Thermodynamics of oligomeric binary mixtures of polyethylene glycol and polypropylene glycol methylethers

G. Allen, Z. Chai†, C. L. Chong, J. S. Higgins and J. Tripathi*
Department of Chemical Engineering and Chemical Technology, Imperial College, London, SW7, UK
(Received 19 January 1983; revised 15 June 1983)

Measurements are reported of the heats of mixing and cloud point curves of binary mixtures of methoxylated polyethylene glycol with methoxylated polypropylene glycol. The data are discussed in terms of the Flory equation of state theory and it is shown that both a temperature and concentration dependent X_{12} parameter and a Q_{12} term are required.

Keywords Thermodynamics; polymers; blends; polyethylene glycol; polypropylene glycol; phase diagram

INTRODUCTION

There is renewed interest in the thermodynamic study of polymer mixtures both from experimental and theoretical points of view. The Flory equation of state accounts for the properties of mixtures on the basis of both the disparity between the equations of state of the pure components and interactions between these species. The theory can describe qualitatively the appearance of *LCST* and *UCST*, the change in volume on mixing and many other properties of the mixture. There is, however, a paucity of accurate experimental data obtained on well-characterized polymer pairs for comparison with theory.

Oligomer mixtures offer some advantage over polymer pairs of high molecular weight. For example, the heats of mixing and cloud point curves of the mixtures can be determined more precisely. However, one disadvantage is that some features of high molecular weight blends may be inaccessible in an oligomer mixture because the *LCST* may be moved to a very high temperature at which the chains become thermally unstable.

In this paper we report measurements on binary mixtures of methoxylated polyethylene glycol (PEGM) and methoxylated propylene glycol (PPGM). This system has already been studied extensively by Booth *et al.*[1,2]. They based the discussion of their results mainly on the Flory–Huggins theory, using a concentration-dependent interaction parameter χ. Some features of the phase behaviour were further examined using the Flory equation of state theory.

THEORY

In the notation as given in the Appendix, the Flory equation of state theory[3,4] gives the following relationships for the free energy of mixing, the heat of mixing and the chemical potential at pressure $p=0$:

$$
\begin{aligned}
\text{‘}G_{\mathrm{m}} &= RT(n_1 \ln \phi_1 + n_2 \ln \phi_2) \\
&\quad + 3\bar{r}Nv^*\left[\phi_1 P_1^* \tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3}-1}{\tilde{v}^{1/3}-1} + \phi_2 P_2^* \tilde{T}_2 \ln \frac{\tilde{v}_2^{1/3}-1}{\tilde{v}^{1/3}-1}\right] \\
&\quad + \bar{r}Nv^*\left[\frac{\phi_1 P_1^*}{\tilde{v}_1} + \frac{\phi_2 P_2^*}{\tilde{v}_2} - \frac{P^*}{\tilde{v}}\right]
\end{aligned}
\tag{1}
$$

$$
\Delta H_{\mathrm{m}} = \bar{r}Nv^*\left[\phi_1 P_1^*\left(\frac{1}{\tilde{v}_1}-\frac{1}{\tilde{v}}\right) + \phi_2 P_2^*\left(\frac{1}{\tilde{v}_2}-\frac{1}{\tilde{v}}\right) + \phi_1\theta_2 X_{12}/\tilde{v}\right]
\tag{2}
$$

$$
\begin{aligned}
\Delta\mu_1 &= \left(\frac{\partial \Delta G_{\mathrm{m}}}{\partial \mathrm{n}_1}\right)_{T,P,n_2} = RT\left[\ln \phi_1 + \left(1-\frac{r_1}{r_2}\right)\phi_2\right] \\
&\quad + P_1^* V_1^*\left[3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3}-1}{\tilde{v}^{1/3}-1} + \left(\frac{1}{\tilde{v}_1}-\frac{1}{\tilde{v}}\right)\right] + \frac{V_1^* X_{12}\theta_2^2}{\tilde{v}}
\end{aligned}
\tag{3}
$$

with

$$
P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2 X_{12}
\tag{4}
$$

$$
\frac{1}{T^*} = \frac{1}{P^*}\left(\frac{\phi_1 P_1^*}{T_1^*} + \frac{\phi_2 P_2^*}{T_2^*}\right)
\tag{5}
$$

and the segment fraction ϕ and the interaction site fraction θ as

$$
\phi_2 = 1-\phi_1 = r_2 N_2/\bar{r}N
\tag{6}
$$

$$
\theta_2 = 1-\theta_1 = S_2\phi_2/(S_1\phi_1 + S_2\phi_2)
\tag{7}
$$

where

$$
\bar{r}Nv^* = r_1 N_1 v_1^* + r_2 N_2 v_2^*, \qquad v^* = v_1^* = v_2^*
\tag{8}
$$

In equation (3) the second and third terms are called the residual chemical potential $\Delta\mu_1^{\mathrm{R}}$.

