Macromolecules **1984**, *17*, 2197–2202 **2197**

Molecular Conformation and Interactions in Oligomeric Mixtures of Poly(ethylene glycol) and Poly(propylene glycol) Methyl Ethers: A Small-Angle Neutron Scattering Study

J. S. Higgins* and A. J. Carter

Department of Chemical Engineering, Imperial College, London SW7, England.

Received July 12, 1983

ABSTRACT: Small-angle neutron scattering measurements are reported from poly(propylene glycol) methyl ether (PPGM) molecules of molecular weight 2100 in binary blends with poly(ethylene glycol) methyl ethers of molecular weight 600. It is shown that the PPGM molecules vary little in average dimensions as their concentration in the blend decreases. Data at two volume fractions are analyzed to obtain values of the interaction parameter from the concentration fluctuation contribution to the scattering. Differences between these values and those obtained from heat of mixing measurements are discussed in terms of entropic contributions to the free energy of mixing.

1. Introduction

There is currently considerable interest in understanding the molecular and thermodynamic behavior governing the partial compatibility observed for many binary polymer mixtures. Because both heat of mixing and cloud point curves can be determined directly and rather precisely, oligomeric mixtures offer some advantages as model systems for such studies over high molecular weight blends, although it is these latter which are more likely to be found in practical applications. One such model oligomeric system is formed by combination of methoxylated poly(ethylene glycol) with methoxylated poly(propylene glycol) with molecular weights less than 2000.[1,2] The mixtures have upper critical solution temperatures just above room temperature and are particularly amenable to study. In a recent paper[3] some of us have reported a thermodynamic study of these blends in which the experimental heat of mixing and cloud point curves are fitted by the Flory equation of state theory.[4] The main conclusions of that work are that because the equation of state contributions (essentially the volume terms) are small, the observed miscibility occurs at temperatures lower than can be predicted on the basis of the observed unfavorable enthalpy of mixing. To reproduce the observed phase behavior an additional favorable entropic term (above the mixing entropy) has to be introduced. The implication of such a favorable entropic term—more random molecular configuration after mixing—is difficult to understand. In the current paper we explore further the question of molecule configuration in these blends using the technique of small-angle neutron scattering[5] (SANS). The conventional use of SANS to study molecular conformation involves labeling some of the molecules with deuterium. In the case of a polymer blend, however, this leads to a three-component system consisting of polymer 1, in both deuterated and hydrogenous analogues, and polymer 2. The scattering from such systems contains contributions both from the molecular shape function and from concentration fluctuations. These latter were originally shown by Einstein[6] to depend on the concentration gradient of the chemical potential, and subsequently related by Debye and Beuche[7] to the interactions in the system via the Flory–Huggins equation.[8-10] Recent papers have examined in detail the neutron scattering from blend systems and shown how to separate and analyze the molecular conformation and interaction terms.[11-13] One problem which has been brought to light is the effect of the deuterated molecules on the phase behavior. For oligomeric mixtures of polystyrene with polybutadiene the compatibility is reduced and the UCST raised by about 20 °C when either component is deuterated.[14,15] High molecular weight blends of polystyrene with poly(vinyl methyl ether) are rendered more compatible by deuteration, which actually raised their LCST by 40 °C or more.[16] Observations in our laboratory indicated that the effect of deuteration is not always as large as for these systems and when strong specific interactions are involved, may indeed be negligible. For the system reported here, the effect is close to negligible.

Table I
Sample Characteristics

sample	M_w	M_n	M_w/M_n	ρ, g/cm^3
PEGM 600		600	narrow	1.065
PPGM 2000	2200	2055	1.07	0.99
PPGMd 2000	2200	1980	1.11	

