A completely miscible ternary blend: poly(methyl methacrylate)–poly(epichlorohydrin)–poly(ethylene oxide)

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The polymer pair poly(epichlorohydrin) (PECH) and poly(ethylene oxide) (PEO) is shown to form completely miscible blends based on the observation of a single glass transition temperature (T_g) by differential scanning calorimetry and lower critical solution temperature (*LCST*) behaviour. Since poly(methyl methacrylate) (PMMA) is known from earlier work to form miscible binary blends with PECH and with PEO, then a ternary system (PMMA–PECH–PEO) has been identified for which all three binary pairs are miscible. Examination of ternary blends for T_g and *LCST* behaviour revealed that complete miscibility exists over the entire ternary composition diagram. Heats of mixing for binary mixtures of liquids whose molecular structures are analogues of the polymers are reported in order to understand better the nature of the interactions operative in each of the binary blends. It is seen that oligomeric analogues for poly(ethylene oxide) give misleading results when they have hydroxyl end groups.

(Keywords: binary blend; ternary blend; miscibility; heats of mixing; lower critical solution temperature)

Examination of the recent literature reveals a rapid growth in the number of pairs of polymers known to form miscible binary blends[1]. Recently there has been some interest in the thermodynamic phase behaviour of ternary blends restricted primarily to a few cases where two of the binary pairs (A + B and A + C) are miscible but the third binary (B + C) is not[2-4]. Generally, the issue in the latter case is to learn how much of polymer A must be added to create a miscible mixture containing both B and C (which are immiscible with each other). To our knowledge, no examples have been reported of ternary polymer blends where all three binary pairs are miscible. For such a system, an immediate question to be answered is whether all ternary compositions form miscible blends, since closed-loop regions of immiscibility are known for polymer–polymer–solvent ternary mixtures where all three binaries are miscible[5-8].

This paper reports an example of a ternary blend where each binary is miscible and examines the entire ternary composition diagram to learn whether the possible closed-loop region of immiscibility exists for this system. The techniques employed for this purpose include differential scanning calorimetry (d.s.c.) for glass transition behaviour and optical observations for phase separation on heating or lower critical solution temperature (*LCST*) behaviour. Heats of mixing for low molecular weight liquid analogues of the polymer repeat units are used to understand more about the interactions responsible for miscibility of the three binary pairs[9-12].

The ternary system involves poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO) and poly(epichlorohydrin) (PECH). The pair PMMA–PEO is well known to be miscible, and numerous studies of this system have appeared in the literature[13-23]. A recent paper from this laboratory documents the miscibility of the PMMA–PECH pair[24]; however, all evidence suggests that the interaction causing miscibility is relatively weak. The fact that PECH and PEO form a miscible pair is a more recent discovery in our laboratory. The evidence for this conclusion is presented here.

MATERIALS AND PROCEDURES

The three polymers used in this work are identified in *Table 1* along with their sources and various characterization information. Binary and ternary polymer blends were prepared by casting from methylene chloride solutions. Blend films with the desired amounts of each component were cast by pouring the solution, total polymer concentration of about 5% by weight, into disposable aluminium pans which were then covered with perforated foil. The solvent was allowed to evaporate at room temperature for 2 days. The resulting films were held under vacuum at 80°C for one week in order to remove any residual solvent and then slowly cooled to room temperature.

A Perkin-Elmer DSC-2 equipped with a thermal analysis data station was used to obtain thermal transition behaviour of the blends. Glass transition temperature (T_g) measurements were conducted on the cast film after first heating to 97°C for 5 min to melt any PEO crystallinity followed by quenching to -133°C. A separate series of experiments using cyclic heating to 87°C for 5 min and cooling at 32°C min^{-1} to a specified crystallization temperature for 10 min were used to obtain information for melting point depression analysis. A heating rate of 20°C min^{-1} was used in all cases.

Lower critical solution temperature (*LCST*) behaviour was observed by using a procedure previously reported[25]. A heating rate of about 5°C min^{-1} was employed in this measurement, and cloud point temperatures were taken as the mean value for three runs.

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Table 1 Polymers used in this study

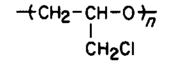
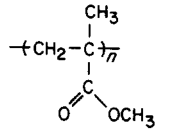
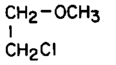
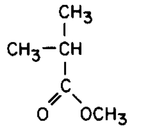
Abbreviation	Polymer	Structure	Molecular weight	T_g (°C)	Source
PECH	Poly(epichlorohydrin)	 $-\!(CH_2-\underset{\substack{\vert\\ CH_2Cl}}{CH}-O)_n-$	$\bar{M}_n=2.83\times10^5$ $\bar{M}_w=5.55\times10^5$	-23	B. F. Goodrich Co. (Hydrin 100)
PEO	Poly(ethylene oxide)	$-\!(CH_2-CH_2-O)_n-$	$\bar{M}_w=3.0\times10^5$	-61	Aldrich Chem. Co.
PMMA	Poly(methyl methacrylate)	 $-\!(CH_2-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ C\\ /\!/\ \ \backslash\\ O\quad OCH_3}}{C}})_n-$	$\bar{M}_n=5.29\times10^4$ $\bar{M}_w=1.3\times10^5$	105	Rohm and Haas Co. (Plexiglas V(811))