At the phase boundary the binodal is defined as

$$
\Delta\mu_1 = \Delta\mu_1' \quad \text{and} \quad \Delta\mu_2 = \Delta\mu_2'
\tag{9}
$$

---

† Institute of Chemistry, Academua Sinica, Beijing, China.
* J. Tripathi died shortly after his return to India.

0032-3861/84/020239-06$03.00

and the spinodal as

$$\left(\frac{\partial(\Delta\mu_1/RT)}{\partial\phi_2}\right)_{T,P}=0 \qquad (10)$$

and the critical point

$$\left(\frac{\partial^2(\Delta\mu_1/RT)}{\partial\phi_2^2}\right)_{T,P}=0 \qquad (11)$$

All the equations for the phase boundary can be seen in their original form in ref. 4.

In order to use the theory, the density d, the thermal expansion coefficient α and the thermal pressure coefficient γ of the pure components are needed to calculate the three characteristic parameters of the theory:

$$v_i^*=v_i/\{1+\alpha_i\mathrm{T}[3(1+\alpha_i T)]\}^3 \qquad (12)$$

$$T_i^*=T\tilde{v}_i^{4/3}/(\tilde{v}_i^{1/3}-1) \qquad (13)$$

$$P_i^*=\gamma_i T\tilde{v}_i^2 \qquad (14)$$

In the calculation, the dependence of these parameters on temperature T must also be considered:

$$d=d_0\exp(-\alpha_0\Delta T) \qquad (15)$$

$$\alpha=\alpha_0+\alpha_0^2(7+4\alpha_0 T)\Delta T/3 \qquad (16)$$

$$\gamma=\gamma_0-\gamma_0(1+2\alpha_0 T)\Delta T/T \qquad (17)$$

S_1/S_2 in the site fraction can be obtained from the crystallographic data or by projecting a molecular model or by the group contribution technique of Bondi for computing van der Waals molecular volume and surface area. X_{12} can be evaluated from the heat of mixing:

$$\Delta H_m=BN_1\phi_2 \qquad (18)$$

$$B=\lim_{\phi_2\to0}\left(\frac{\Delta H_m}{N_1\phi_2}\right)=\lim_{N_2\to0}\left(\frac{\Delta H_m}{N_2}\right)\left(\frac{V_1^*}{V_2^*}\right)$$

$$=\left(\frac{V_1^*}{\tilde{v}_1}\right)\left\{P_2^*\left[\frac{\tilde{v}_1}{\tilde{v}_2}-1-\alpha_1 T\left(1-\frac{\tilde{T}_2}{\tilde{T}_1}\right)\right]\right.$$

$$\left.+(1+\alpha_1 T)\left(\frac{S_2}{S_1}\right)X_{12}\right\} \qquad (19)$$

or the change of volume on mixing.

For the Flory–Huggins theory χ can be calculated from the residual chemical potential $\Delta\mu_1^R$.

$$\chi=\frac{\Delta\mu_1^R}{RT\phi_2^2}$$

$$=\frac{P_1^*V_1^*}{RT\phi_2^2}\left[3\tilde{T}_1\ln\frac{v_1^{1/3}-1}{\tilde{v}^{1/3}-1}+\left(\frac{1}{\tilde{v}_1}-\frac{1}{\tilde{v}}\right)\right]+\frac{V_1^*X_{12}\theta_2^2}{RT\tilde{v}\phi_2^2} \qquad (20)$$

To a first approximation the first term in equation (20) is the contribution from the equation of state. The second term is the interaction contribution. Because the reduced volume of the mixture, $\tilde{v}$, includes both contributions, a clean separation is impossible.

EXPERIMENTAL

Narrow molecular weight samples of the PEG and PPG obtained from Shell Chemicals Ltd. were methoxylated by the method described in ref. 1, the hydroxyl end group being reacted with methyl iodide in alkaline medium. Heats of mixing were measured in a modified NBS batch-type calorimeter, the construction of which has been described in detail elsewhere[5]. The calorimeter has a limiting accuracy of ±1% when calibrated by the acid-base neutralization reaction. The enthalpies of mixing of the oligomers were measured with a precision of ±4 to ±8% depending on the viscosities of the mixture according to composition and temperature. At low temperatures the oligomers become viscous which inhibits the mixing process, and thus lowers the precision.

Phase boundaries were determined by observing cloud points[6]. The oligomers were mixed at an elevated temperature to form a homogeneous solution. Each sample was then cooled at a fixed rate and the temperature at which the onset of turbidity occurred was measured. Various rates of cooling were employed and the cloud point was taken as the temperature at which theonset of turbidity is independent of the cooling rate.

