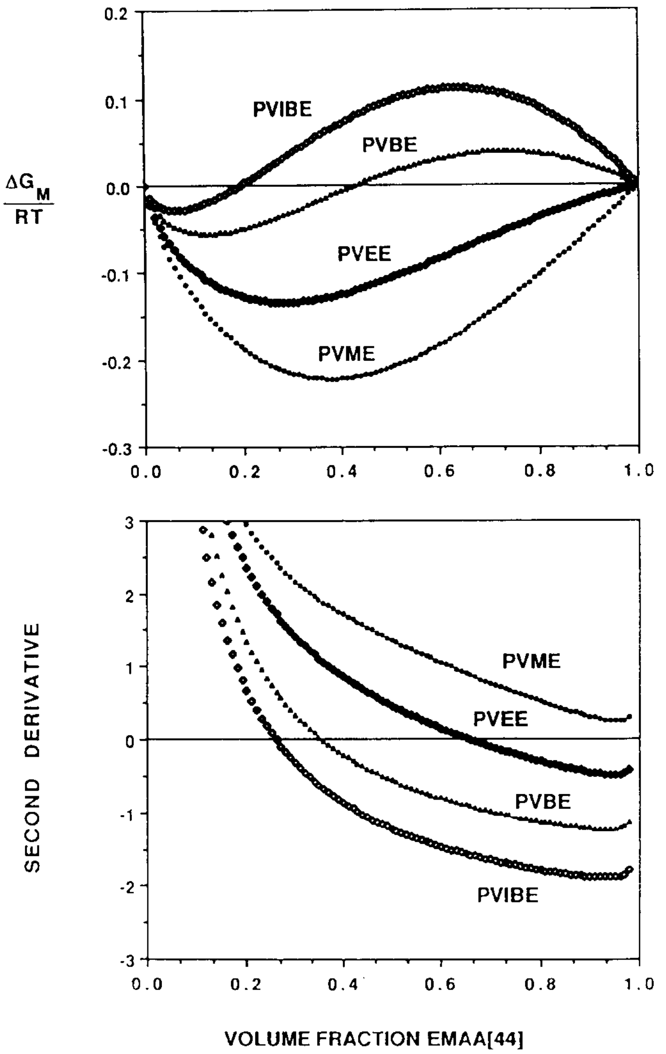

Figure 5 Calculated free energy of mixing and second derivatives of the free energy for EMAA[44]–Poly(vinyl alkyl ether) blends at 25°C

14.4 kcal mole^{-1} of carboxylic acid dimers. The corresponding value for the carboxylic acid–ether interaction (6 kcal mole^{-1}) was obtained from the literature[12]. Finally, the temperature dependence of the interaction parameter, χ, was assumed to follow a simple inverse temperature relationship in this study. *Figure 6* shows the calculated results, which predict that the PEO and EPO blends are miscible at 70°C, and is in concert with experiment. The free energy of mixing is negative and the second derivative is positive throughout the whole composition range. The PTHF blend system is predicted to be on the margins of miscibility. Although the free energy curve is everywhere negative, the second derivative exhibits negative values at high EMAA[55] content.

Phase diagrams

A spinodal phase diagram may be determined over a specific temperature range by equating the second derivatives of the free energy of mixing (equation (15)) to zero. Such an exercise yields no spinodal information over a range from about −25–300°C for the EMAA[55] blends with PEO and EPO (*Figure 7*). This implies that these blends are theoretically single phase systems over the entire range of experimentally accessible temperatures (i.e. above the T_g and below the onset of degradation). The same holds true for the PTHF blends except that an upper critical boundary may just come into play in rich EMAA[55] blends at ambient temperature. In terms of a trend for the EMAA[55] blends, multiphased systems might be predicted as the number of methylene groups is increased in the polyether.