2. Experiments

2.1. Oligomeric Blends of Methoxylated Poly(ethylene glycol) with Poly(propylene glycol). Narrow molecular weight fractions of poly(ethylene glycol) were obtained from Shell Chemicals Ltd. A hydrogenous poly(propylene glycol) sample was prepared in the laboratory from propylene oxide by heating with a catalytic amount of sodium dissolved in ethane-1,2-diol at ca. 95 °C under pressure for 48 h. Both ethylene and propylene glycols were methoxylated by a method previously described,[1,3] the hydroxyl end group being reacted with methyl iodide in alkaline medium. Infrared spectroscopy confirmed the absence of OH groups in the products. Deuterated poly(propylene glycol) was prepared as previously described[17] by a four-stage synthesis starting from propan-2-one-d_6. Proton NMR confirmed the absence of C–H bonds to a limiting observation level of 5%. Methyl-d_3-oxylation followed the same method as for the hydrogenous species using methyl-d_3 iodide obtained from Merck Sharp and Dohme (99.5 atom % D). The molecular weights of these materials were measured by GPC calibrated against a commercial sample from Shell Chemicals Ltd. The number-average molecular weight of this sample was found both by hydroxyl analysis and by vapor phase osmometry to be 2100. The polydispersity M_w/M_n was better than 1.05 and the laboratory-prepared samples were only slightly worse. Sample characteristics are listed in Table I.

For neutron measurements samples were weighed into flat-sided quartz cells with a cross-section of 15 × 20 mm and with 2-mm path length, degassed, and sealed under vacuum. A small metallic strip was included in each cell to allow magnetic stirring. Samples were heated above the phase boundary, stirred, and then left for several hours at required temperatures to attain equilibrium before measurements were made. Cloud point curves were measured by slowly cooling stirred samples and measuring the intensity of transmitted light. The cooling rate was reduced until a rate-independent cloud point was achieved. The cloud point curve for the hydrogenous blend is shown in Figure 1a. The effect of

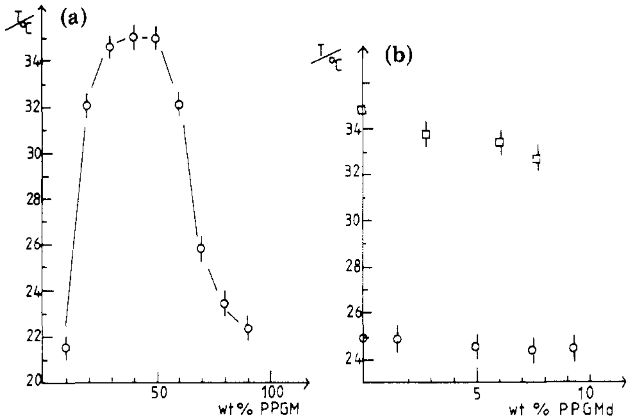

Figure 1. (a) Cloud point temperatures for blends of PEGM 600 with PPGM 2000. (b) Effect of deuterating the PPGM component up to 10% by weight of the total sample. (□) 30% PPGM; (○) 70% PPGM.

Table II
Details of Scattering Experiments

apparatus	S–D distance, m	wavelength, Å
D11	2.603	9.91
D17	1.4	12.0
SAS	2.0	4.5

deuteration on the cloud points of the 30% and 70% PPGM blends is shown in detail in Figure 1b, where is can be seen that the maximum effect of deuteration is less than 2 °C shift—barely outside the error bars of the experiments. The slight tendency toward increased compatibility as the deuterated molecules are added could well be explained by the lower degree of polymerization calculated from Table I. Reference 3 shows that reducing the molecular weight of the PPGM component has a more marked effect at the lower concentrations of this polymer. Not shown in Figure 1b is the error in the concentration, which will be of order 1 or 2%. More serious is the error in the deuterated fraction c, which may be as high as 10%. This is largely due to small losses on the sides of the filling ports when introducing the viscous samples. The implications of this error will be discussed in section 3.

2.2. Neutron Scattering Experiments. Experiments were carried out at 45 and 51 °C using the D11 and D17 small-angle scattering spectrometers at the Institut Laue-Langevin, Grenoble[18,19] and the SAS spectrometer at AERE Harwell. The experimental conditions are summarized in Table II. Data were normalized for geometrical and flux factors using the isotropic incoherent scattering from water. The corrected scattered intensity $I(Q)$ is then related[20] to the scattering law $S(Q)$

$$S(Q) = \frac{I(Q)(1 - \mathrm{TRW})g(\lambda)}{4\pi \times \mathrm{TRS} \times d}$$

where TRS and TRW are transmissions of sample and water, respectively, and d is the sample thickness. The factor $g(\lambda)$ takes account of effects in the water scattering due to inelastic terms. A theoretical function for $g(\lambda)$ was discussed in ref 20 but the experimental value has recently been measured rather accurately[21] for the D11 spectrometer. There is some evidence that this factor is not transferable to other spectrometers since molecular weights obtained for homopolymers gave systematically lower values than at D11. For this reason the molecular weight observed from the deuterated PPGM dispersed in hydrogenous PPGM was used to normalize the scattered intensity in each series of experiments.