RESULTS AND DISCUSSION

In *Table 1* all the parameters required for use in subsequent calculations of the phase behaviour of the binary mixtures are listed[1,7]. The parameters are either measured directly or computed from measurements of specific properties.

X_{12} was evaluated using equation (19) and the ΔH_m as a function of composition was simulated using these values. The value of X_{12} obtained for each pair was small. An independent estimate of X_{12} was calculated by fitting the ΔH_m values over the whole range of composition. The values of X_{12} thus determined directly from the calorimetric measurements are some 10% larger than those calculated from equation (19). The calculations were carried out for ΔH_m at 30°, 50° and 70°C as shown in *Figure 1*.

Using these data ΔG_m values were calculated and the results are shown in *Figure 2*. The curves obtained predict that, with the exception of PEGM 600/PPGM 400, each polymer pair should be immiscible at 30° and 50°C. However, the cloud point measurements in *Figure 3* show that all oligomer pairs are in fact miscible at these temperatures.

To make the calculated phase boundaries fit the experimental measurements we have to adopt the practice of Eichinger and Flory (3) and introduce the term

$$-TQ_{12}V_1^*\theta_2^2$$

into the equation for the residual chemical potential.

With the values of Q_{12} in *Table 1* the calculated phase boundaries have a best fit with the experimental cloud point. One example is given in *Figure 4*. The theory predicts a reasonable upper critical solution temperature and a correct range for phase separation. The calculated curves are always much narrower than the rather flat-toppedd cloud point curves. A similar discrepancy is often found if Flory–Huggins theory[8] is applied and can only be resolved by allowing X_{12} and/or Q_{12} to be concentration dependent. The fitting in any case shows the importance of the parameters Q_{12} for these systems.

Table 1 Parameters of PEGM 600 and various PPGMs at 30°C

		M	d (g cm^{-3})	α (x10^4/K)	γ (atm/K)	X_{12} (atm) 1	2	Q_{12} (atm/K)	x_H^0	x_S^0 3	4
PEGM	600	600	1.0718	7.8	15.35	–	–	–	–	–	–
PPGM	400	400	0.9551	8.7	9.97	112	130	−0.051	2.11	−0.34	−0.09
	1000	1000	0.9775	8.5	10.17	107	130	0.065	2.12	−0.36	−0.67
	1500	1500	0.9851	8.15	10.76	106	115	0.061	1.89	−0.34	−0.64
	2000	2000	0.9881	7.8	11.36	97	105	0.054	1.73	−0.33	−0.59

$S = S_1/S_2 = S_{\mathrm{PEGM}}/S_{\mathrm{PPGM}} = 1.08$

1, From equation (19); 2, from equation (2); 3, from equation (25); 4, from equation (25) + Q_{12} term