Table 2 Analogues used in this study[a]

Abbreviation	Compound	Structure	Density (g cm^{-3})	*MW*	B.p. (°C)
CEME	2-Chloroethyl methyl ether	 $\underset{\substack{\vert\\ CH_2Cl}}{CH_2}-OCH_3$	1.035	94.5	89–90
MIB	Methyl isobutyrate	 $CH_3-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ C\\ /\!/\ \ \backslash\\ O\quad OCH_3}}{CH}}$	0.891	102.1	90
TGME	Tetraethylene glycol dimethyl ether	$CH_3O\!-\!(CH_2CH_2O)_4\!-\!CH_3$	1.009	222.3	275–276
PGM	Poly(ethylene glycol methyl ether)[b]	$CH_3O\!-\!(CH_2CH_2O)_{(7)}\!-\!H$	1.094	350 (avg.)	–
PEG	Poly(ethylene glycol)[b]	$HO\!-\!(CH_2CH_2O)_{(4)}\!-\!H$	1.125	200 (avg.)	–

[a] All chemicals were obtained from the Aldrich Chemical Corporation

[b] Subscript corresponds to average degree of polymerization

Heats of mixing ΔH_{mix} and binary interaction parameters B for low molecular weight analogues of the corresponding polymer were measured at 30 ± 0.1°C using an LKB model 2197 batch microcalorimeter. *Table 2* gives a list of the analogue compounds used in this study. In these experiments the cells were dried thoroughly before adding the two liquids whose exact proportions were determined by weighing injection syringes.

RESULTS FOR PECH-PEO BINARY BLENDS

Thermal behaviour for blends of PECH and PEO are described in this section, which documents that this binary pair is completely miscible for all compositions. Binary blends rich in PECH were optically transparent at room temperature; however, at higher PEO contents the blends became increasingly less transparent owing to PEO crystallinity. All blends were transparent just above the melting point of PEO. D.s.c. thermograms (second heat) shown in *Figure 1* revealed a single glass transition temperature which varied with overall blend composition as indicated by the full circles in *Figure 2*.

Figure 1 also shows the melting endotherm for PEO and a crystallization exotherm which occurred for blends rich in PECH. The upper line in *Figure 3* shows the heat of fusion for the PEO, based on total sample mass, during a first heat. The melting endotherm for a second heat was somewhat smaller (open circles in *Figure 3*). The heat of crystallization during second heats is also shown in *Figure 3* as negative values. This quantity goes to zero at low PEO contents as expected and also at high PEO contents since crystallization was sufficiently rapid to occur completely during cooling after the first heat. The algebraic sum of the second scan values for the heats of crystallization and melting, i.e. $\Delta H_f+\Delta H_c$, is also shown in *Figure 3* since this is indicative of the amount of crystallinity that existed while heating through the glass transition region[26,27]. This fractional crystallinity X_c was

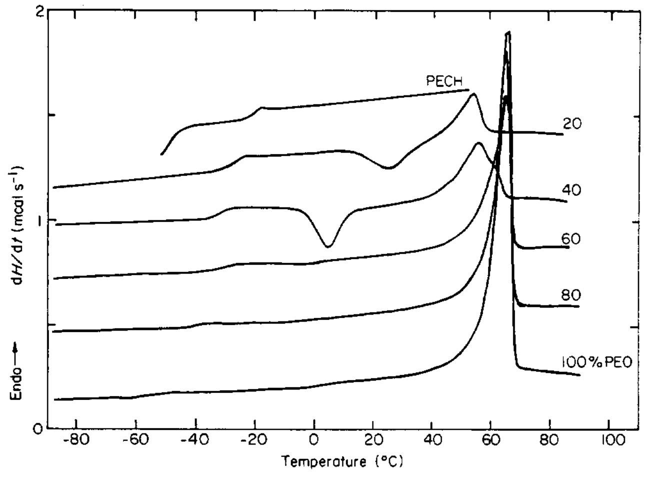


Figure 1 D.s.c. thermograms for binary poly(epichlorohydrin)–poly(ethylene oxide) blends

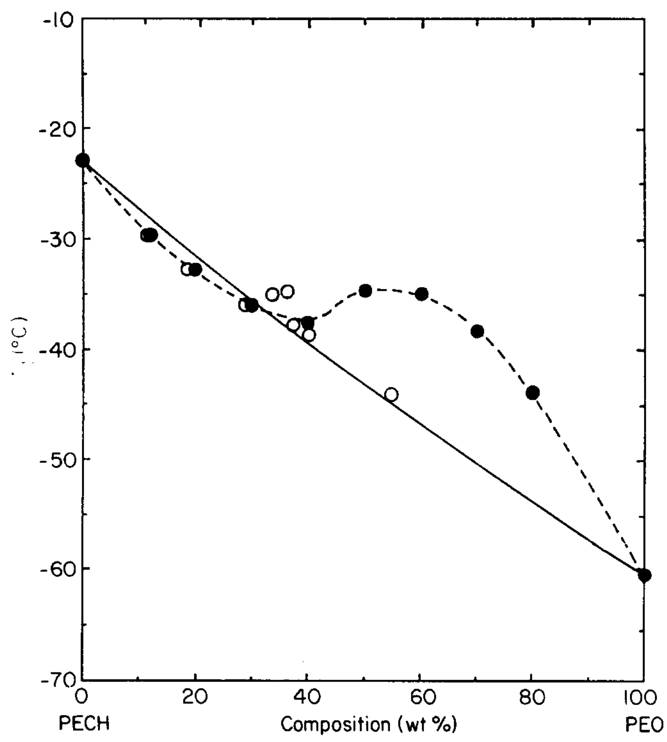


Figure 2 Glass transition temperatures for PECH–PEO blends plotted *versus* overall blend composition (●) and *versus* calculated amorphous phase composition (○). Full curve is Fox equation prediction