In a previous publication[11] we have derived an expression for scattering from a sample containing volume fractions ϕ_1 and ϕ_2 of two polymers, a fraction c of the 1-type segments being deuterated. (A segment is conveniently identified as a monomeric repeat unit. In the present case PPGM is polymer 1.)

$$S(Q) = \frac{(cd + (1 - c)h - b')^2}{\chi_1^{-1}(Q) + \beta^2\chi_2^{-1}(Q) - 2\beta U} + c(1 - c)(d - h)^2\chi_1(Q) \quad (1)$$

where d and h are the sums of neutron scattering lengths for deuterated and hydrogenous segments of polymer 1, $b' = \beta b$, and b is the scattering length per segment of polymer 2. $\beta = v_1/v_2$, where v_1 and v_2 are segment specific volumes for polymers 1 and 2, respectively.

$$\chi_n(Q) = \phi_n N_n f_D(QR_g^{\,n}) \quad (2)$$

ϕ_n is the segment concentration, N_n the degree of polymerization, and $R_g^{\,n}$ the radius of gyration of the nth component. In more familiar terms the volume fraction $\phi_n' = \phi_n[m_n/(\rho_n N_A)]$. m_n is the segment mass and ρ_n the density of polymer species n. $f_D(QR_g^{\,n})$ is the Debye scattering curve for ideal polymers, which at low Q can be approximated to

$$f_D(QR_g^{\,n}) \rightarrow 1 - (QR_g^{\,n})^2/3 \quad (3)$$

U is the Flory interaction parameter,[22] here expressed per polymer segment volume. In terms of the conventional χ_{12} per lattice segment mole

$$U = \chi_{12}v_1/N_A \quad (4)$$

The first of the terms in eq 1 arises from concentration fluctuations; the second is the scattering from the labeled chains. In these calculations the assumption has been made that the d segments exactly replace the h segments (i.e., (density of d polymer) = (density of h polymer) × (ratio of segment weights)).

2.3. Data Analysis and Design of Experiments. As previously described[11] there are a number of ways of manipulating eq 1 in order to obtain $R_g^{\,1}$ and U. They all depend on the invariance of the blend characteristics with deuteration. It is essential, if weighted subtractions are to be carried out, that concentration fluctuations be the same in each sample. Careful temperature control and equilibration are important. To avoid as far as possible effects of deuteration in shifting the phase boundary, levels of deuteration were kept to around 10%.

Before the data can be manipulated in order to separate the two terms in eq 1 the incoherent background must be removed. This is not a trivial procedure, as has recently been shown[23] since the cross section of hydrogenous molecules (including polymers) is strongly temperature dependent. This temperature dependence reflects the effect of molecular mobility. Thus careful measurement of the incoherent contribution of the separate constituents of a blend may not be sufficient since the combination may not be adequately described by a simple summation if there is a strong effect of each polymer on the other's mobility. There is currently some effort being expended to ascertain the best method of estimating the incoherent contribution from heterogeneous systems. In the meantime however we have preferred to take direct subtractions of data with approximately similar levels of hydrogen, thus removing the incoherent contribution, and to deal with the resulting scattering in terms of eq 1. For deuteration levels of order 10% or less the error in the incoherent subtraction is certainly no more than that introduced by other methods of estimating this contribution. On the other hand, an error in the $S(Q)$ in eq 1, introduced via the estimation of the incoherent level subtracted, will cause very large errors in any subsequent weighted subtraction of data for different values of c aimed at extracting separately either the first or second term of the equation.