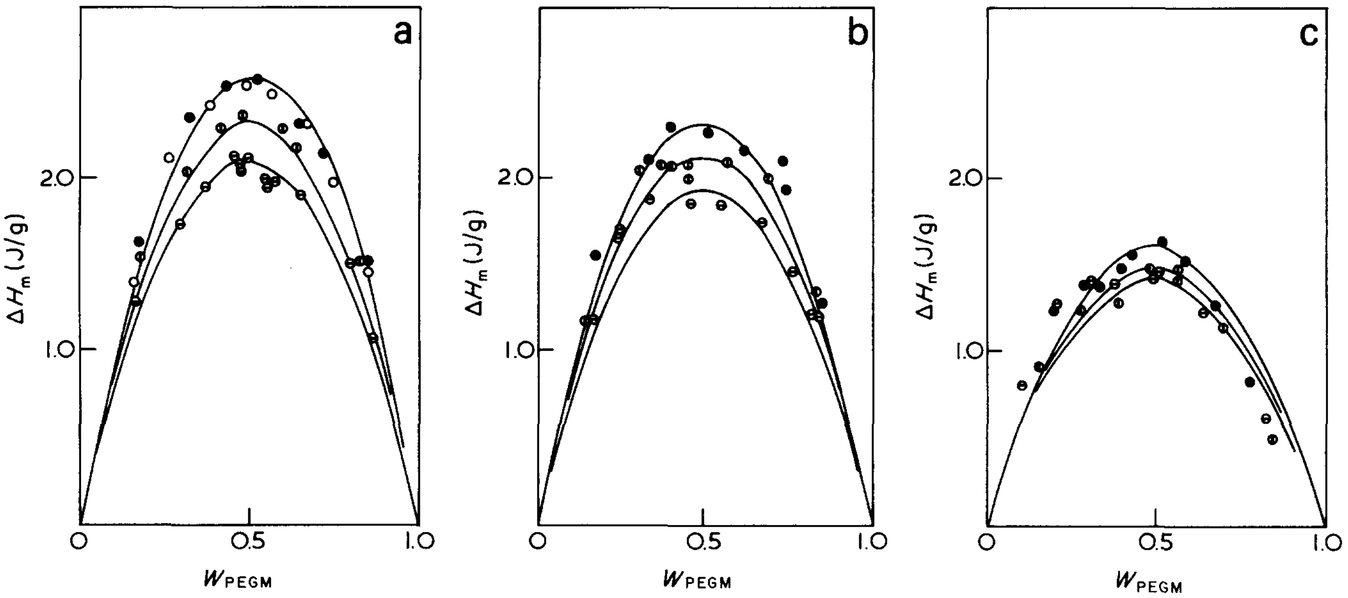

Figure 1 Heats of mixing of PEGM 600 with PPGM: (a) at 30.1°C; (b) at 50.1°C and (c) at 70.1°C. (○) PPGM 400; (●) PPGM 1000; (⦶) PPGM 1500 and (⊖) PPGM 2000. Theoretical curves are calculated from equation (2)

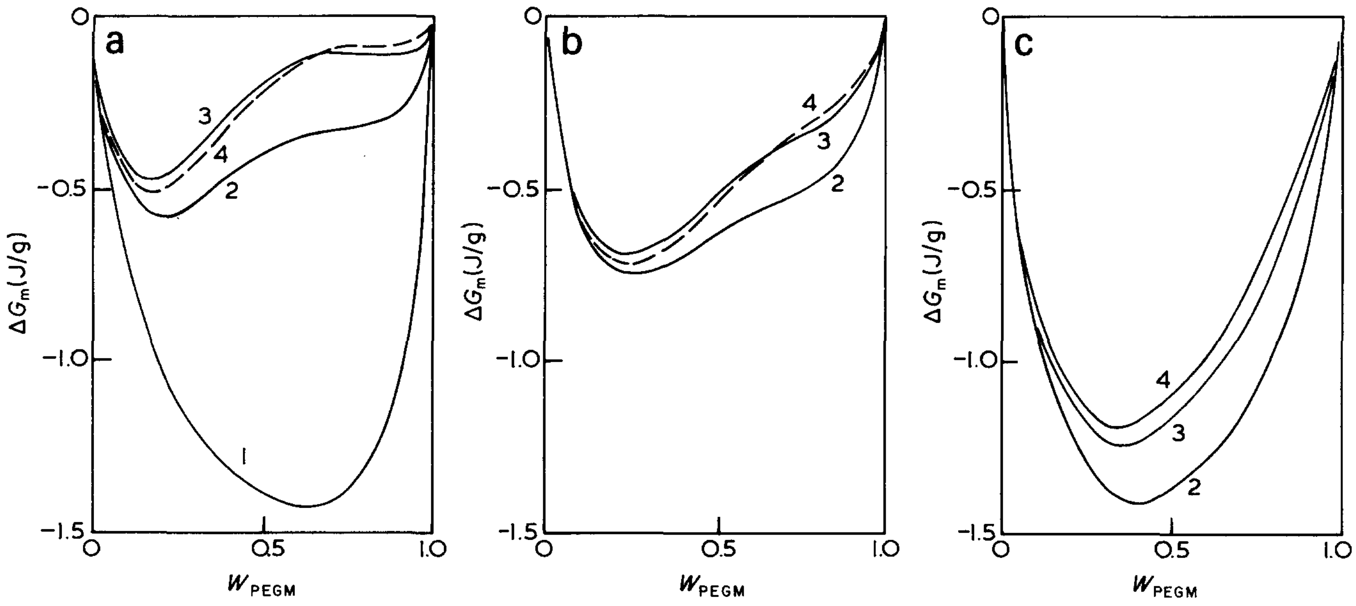

Figure 2 Free energies of mixing of PEGM 600 with PPGM: (a) at 30.1°C; (b) at 59.1°C and (c) at 70.1°C. (1) PPGG 400; (2) PPGM 1000; (3) PPGM 1500 and (4) PPGM 2000