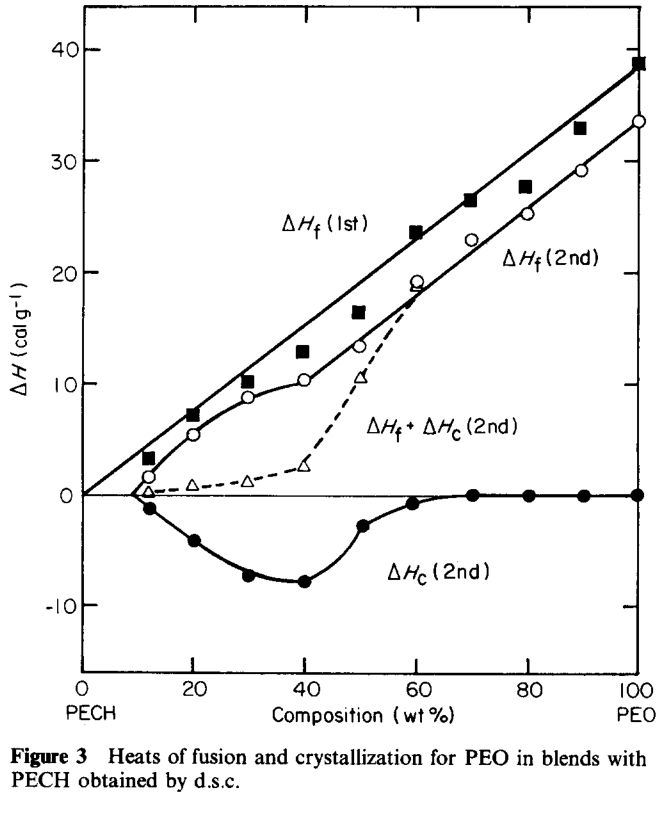


Figure 3 Heats of fusion and crystallization for PEO in blends with PECH obtained by d.s.c.

computed from:

$$X_c = \frac{\Delta H_f + \Delta H_c}{\Delta H_f^\circ} \tag{1}$$

where $\Delta H_f^\circ = 45\,\mathrm{cal\,g^{-1}}$ is the heat of fusion for 100% crystalline PEO[28]. Because of this crystallinity, the weight fraction of PEO in the amorphous phase, W', does not equal the overall weight fraction of PEO in the blend, W. These quantities are related by[27]:

$$W' = \frac{W - X_c}{1 - X_c} \tag{2}$$

The open circles in *Figure 2* represent a replot of the T_g values *versus* the amorphous fraction of PEO. These data conform well to the Fox equation whereas the plot *versus* overall PEO content does not. The latter shows a maximum similar to that noted for other systems[26,27] where crystallization significantly alters the composition of the amorphous phase.

Figure 4 shows the PEO melting point as a function of crystallization temperature T_c for several blends. These linear relations were extrapolated to $T_m = T_c$, as suggested by Hoffman and Weeks[29], to obtain an equilibrium melting point for each composition. The equilibrium melting points estimated by the extrapolation procedure are plotted in *Figure 5*, as suggested by the Nishi–Wang equation[30–32]:

$$(1 - T_m/T_m^\circ) = -B\phi_1^2(V_{2u}/\Delta H_{2u}) \tag{3}$$

to obtain the interaction parameter B. In this equation, T_m° is the melting temperature of the pure crystalline PEO, T_m is the value for a blend containing ϕ_1 volume fraction of the amorphous component, and $(\Delta H_{2u}/V_{2u})$ characterizes the heat of fusion per unit volume for 100% crystalline PEO. The latter was computed from the following literature values[33]: $V_{2u} = 38.9\,\mathrm{cm^3\,mol^{-1}}$ and $\Delta H_{2u} = 2100\,\mathrm{cal\,mol^{-1}}$. The slope of the linear relation in *Figure 5* gives a value for B of $-0.94\,\mathrm{cal\,cm^{-3}}$. Note that this line does not extrapolate to zero melting point