For the results reported here the initial data treatment therefore involved the subtraction $S'(Q) = S_c(Q) - S_0(Q)$ for fixed blend concentration ϕ_1. The resulting scattering still contains two terms as in eq 1, but the coefficient of the first is now

$$(cd + (1 - c)h - b')^2 - (h - b')^2$$

which becomes

$$c^2(d - h)^2 + 2c(h - b')(d - h) \quad (5)$$

This coefficient is parabolic in c as is shown in Figure 2. It has zero values both trivially at $c = 0$ and for a positive value of c if h is less than b'. We identify this "null point" as $\hat{c}$.

For the PEGM/PPGM system reported here $h < b'$ and such a null point occurs. In Figure 2 the coefficients of the fluctuation term for PEGM/PPGM are compared with those of the single-chain term for various values of ϕ. For all values of $c < 0.1$ the fluctuation term has a very small coefficient, but by working as close as possible to $\hat{c}$ it can be removed completely and the sin-

Table III
Concentration Effects[a]

	ϕ_1	c_D, g/g	c	"R_g"/R_g(Θ)	"M_w"/M_w(Θ)	S_p	χ_{12}
SAS, T = 45 °C	0.31	0.021	0.063	0.96	1.0		
	0.31	0.042	0.127	1.16	1.32		
	0.31	0.056	0.173	1.25	1.41	2.5×10^{-2}	0.073
	0.32	0.080	0.247	1.33	1.78	2.66×10^{-2}	0.073
	0.33	0.126	0.374	1.44	2.38	3.49×10^{-2}	0.070
	0.32	0.133	0.417	1.61	2.92	2.96×10^{-2}	0.072
D11, 50 °C	0.72	0.019	0.027	1.12	0.77		
	0.72	0.054	0.077	0.91	1.05		
	0.72	0.079	0.103	0.94	1.09	0.73×10^{-2}	0.14
	0.72	0.097	0.127	0.94	1.09	1.69×10^{-2}	0.14
SAS, 45°	0.72	0.079	0.103	1.07	1.03	2.13×10^{-2}	0.13
	0.72	0.097	0.127	0.99	1.06	2.94×10^{-2}	0.13

[a] Apparent R_g and apparent M_w obtained by analyzing data for a 30% and a 70% blend using eq 1 without the concentration fluctuation term. The values are shown as ratios compared to values for a pure PPGM sample observed in the same experiment.

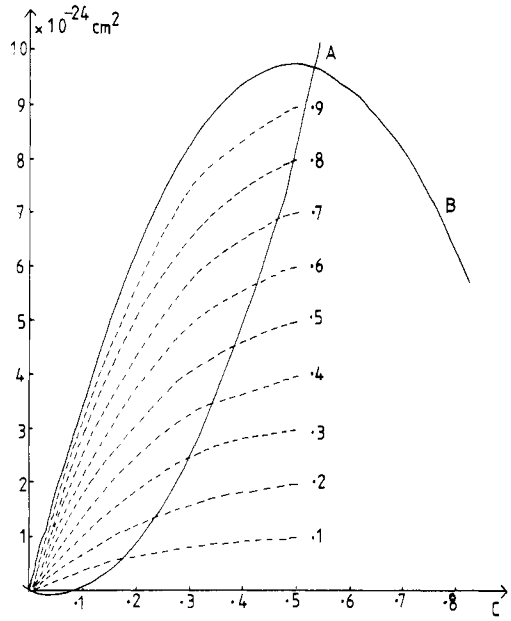

Figure 2. Calculated contrast coefficients of the single-chain and concentration fluctuation terms as a function of deuterated segment fraction, c, for the PEGM 600/PPGM 2000 blend. Solid line A, concentration fluctuation contrast (eq 5); solid line B and dashed lines, single-chain factor, $\phi_1 c(1 - c)(d - h)^2$ for various values of the volume fraction ϕ_1.

gle-chain term obtained directly.

We report here two sets of experiments. In one series $c \approx \hat{c}$ and we obtain directly the second term in eq 1 and hence the dimensions of the deuterated chains. In a separate set of experiments c was varied away from $\hat{c}$ and we analyze the forward scattering in order to obtain the interaction parameters.

3. Results

3.1. 30% Blend: Variation of Deuterated Fraction.