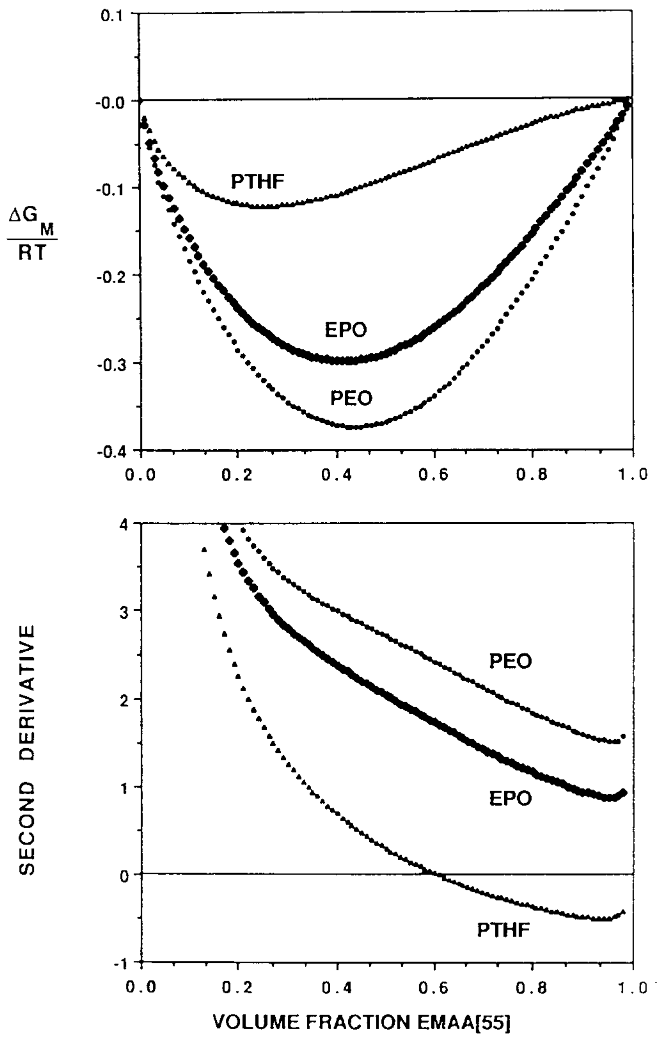

Figure 6 Calculated free energy of mixing and second derivatives of the free energy for EMAA[55]–Poly(alkylene oxide) blends at 70°C

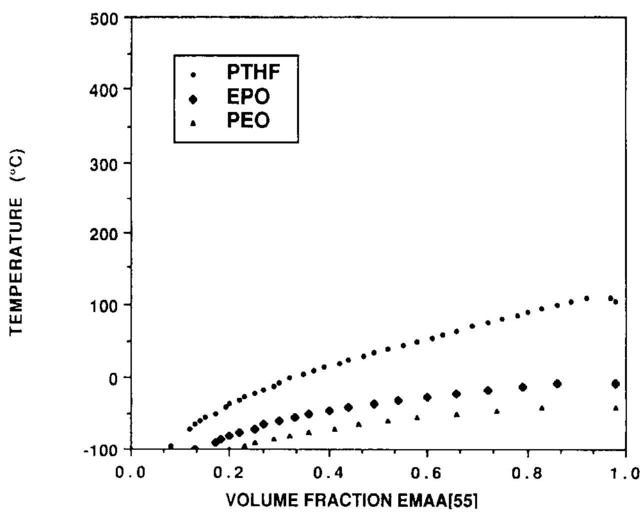

Figure 7 Theoretical spinodals for EMAA[55]–Poly(alkylene oxide) blends

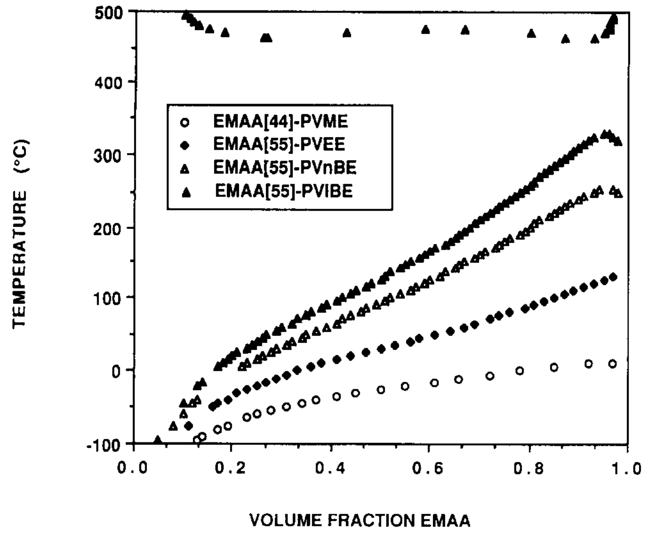

Figure 8 Theoretical spinodals for EMAA–Poly(vinyl alkyl ether) blends

A similar calculation for the EMAA blends with PVME, PVEE, PVBE and PVIBE, on the other hand, yields theoretical phase diagrams shown in *Figure 8*. For the EMAA[44] blends containing PVME an upper critical solution phase boundary is calculated. No other spinodal information is generated in this temperature range implying single phased systems above 0°C. The phase diagrams for the EMAA[55] blends containing PVEE and PVBE are similar in appearance, except that the upper critical boundary occurs at higher temperatures. The trend continues for the EMAA[55]–PVIBE blends and now in addition to the upper critical boundary a lower critical solution boundary is evident at very high temperatures (much too high, however, to ever come under the scrutiny of experimental verification!). The merging of these two boundaries is predicted to occur with the addition of a few more aliphatic groups to the poly(vinyl alkyl ether) and leads to an essentially immiscible system. Although we cannot test the subtleties of these phase diagrams the gross behaviour is consistent with experiment.