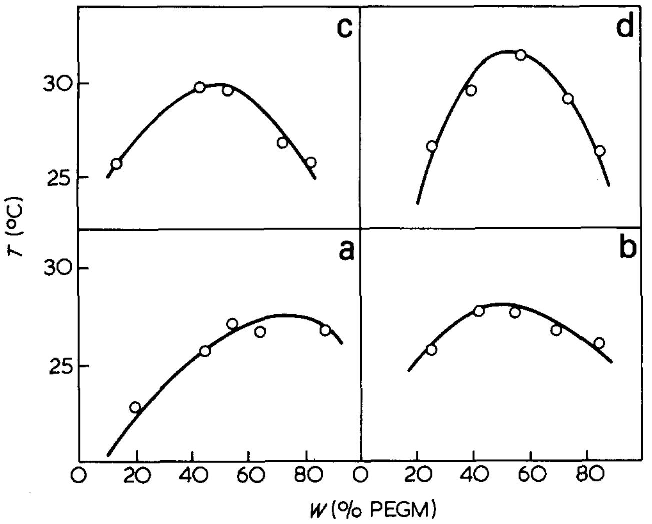

Figure 3 Cloud point curves for PEGM 600 with (a) PPGM 400; (b) PPGM 1000; (c) PPGM 1500; (d) PPGM 2000

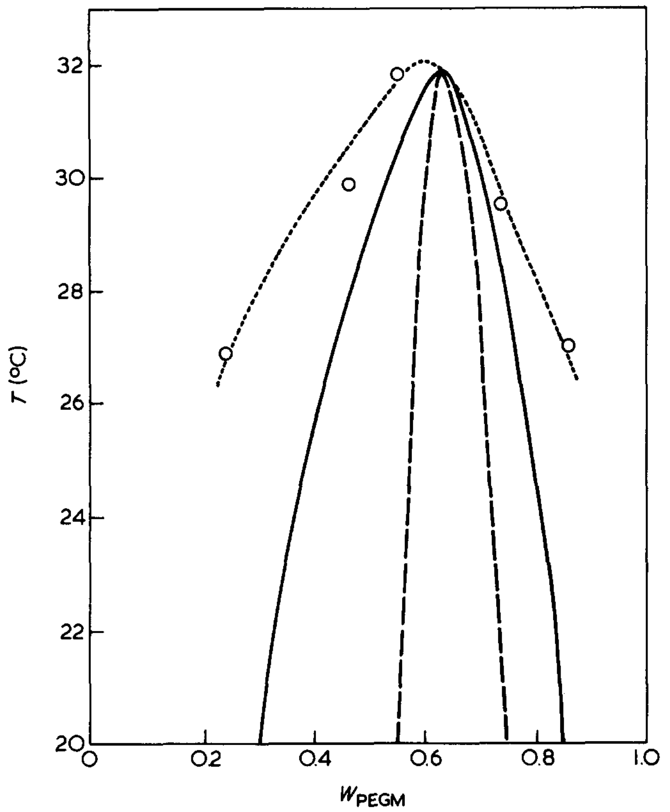

Figure 4 Experimental phase boundary of PEGM 600/PPGM 2000 mixture (...O...). The binodal (——) and spinodal (– – –) are calculated from equations (9) and (10)

Q_{12} is defined as an interaction entropy parameter since it is presumed that the interaction between the different species may also result in an entropy change as well as energy change on mixing. Thus Q_{12} is an empirical parameter which is related to ΔS_m. Values of $Q_{12} > 0$ mean that the interaction entropy term between unlike segments favours mixing.

X_{12} is a measure of enthalpy of interaction between segments. In the PEGM/PPGM system X_{12} is dependent on both molecular weight and temperature as shown in *Figure 5*. The decrease with molecular weight is in line with findings for mixtures of polyisobutene and n-alkanes[9]. Plots of X_{12} and Q_{12} as a function of M^{-1} (the reciprocal molecular weight of the PPGM component) show that the degree of polymerization has a substantial influence at low molecular weight on the phase separation behaviour (*Figure 6*).

It has been noted that the parameter Q_{12} is introduced to make the calculated phase boundaries fit the experimental data. Except for PPGM 600/PGGM 400, Q_{12} is positive.

In an earlier study of this system using PPGM oligomers up to molecular weight 1000, Cooper and Booth[1] found that X_{12} increased with increase in molecular weight. This arises from the fact that up to molecular weight 1000 ΔH_m increases with increase in molecular weight of the PPGM component. Our extension of their measurement shows that in the molecular weight range of 1000–2000 ΔH_m actually falls as the molecular weight of PPGM increases. Our data yield a value of X_{12} for PEGM 600/PPGM 1000 close to