Combining eq 1 and 5 the treated data are described by

$$S'(Q) = \frac{c^2(d-h)^2 + 2c(h-b')(d-h)}{\chi_1^{-1}(Q) + \beta^2\chi_2^{-1}(Q) - 2\beta U} + c(1-c)(d-h)^2\chi_1(Q) \tag{6}$$

If the leading, concentration fluctuation, term were negligible, then we would obtain

$$S'(Q) = c(1-c)(d-h)^2\phi_1 N_1\left(1 - \frac{Q^2(R_g^{\ 1})^2}{3}\right) \tag{7}$$

and the molecular dimensions, $R_g^{\ 1}$ and molecular weight N_1, could be obtained in the conventional way.

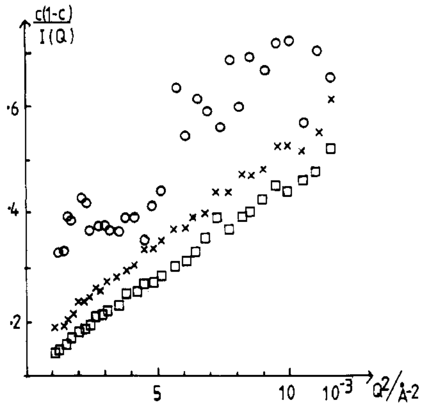

Figure 3. $c(1 - c)/I(Q)$ vs. Q^2 for blends of PEGM 600 with PPGM 2000 with ϕ_1 = 0.3162: (○) c = 0.063; (×) c = 0.247; (□) c = 0.417.

Figure 3 shows the result of such a conventional analysis for several deuteration levels where the data are plotted as $[c(1 - c)]/S(Q)$ vs. Q^2. If the concentration fluctuations were negligible and eq 7 applied, the curves in Figure 3 should at the very least show an identical value at Q = O($S(0) = N_1\phi_1$), and unless R_g varies with deuteration level, the data should superimpose for all Q values. In Table III we list the apparent values of R_g and N_1 obtained by analyzing the data as though eq 7 applied. Values are expressed as ratios to those obtained for a sample of deuterated PPGM dispersed in hydrogenous PPGM in the same experiment.

In both Figure 3 and Table III the effect of the concentration fluctuation term clearly becomes significant as c varies away from $\hat{c}$ (=0.081) as would be predicted from Figure 2. We must therefore analyze the scattering in terms of the full expression in eq 6. The scattering extrapolated to Q = 0 is then given by

$$S'(0) = \frac{c^2(d-h)^2 + 2c(h-b')(d-h)}{(N_1\phi_1)^{-1} + \beta^2(N_2\phi_2)^{-1} - 2\beta U} + c(1-c)(d-h)^2\phi_1 N_1 \tag{8}$$

In this expression everything is known except U and thus the denominator of the first term

$$S_p = (N_1\phi_1)^{-1} + \beta^2(N_2\phi_2)^{-1} - 2\beta U \tag{9}$$

and interaction parameter χ_{12} (=U(N_A/v_1)) can be obtained. Values of χ_{12} and S_p obtained for the larger deuterium concentrations are included in Table III.

A discussion of the accuracy of these values is given in section 3.4.

Table IV
Results from D11 at 45 °C

wt % PPGM	% dPPGM	ϕ_1	c (±10%)	R_g^1	M_w^1	R_g^1/R_g	M_w^1/M_w
9.98	0.74	0.106	0.067	11.1	2260	0.83	0.95
19.75	1.29	0.209	0.059	12.7	1840	0.95	0.77
30.56	2.11	0.322	0.063			0.96[a]	1[a]
39.83	2.74	0.417	0.063	12.5	2420	0.94	1.01
49.32	3.26	0.512	0.060	11.9	2300	0.89	0.97
59.64	4.13	0.614	0.062	13.8	2200	1.04	0.92
70.08	5.38	0.717	0.068	12.1	2490	0.91	1.04
79.06	5.41	0.803	0.062	14.1	2190	1.06	0.92
88.8	6.24	0.895	0.064	14.5	2220	1.09	0.93
100	7.04	1	0.0654	13.3	2390	1	1

[a] Taken in a separate experiment as in Table III.