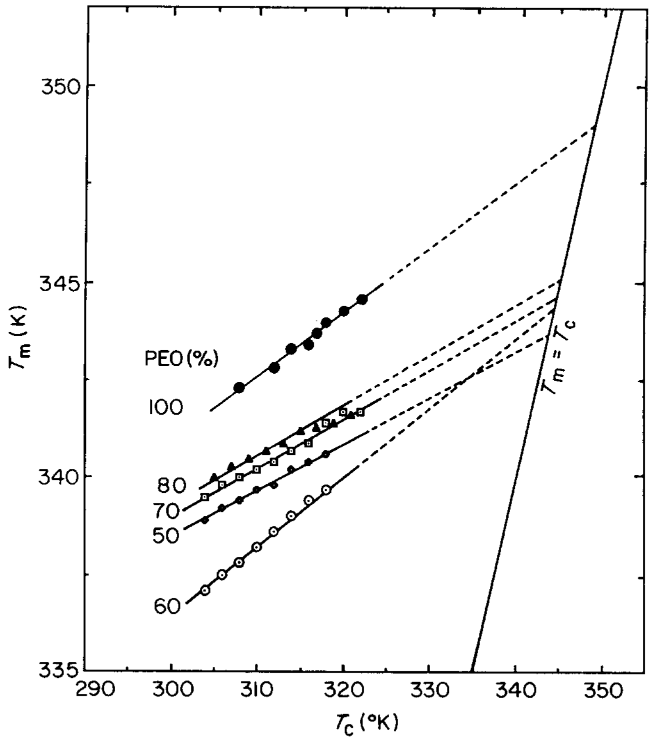


Figure 4 Hoffman–Weeks plot to obtain equilibrium melting point for PEO in blends with PECH. All samples quenched from 360 K to T_c

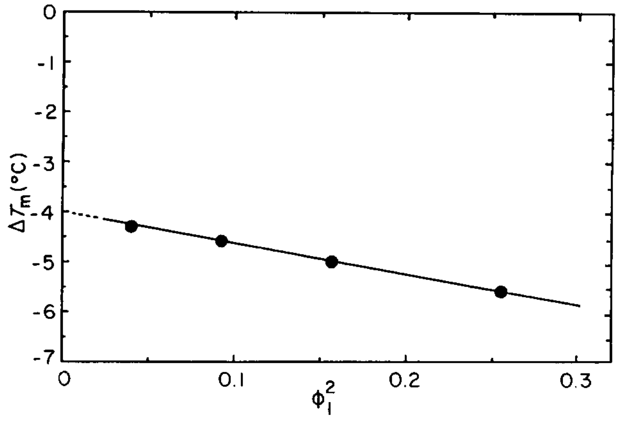


Figure 5 Melting point depression analysis to obtain interaction parameter B for PEO–PECH blends. Slope gives $B = -0.94 \text{ cal cm}^{-3}$

depression as $\phi_1 \rightarrow 0$. Finite intercepts of this type have been noted in other cases[34] and may result from a variety of issues.

PECH–PEO blends exhibited phase separation on heating or *LCST* behaviour. The cloud points are shown later (centre panel of *Figure 8*).

Based on all of the above, it is evident that PECH–PEO blends are entirely miscible.

RESULTS FOR TERNARY BLENDS

The primary reason for examining blends containing all three of the polymers (PMMA, PECH and PEO) was to learn whether miscibility exists over the entire ternary composition diagram. Ternary glass transition and *LCST* behaviour were investigated for this purpose.

First, it is useful to summarize the T_g and cloud point data for the various binaries in the graphical manner shown in *Figures 6* and *7*, which amounts to unfolding the

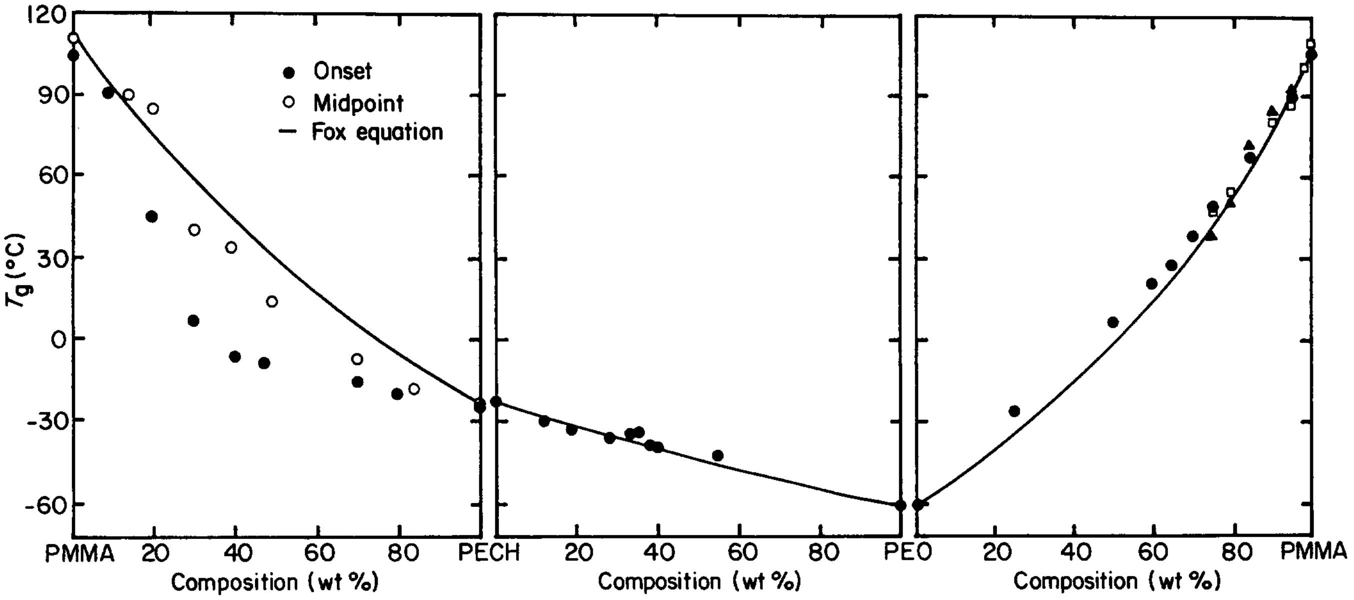


Figure 6 Summary of glass transition behaviour for the three binary blend systems. Data for PMMA–PECH from ref. 24. Data for PECH–PEO from *Figure 2*. Data for PMMA–PEO from ref. 13 (▲), ref. 24 (□) and ref. 21 (●)