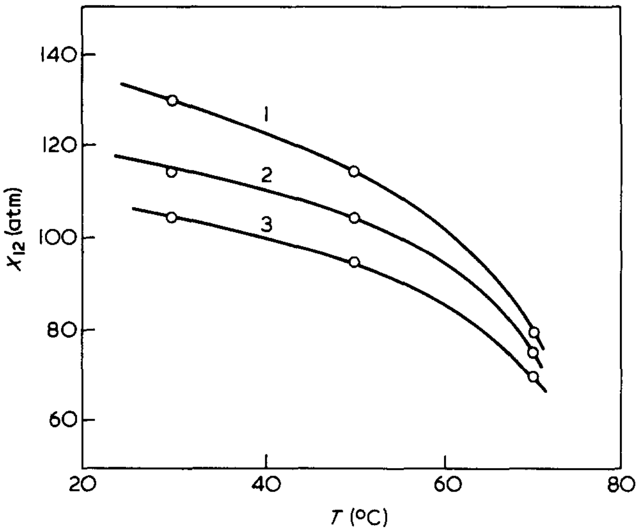

Figure 5 X_{12} as a function of molecular weight and temperature for: (1) PEGM 600/PPGM 1000; (2) PEGM 600/PPGM 1500 and (3) PEGM 600/PPGM 2000 mixtures

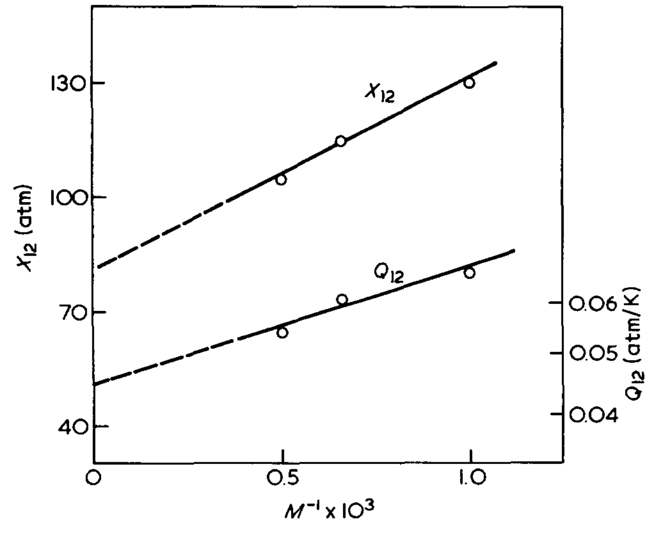

Figure 6 The molecular weight dependence of X_{12} and Q_{12} for PEGM 600/PPGM system as 30.1°C

that obtained by Cooper and Booth, and for PPGM 400 a somewhat higher value than theirs.

Friday, Cooper and Booth interpreted their phase boundary data in terms of the Flory–Huggins equation with a concentration dependent χ parameter:

$$\chi = \chi_c + \chi_1 \phi_1$$

where ϕ_1 is the volume fraction of PEGM. From their measurements $\chi_c = 0.1$ and $\chi_1 = -0.02$, and thus χ decreases with increase in the volume fraction of PEGM. This was attributed to the surface volume ratio factor S_1/S_2.

The same conclusion could be drawn from equation (20) if the equation of state contribution is negligible. However, the value of χ obtained directly from the heat of mixing measurements is much larger than χ_c. Furthermore, phase separation occurs at a much higher temperature than would be predicted. Only when the positive value of Q_{12} is introduced can be system by modelled simultaneously for both the ΔH_m and the phase boundary dependence on ϕ_1. It is plausible to introduce Q_{12} in this manner but a third independent experiment on phase separation behaviour (for example, SANS or SAKS) would be needed to establish its validity.

At weight fraction 0.5, χ was calculated as a function of temperature using equation (20) and the results are shown in *Figure 7*. It decreases with temperature, hence the system gives a *UCST* behaviour. It is shown that the contribution of the equation of state terms to χ is small, although it does increase with temperature. This excludes the possibility of finding an *LCST* at an elevated temperature.