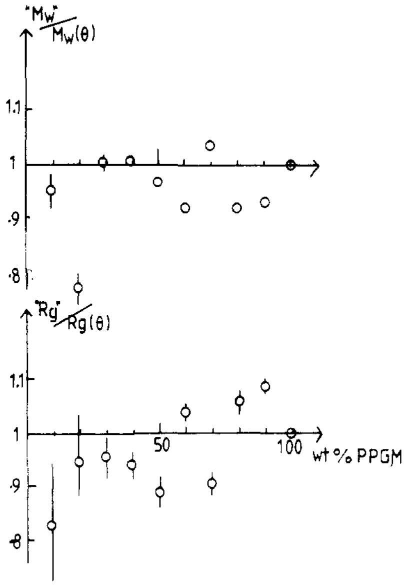

Figure 4. Single-chain radius of gyration R_g^1 and molecular weight M_w^1 plotted against ϕ_1 for the PPGM molecules in a blend with PEGM at 45 °C shown as ratios to the equivalent values for dPPGM in hPPGM.

3.2. 70% Blend: Variation of Deuterated Fraction. Table III also includes values of apparent radii of gyration and molecular weights for a 70% PPGM blend. In this case our self-imposed restriction to levels of deuteration below 10% has limited us to lower values of the deuterated fraction c than for the 30% blend. (On the other hand, the total deuteration level governs the counting statistics and these are equally as good.) In this case the effects of the concentration fluctuation term are very small but there does appear to be a systematic deviation from the single-chain values of R_g and M_w as c increases from $\hat{c}$. Measurements on the two higher concentration samples were therefore repeated on the SAS at Harwell because the longer experiment times (~8 h as compared to 30 min on the D11 spectrometer) allow better temperature equilibration of the samples.

3.3. Single-Chain Dimensions. A further series of measurements were made for a number of different blend concentrations ϕ_1, choosing c in each case to lie close to $\hat{c}$ as defined by setting expression 5 (the numerator of the concentration fluctuation term) equal to zero. Equation 7 should then apply; R_g^1 and N_1 can be obtained. The data are summarized in Table IV and in Figure 4. The error bars in the figure are purely these that arise from fitting eq 7 to the data. The sources of the other variation evident from the data are discussed in the following section. Within these limitations it is possible to detect a very slight downward trend in the molecular dimensions as the PPGM concentration decreases. If this effect were due to residual contributions from the concentration fluctuation term, a similar variation in apparent molecular weight would be expected (as seen in Table III as c increases from $\hat{c}$).

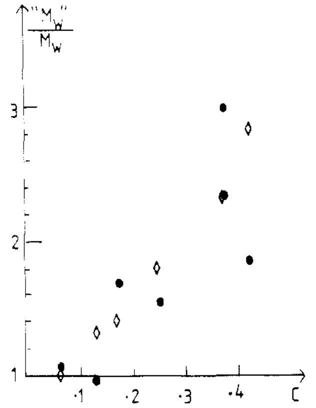

Figure 5. Apparent molecular weight divided by molecular weight of the PPGM molecules measured in the same experimental series and plotted as a function of deuterated segment fraction, c ($\phi_1 = 0.3162$): (●) D17 experiments; (◊) SAS experiments.

3.4. Sources of Errors. The data are subject to three major sources of errors—sample preparation, temperature equilibration, and neutron counting statistics and spectrometer normalization.

The errors arising from neutron counting statistics are generally small as seen both in Figure 3 and from the error bars obtained when fitting such data as shown in Figure 4. Systematic errors arising from spectrometer normalization factors have been largely eliminated by normalizing each set of data to the results for the pure PPGM molecules. Errors in sample preparation arise because of the difficulty of weighing small quantities of viscous liquids into the sealed quartz cells. These errors are estimated to range from as much as 10% for the lowest deuteration levels down to a few percent for the highest levels. Since the data are always analyzed as differences between two experiments and c appears as a squared term in eq 5, this error accounts to a large extent for the random variation shown in Figure 4, especially at low PPGM concentrations, where the deuteration level of $\hat{c}$ is very low (see Table IV).