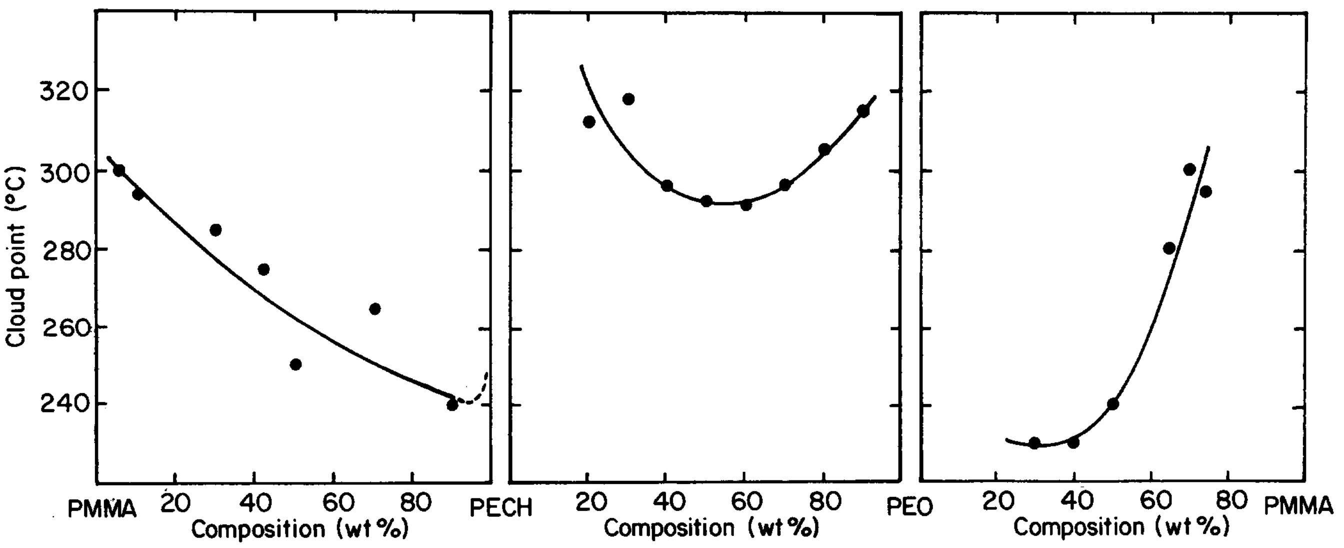


Figure 7 Cloud point curves for the three binary blend systems. Data for PMMA with PECH and PEO from ref. 24. Data for PECH–PEO from present work

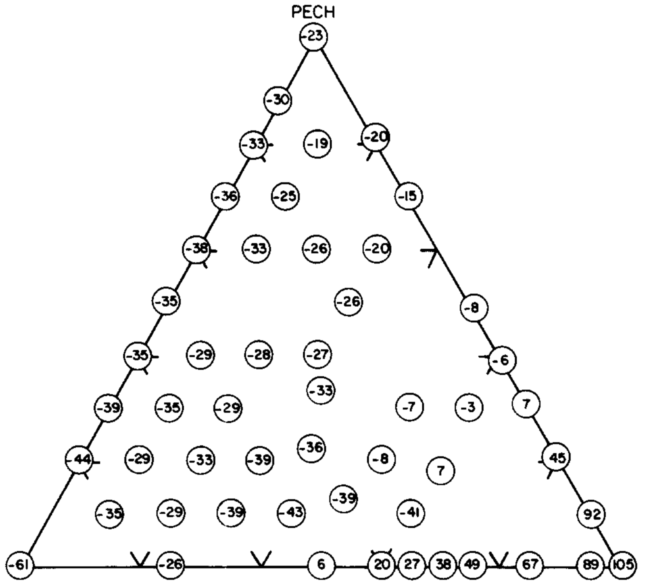


Figure 8 Glass transition temperatures (in °C) for ternary blends as determined by d.s.c. using onset method. Only one value observed for each composition

three binary planes of a three-dimensional ternary diagram. The glass transitions by d.s.c. for PMMA–PECH blends[24] are very broad so we show values for T_g defined by both the onset and midpoint methods. The former depart markedly from the Fox equation while the latter conform somewhat more closely with this prediction. The PECH–PEO data are those from *Figure 2* after correction for the change in amorphous phase composition by crystallinity. Without this adjustment, these results do not agree well with the Fox equation as noted earlier. The data for PEO and PMMA were taken from several sources[13,21,24]. It is usually difficult to obtain T_g data over the entire composition range for this system owing to PEO crystallinity. However, one of these data sets spans nearly the entire range, and since these results agree rather well with the Fox prediction, it would appear that they have been adjusted for the effect of PEO crystallinity on composition although this is not mentioned in the original reference[21]. In summary, the ternary system is complicated by PEO crystallinity and the breadth of the transitions for the PMMA–PECH binary. For these reasons, the T_g surface for ternary mixtures would not be expected to conform to any simple relation like an extended Fox equation without extensive consideration of each of these issues, which was beyond the scope of our investigation.