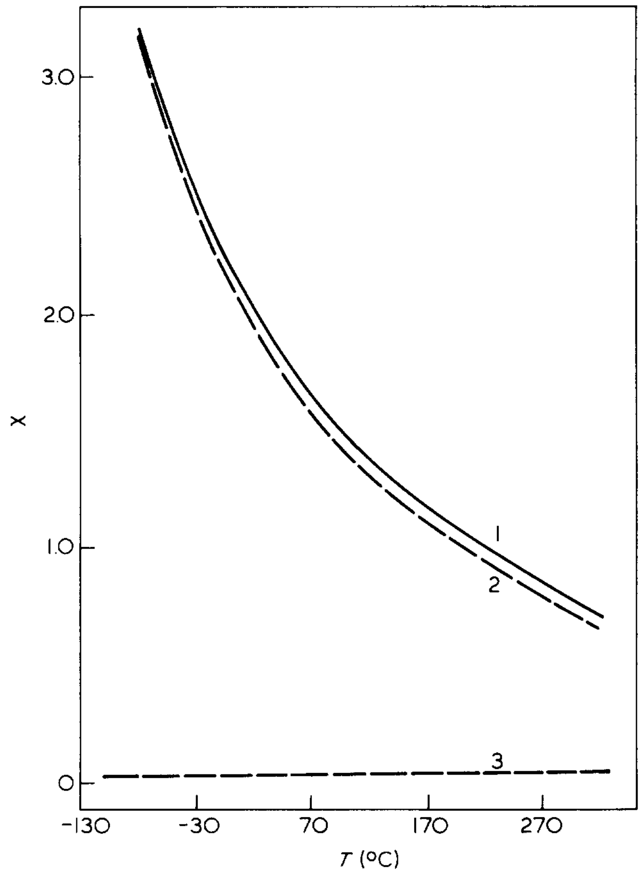

Figure 7 χ decreases with increasing temperature for PEGM/PPGM system. (1) χ; (2) the interaction contribution and (3) the equation of state contribution

Finally, an alternative analysis of the behaviour of χ is to treat it as a free energy parameter and to separate it into an enthalpy term χ_H and an entropy term χ_S.

$$\chi = \chi_H + \chi_S \tag{21}$$

In the equations of state formulations given above:

$$\chi_H = \bar{H}_1^{\mathrm{R}}/RT\phi_2^2$$

$$= \frac{1}{RT\phi_2^2}\left\{P_1^* V_1^*\left[\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \left(\frac{\alpha T}{\tilde{v}}\left(\left(\frac{\tilde{T}_1 - \tilde{T}}{\tilde{T}}\right)\right]\right.\right.$$

$$\left. + \frac{v_1^* X_{12}}{\tilde{v}}(1 + \alpha T)\theta_2^2\right\} \tag{22}$$

$$\chi_S = -T\bar{S}_1^{\mathrm{R}}/RT\phi_2^2$$

$$= \frac{\dfrac{1}{RT\phi_2^2}\left\{P_1^* V_1^*\left[3\tilde{T}_1 \ln\left(\dfrac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) - \dfrac{\alpha T}{\tilde{v}}\left(\dfrac{\tilde{T}_1}{\tilde{T}}\right)\right]\right.}{\tilde{T}}$$

$$\left. - \frac{V_1^* X_{12}}{\tilde{v}}\alpha T\theta_2^2 - TQ_{12}V_1^*\theta_2^2\right\} \tag{23}$$

The computational difficulty presented by equations (22) and (23) lie in the evaluation of the expansion coefficient α of the mixture. We have estimated χ_H and χ_S for the mixture PEGM 600/PPG 200 in which α_i is similar for both components. Typical results are shown in *Figure 8* again setting $Q_{12} = 0$. Series expansion of H_1^{R} and $T\bar{S}_1^{\mathrm{R}}$ yields:

$$\bar{H}^{\mathrm{R}1} = \left(\frac{P_1^* V_1^*}{\tilde{v}_1}\right)[Y_{12}(1 + \alpha_1 T)$$

$$-\tfrac{2}{3}(A_1\alpha_1 T)^2(1 + \alpha_1 T)]\phi_2^2 + 0(\phi_2^3) \tag{24}$$

$$T\bar{S}_1^{\mathrm{R}} = \left(\frac{P_1^* V_1^*}{\tilde{v}_1}\right)\left\{Y_{12}\alpha_1 T - \left(\frac{A^2\alpha_1 T}{2}\right)\right.$$

$$\left. \times [1 + \tfrac{4}{3}\alpha_1 T(1 + \alpha_1 T)]\right\}\phi_2^2 + 0(\phi_2^3) \tag{25}$$

where

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (S_2/S_1)X_{12}/P_1^* \tag{26}$$

$$Y_{12} = (S_2/S_1)^2 X_{12}/P_1^* \tag{27}$$

Thus the limiting values of χ_H^0 and χ_S^0 at $\chi_2 = 0$ can be calculated. From the values reported in *Table 1*, it can be seen that χ_s calculated without the inclusion of a Q_{12} term makes a negative contribution to χ (i.e. it increases compatibility) and its magnitude is about 15% of χ_H. With the inclusion of Q_{12}, χ_S makes an even larger negative contribution to χ as must be expected since the role of Q_{12} is to provide a better fit with the observed high degree of compatibility.