Another interesting facet of this work concerns the number of interaction sites that are necessary to ensure molecular mixing. In other words, using a specific example relevant to this current study, can we estimate the lowest concentration of MAA units that we must incorporate into an otherwise polymethylene chain to ensure molecular mixing with PEO at a given temperature? The key parameters that are going to have a major effect on where this limit occurs are:

1. The ratio of the molar volumes, r, which becomes smaller as V_{A} is constant and V_{B} becomes increasingly larger with decreasing concentration of MAA units in the copolymer. This is favourable to mixing.

2. The value of the interaction parameter, χ, and how it varies as a function of MAA concentration in the copolymer. This in turn, is determined by the change in solubility parameter, δ_{B}, with MAA content of the EMAA copolymer and its value relative to δ_{A}, the solubility parameter of the polyether. For example, the solubility parameter of EMAA[100] (polymethacrylic acid) is calculated to be $\delta_{\mathrm{B}}=12.98$ (cal cm^{3})$^{0.5}$. As the concentration of MAA decreases in the copolymer the value of δ_{B} decreases monotonically (*Table 4*) and would eventually approach the calculated solubility parameter of polymethylene (7.99 (cal cm^{3})$^{0.5}$). Consider PEO, which has a value of $\delta_{\mathrm{A}}=9.13$ (cal cm^{3})$^{0.5}$ (*Table 5*). The calculated value of χ first decreases and then increases as the amount of MAA in the copolymer decreases (*Table 6* and *Figure 9*). Starting again with EMAA[100], the calculated value