All ternary compositions gave a single T_g by d.s.c. and these values are digitally recorded on the ternary diagrams in *Figure 8*. The values represent determinations by the onset method and are positioned at the overall blend composition without adjustment to give the amorphous phase composition. For the reasons outlined above, the surface defined by these data is complex in shape. However, the central point is that each composition has only one T_g (within the sensitivity of the d.s.c.) located at a temperature in the general vicinity that might be expected for a miscible system.

As seen in *Figure 7*, all three binaries exhibit *LCST* behaviour with the PECH–PEO pair (present data) showing the highest cloud points. The data for the PMMA–PECH and PEO–PMMA pairs have been reported previously[24]. All ternary compositions were clear just above the PEO melting point but became cloudy on further heating at the temperatures recorded digitally in *Figure 9*. The surface defined by these data is also complex and no attempt is made here to model it or to represent it graphically.

From all of the evidence given above we conclude that this ternary system forms miscible mixtures for all compositions.

BINARY HEATS OF MIXING FOR LIQUID ANALOGUES

Previous work has shown that the heat of mixing of liquids having molecular structures analogous to units in the polymer chains can yield useful information about the interactions that drive miscibility in blends[9–12]. *Table 2* lists such analogues for the three polymers of interest here. Methyl isobutyrate (MIB) was selected to model PMMA while the three oligomeric glycols have repeat units like that in PEO. The latter differ from each other in the important regard of their end groups. The poly(ethylene glycol) (PEG) has hydroxyl groups at both ends, poly(ethylene glycol methyl ether) (PGM) has a hydroxyl group at one end, while tetraethylene glycol methyl ether (TGME) has no hydroxyl end groups. Heats of mixing for each of the latter three liquids were measured with MIB, and the results are shown in *Figure 10* in terms of the interaction parameter computed from:

$$\Delta H_{\text{mix}} = B\phi_1\phi_2 \tag{4}$$

where ϕ_1 is the volume fraction of component 1. Interestingly, the oligomers having hydroxyl end groups exhibited endothermic mixing with MIB while the compound without any hydroxyl groups mixes exothermically. We speculate that the former behaviour is the result of self-association in the pure liquids via hydrogen bonding that is broken up (an endothermic process) by mixing with MIB and this outweighs the

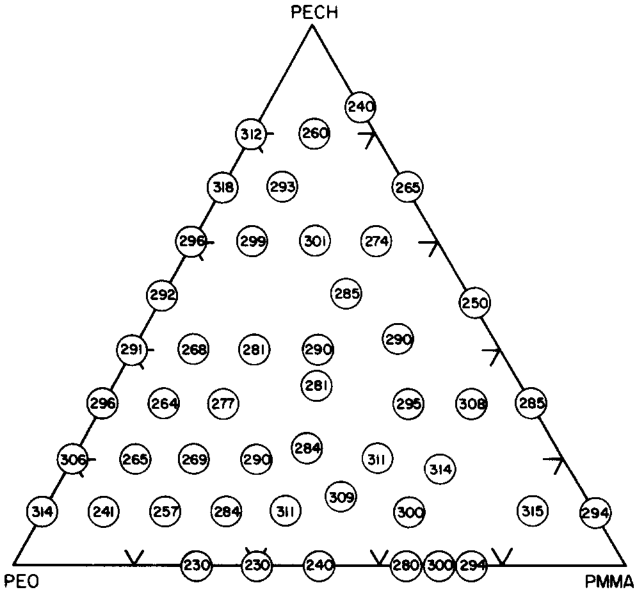


Figure 9 Cloud point temperatures (in °C) for ternary blends

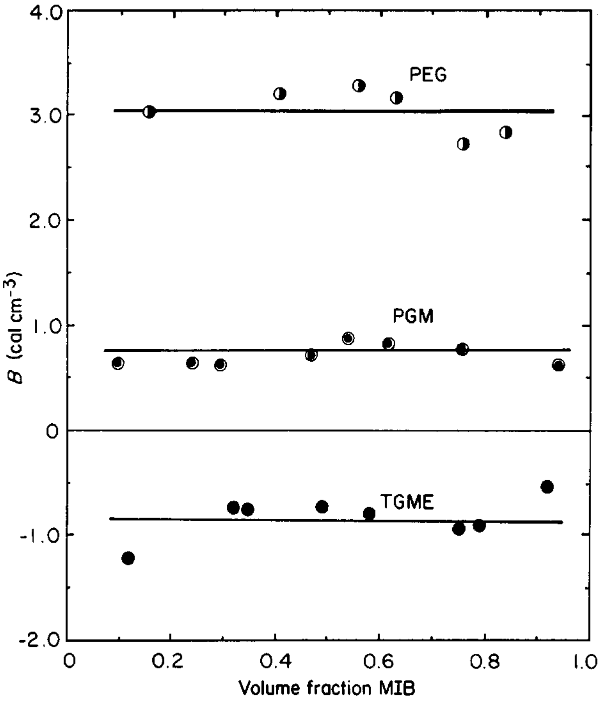


Figure 10 Binary interaction parameters computed from heat of mixing, using equation (4), for mixing MIB with various oligomeric analogues of PEO (see *Table 2* for abbreviations)