CONCLUSION

The Flory equation of state theory requires an X_{12} parameter with both molecular weight and temperature

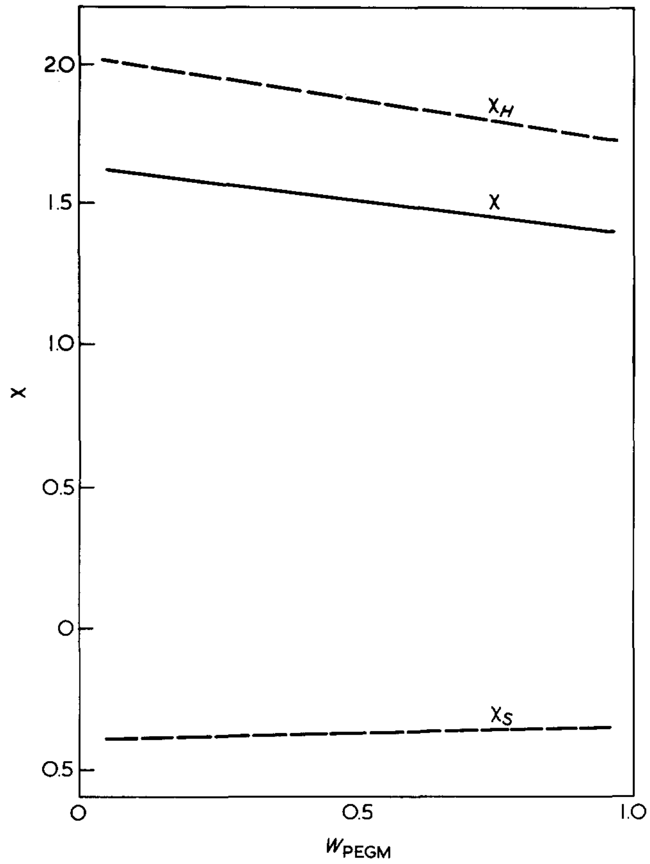

Figure 8 χ, χ_H and χ_S for PEGM 600/PPGM 2000 mixtures at 30.1°C

dependence to fit the observed heat of mixing behaviour of the binary system PEGM/PPGM. To reproduce the phase boundary results an additional term Q_{12} appears to be necessary. It's sign can be interpreted to suggest that the molecules in the mixture PEGM/PPGM are 'more random' after mixing. This is the first report of a conclusion of this kind, but we shall report later several binary mixtures which show this behaviour. The χ parameter is a decreasing function of temperature which thus leads to *UCST* behaviour. Even though the disparity between the two pure components is not great, χ_S is not a negligible part of χ.

REFERENCES

1 Cooper, D. R. and Booth, C. *Polymer* 1977, **18**, 164
2 Friday, A., Cooper, D. R. and Booth, C. *Polymer* 1977, **18**, 171
3 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.*, 1968, **65**, 2035
4 Abe, A. and Flory, P. J. *J. Am. Chem. Soc.*, 1966, **88**, 2887
5 Chong, C. L., *Ph.D. Thesis*, Imperial College, 1981
6 Jai Tripathi, *Ph.D. Thesis*, Imperial College, 1980
7 Booth, C. and Pickles, C. J. *J. Polymer Sci., Polym.-Phys. Edn.*, 1973, **11**, 595
8 Flory, P. J. Principles of Polymer Chemistry. See for example Fig. 121
9 Flory, P. J., Ellensen, J. L. and Eichinger, G. E. *Macromolecules* 1968, **1**, 279

APPENDIX

Symbolus used in equations (1)–(2)

B	an assumed constant as defined in equation (18)
d	density
ΔG_{m}	free energy of mixing
ΔH_{m}	heat of mixing
ΔS_{m}	entropy of mixing
N	total of molecules in mixture
N_i	number of molecules in species i
n_i	molar numer of species i
P	pressure
P_i^*	characteristic pressure of species i
$\tilde{P}_i$	reduced pressure of species i, $\tilde{P}_i = P/P_i^*$
P^*	characteristic pressure of mixture
$\tilde{P}$	reduced pressure of mixture
Q_{12}	interaction entropy parameter
R	gas constant
r_i	number of segments in chain molecule i
$\bar{r}$	average number of segments in mixture defined as $\bar{r}N = \Sigma r_i N_i$
S_i	number of contact sites per segment in species i
T	temperature
T_i^*	characteristic temperature of species i
$\tilde{T}_i$	reduced temperature of species i, $\tilde{T}_i = T/T_i^*$
T^*	characteristic temperature of mixture
$\tilde{T}$	reduced temperature of mixture
v	specificis volume
v_i^*	segmental characteristic hard core volume of species i
$\tilde{v}_i$	reduced volume of species i, $\tilde{v}_i = v_i/v_i^*$
v^*	segmental characteristic hard core volume of mixture
V_i^*	molar characteristic hard core volume of species i
$\tilde{v}$	reduced volume of mixture
α	thermal expansion coefficient
γ	thermal pressure coefficient
κ	isothermal compressibility coefficient
$\Delta\mu_i$	chemical potential of species i
ϕ_i	segment fraction of species i
θ_i	site fraction of species i
χ	Flory–Huggins interaction parameter
X_{12}	interaction energy parameter