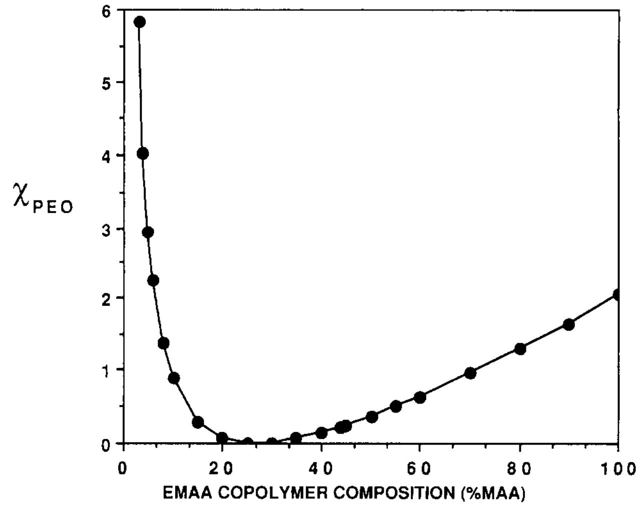

Figure 9 Variation of χ with EMAA copolymer composition in blends with PEO

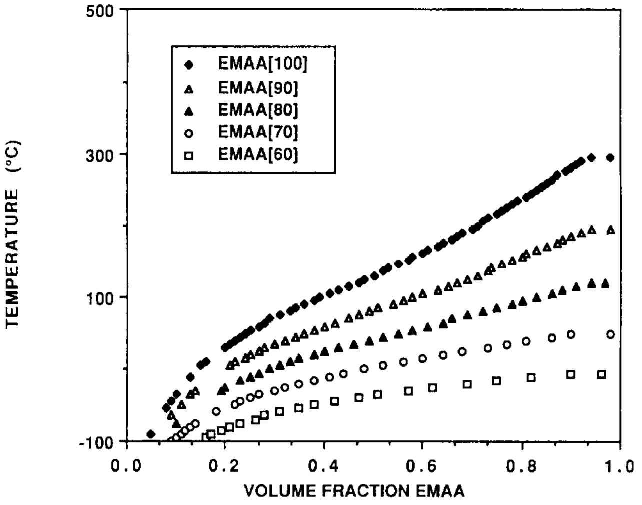

Figure 10 Theoretical spinodals for EMAA–PEO blends

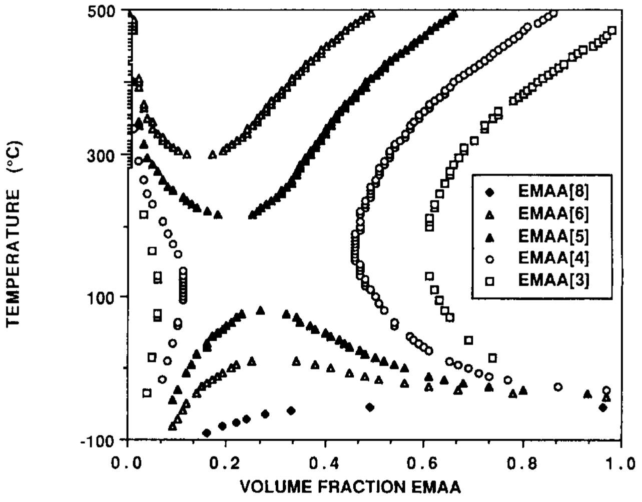

Figure 11 Theoretical spinodals for EMAA–PEO blends

of χ decreases with decreasing MAA content of the copolymer (*Table 6*) as the difference between the two solubility parameters gets progressively smaller. In fact, there is a point where theoretically the solubility parameters are identical and the value of $\chi = 0$. At this particular MAA concentration molecular mixing is assured in the absence of an unfavourable free volume contribution to the free energy of mixing (see below). Further decreasing the MAA content in the copolymer leads to increasing values of χ as the difference between the two solubility parameters now gets progressively larger.

It must be emphasized that our theoretical equation describing the free energy of mixing (equation (12)) does not presently include a contribution from the so-called free volume effect[13]. As the average repeat unit of the EMAA copolymer increases with decreasing MAA content, the contribution per unit volume from $\Delta G_H/RT$ decreases. Thus it follows that the absolute value of the favourable (negative) contributions to the free energy of mixing from combinatorial entropy and hydrogen bonding becomes progressively smaller. It is therefore possible to conceive of a case where the value of χ is fortuitously very close or equal to zero and where we would predict molecular mixing with only a very small total negative free energy of mixing. Here, the unfavourable free volume contribution could be dominant and overwhelming. Accordingly, the results of our subsequent calculations for the minimum number of interaction sites necessary for molecular mixing will be underestimated to some degree and must be tempered by the statement 'in the absence of free volume effects'.

As we have shown above, we can estimate K_B for hypothetical EMAA copolymers containing different concentrations of MAA units from experimental infrared data derived from one specific EMAA copolymer (equation (10)). In addition, the corresponding K_A can be estimated using the experimentally obtained value of the parameter Z $(=K_A/K_B)$. Estimates of δ, χ, and V_B are readily determined from the structure of the average repeat unit (*Tables 4* and *5*). We are now in a position to perform theoretical calculations of spinodal phase diagrams corresponding to the hypothetical EMAA–PEO blends. These are displayed in *Figures 10* and *11*.

Above about 70% MAA the results predict that the blends are multiphased at temperatures above ambient through to about 200–300°C over a wide composition range (*Figure 10*). Between about 10 and 50 weight % MAA no spinodal information is calculated indicating that the blends with PEO are miscible over a wide range of temperatures (theoretically, −100–500°C). At the other extreme, hour glass shaped spinodals are calculated for PEO blends with EMAA copolymers containing less than about 5% MAA (*Figure 11*). We conclude, therefore, that about 6–8 weight % MAA is the lower limit in EMAA copolymers that is necessary to ensure significant molecular mixing with PEO in the amorphous state. In addition, we conclude from our calculations that the corresponding upper limit is about 70 weight % MAA. Hence, there is a window of miscibility from about 6 to 70 weight % EMAA where blends with PEO are mixed at the molecular level.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation, Polymers Program and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also wish to acknowledge the support and assistance of Drs Barbara Varnell and Peter Plimmer of the E.I. du Pont de Nemours Co.

REFERENCES

1 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 570

2 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 580

3 Coleman, M. M., Lichkus, A. M., Serman, C. J. and Painter, P. C. *Macromolecules* 1989, **22**, 586

4 Coleman, M. M., Hu, J., Park, Y. and Painter, P. C. *Polymer* 1988, **29**, 1659

5 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 346

6 Sandler, S. R., Karo, W., 'Polymer Synthesis', Vol. II, Academic Press, New York, 1977

7 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228

8 Lee, J. Y., Ph.D. Thesis, The Pennsylvania State University, 1988

9 van Krevelen, P. W. 'Properties of Polymers', Elsevier, Amsterdam, 1972

10 Hoy, K. L. *J. Paint Technol.* 1970, **42**, 76

11 Kraus, S. *J. Macromol. Sci., Revs. Macromol. Chem.* 1972, **C7**, 251

12 Pimentel, G. C. and McClellan, A. L. 'The Hydrogen Bond', W. H. Freeman and Co., London, 1960

13 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690