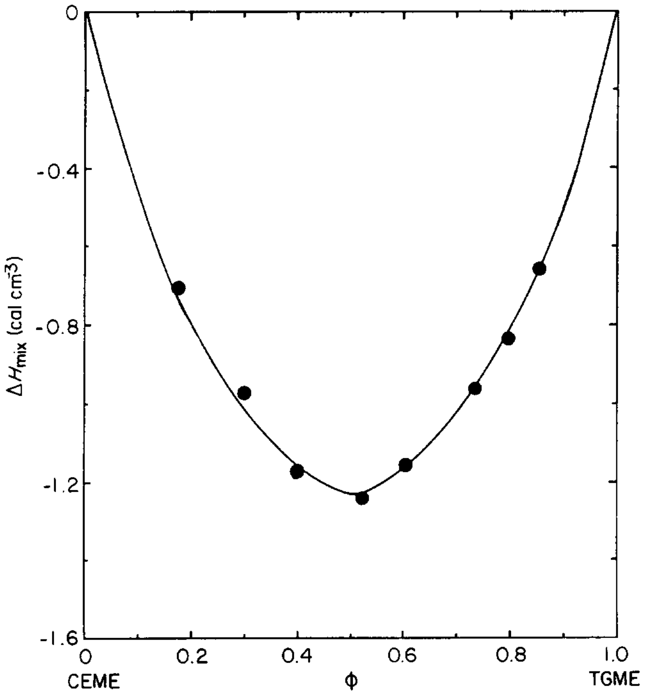


Figure 11 Heat of mixing of CEME and TGME (see *Table 2* for abbreviations)

exothermic interaction of their repeat units with MIB to give a net endothermic mixing. This hypothesis is supported by the nearly constant positive increment in the interaction energy density *B* by going from zero to one and then to two hydroxyl end groups. Clearly, TGME is a more realistic analogue for the high molecular weight PEO, which has a very low content of hydroxyl groups on a mass or volumetric basis, if any at all. These results point out the extreme importance of end groups when using oligomers or calorimetric analogues for polymers.

The results for the analogue pair TGME–MIB demonstrate that there is an exothermic interaction to drive miscibility of the polymer pair PEO and PMMA. The interaction energy density derived from model compounds is just under $-0.9\,\mathrm{cal\,cm^{-3}}$.

2-Chloroethyl methyl ether (CEME) was selected as an approximate analogue for poly(epichlorohydrin). The liquid pair CEME–TGME gave a strong exothermic heat of mixing as shown by the data in *Figure 11*. This suggests that an exothermic interaction is also the basis for miscibility of blends of PECH and PEO. In contrast, CEME and MIB mix in a mildly endothermic manner as shown in *Figure 12*. If these liquids are accurate calorimetric analogues for PECH and PMMA, then the basis for miscibility of the latter polymer pair must be entropic in origin rather than an exothermic interaction. Evidence described previously[24] suggests that the net driving force for miscibility of the PECH–PMMA pair is weak. Whether the interaction in the blend is actually endothermic, as the analogue results suggest, or a very small exothermic value is not known presently. An answer to this difficult question would be valuable as it would help assess the degree to which the selected analogues actually model interactions in the blend. Two approaches can be suggested for future work on this issue. If the polymer–polymer interaction is indeed endothermic, then the blends should phase-separate if the polymer molecular weights are increased significantly. Tracking *LCST* behaviour as a function of molecular weight might be a most useful avenue. On this point, one must realize that if the interaction is positive then other factors like equation-of-state effects[12] must be significant because of the *LCST* behaviour noted. Further information could be obtained by selection of alternative analogues that differ slightly from the ones used, to gauge the sensitivity of their choice. In any case, it is clear that

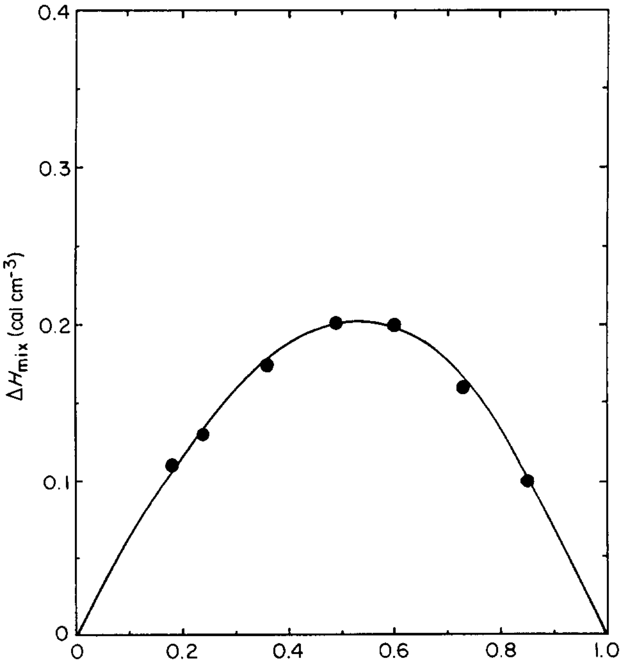


Figure 12 Heat of mixing MIB with CEME (see *Table 2* for abbreviations)

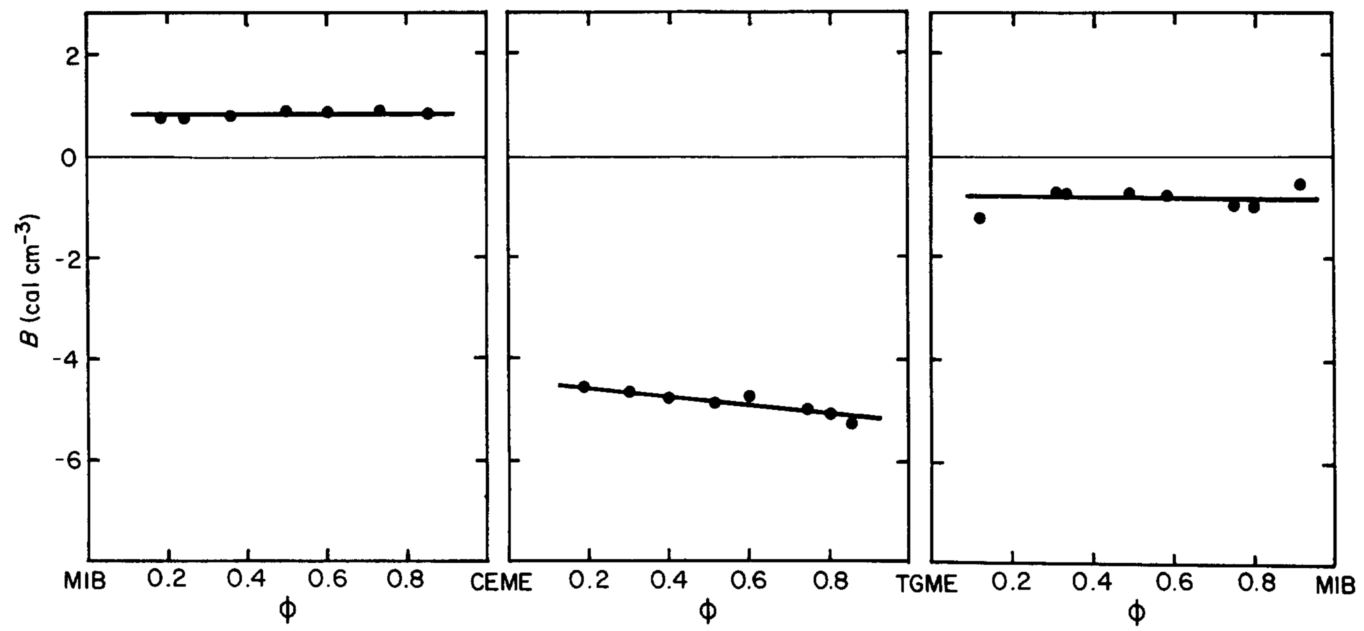


Figure 13 Summary of interaction parameters, estimated from heats of mixing of analogues, for each binary blend system

the enthalpic interactions in PECH–PMMA blends are quite weak.

Figure 13 provides a useful summary of the calorimetric data by showing interaction parameters for all those binaries on the same scale. Clearly the interactions for the PMMA–PECH (analogues MIB–CEME) and the PEO–PMMA (analogues TGME–MIB) pairs are weak relative to the PECH–PEO (analogues CEME–TGME) pair. It is interesting to note that the cloud points shown by *Figure 7*, in a similar representation, reflect this trend, as might be expected[34].

SUMMARY

On the basis of glass transition temperature and *LCST* behaviour, binary blends of poly(ethylene oxide) and poly(epichlorohydrin) have been shown to be miscible, i.e. a single amorphous phase is formed for all blend proportions. Since poly(methyl methacrylate) was previously known to be miscible with both polymers, the possibility for a first example of a completely miscible ternary blend system arose. Similar studies demonstrate that miscibility does indeed exist across the entire ternary composition diagram for the system PMMA–PECH–PEO.

Heats of mixing for binary pairs of low molecular weight liquids with structures analogous to the three polymers confirm exothermic mixing as the basis for miscibility of the polymer pairs PEO–PMMA and PEO–PECH. However, similar results suggest that the interaction for the PECH–PMMA pair is very weak and possibly endothermic. To model PEO, it was found very important to select oligomers without any hydroxyl end groups since self-association effects in the pure oligomers completely masks the interaction between unlike repeat units.

The analogue calorimetry results do not agree well with estimates of interaction parameters made for blends using melting point depression analysis. For the PEO–PECH system, calorimetry gave a value of about -5 cal cm^{-3} while the melting point technique gives -0.94 cal cm^{-3}. For the PEO–PMMA case, calorimetry gives about -0.9 cal cm^{-3} while values from melting point depression range from -1.0 to -2.8 cal cm^{-3} (refs. 14, 20 and 24). Since neither PMMA nor PECH crystallize, no comparison for this system is possible. At this point, no definitive rationalization of the disparities between the two approaches for estimating interaction strengths is available, but this issue is being actively explored.

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