It can be shown however that temperature equilibration is a further important effect. Figure 5 compares results for an earlier series of measurements using the D17 spectrometer with those listed in Table III for the 30% blend. The D17 experiments are short because of the much higher flux and clearly show extra random errors which we attribute largely to poor temperature equilibration. It is for this reason that the longer SAS experiments were used to extract the interaction parameter χ_{12}.

Since the denominator S_p (eq 9) of the concentration fluctuation term arises purely from thermodynamic considerations, it should be invariant with c for a given blend concentration. Table III shows that this is true for the two

Table V
Interaction Parameters and Free Energies for PPGM/PEGM Blends at 45 °C

vol % PPGM	χ_{12} (neutrons)	$\Delta H_m{}^{a,b}$ (±5%)	χ_{12} (heats) (±5%)	$-T\Delta S_m{}^{a,b}$ (calcd[c])	$\Delta G_m{}^{a,b} = \Delta H_m - T\Delta S_m$
0.3162	0.072 ± 0.02	1.8	0.12	−1.55	+0.25
0.71	(0.13 ± 0.02)	1.75	0.13	−1.98	−0.23

[a] In J/mL. [b] Values from ref 3 and 24. [c] ΔS_m is the combinatorial entropy based on the Flory–Huggins model.

sets of SAS results within experimental error in determining c and normalizing intensities. In both cases S_p is a more sensitive measure of the reproducibility of the data than χ_{12}.

In order to put into perspective the reliability of these values of χ_{12}, we consider the value $\chi_{12} = 0.072$ obtained for the 30% blend with $c = 0.417$ (see Table III). In this case the scattered intensity was nearly 3 times that which would be observed from this concentration of deuterated PPGM dispersed in hydrogenous PPGM (i.e., without concentration fluctuations). In order to increase the value of χ_{12} by 10%, i.e., to 0.08, the apparent molecular weight would have to be over 7 times the PPGM molecular weight. This is well outside any experimental error.

The results for the 70% blend are clearly subject to larger uncertainty because of the smaller values of c. Nevertheless the reduction of χ_{12} again by as little as 10% to 0.12 would mean that the observed intensity would have to be within 2% of that for pure PPGM. Since the observed intensity is systematically higher than for pure PPGM, a reasonable degree of reliability can also be attributed to the 70% values.

4. Discussion

Table V contains values of χ_{12} obtained in these experiments together with those obtained from heat of mixing experiments.[3,24] The measured enthalpies of mixing ΔH_m from which the χ_{12} values are obtained are also included. The free energy of mixing can be calculated by combining this unfavorable enthalpic term with the favorable entropic term ΔS_m based on the Flory–Huggins model. Clearly, something is wrong since the resulting free energy predicts immiscibility of a 30% blend at 45 °C, in contradiction to the cloud point curve in Figure 1a. The much smaller neutron χ_{12} obtained at 30% would produce a negative free energy of mixing and miscibility as required. The difference between neutron and heat of mixing results arises because the latter is a purely enthalpic measurement whereas the former comes from the free energy of mixing via the concentration gradient of the chemical potential and therefore includes both enthalpic and entropic contributions. In this case both the neutron value and the temperature of the cloud point show there must be an entropic contribution of order 40% of the enthalpic contribution and that it is favorable for mixing. A similar conclusion was reached when fitting equation of state theory to the heat of mixing and cloud point data for this blend.[3]

In the equation of state theory[4] the interaction term, X_{12} obtained by fitting the heat of mixing data leads automatically to an entropic contribution because of the inclusion of volume changes but this contribution, though vavorable for mixing in this case, was not large enough to counteract the unfavorable X_{12} term so that an extra interaction entropy term Q_{12} had to be introduced. In ref 3 values of an effective χ term calculated from X_{12} and Q_{12} were separated into enthalpic χ_H and entropic χ_S contributions. For a blend similar to that studied here the values were $\chi_H = 0.123$ $\chi_S = -0.042$. These values are obtained by fitting the cloud point curve and therefore apply at a lower temperature than our neutron values. No allowance for concentration dependence of Q_{12} was made, but the calculated phase boundary was a poor fit to the shape of the experimental curve, which could have been improved by inclusion of an arbitrary concentration dependence of this entropic contribution.

This entropic contribution must be favorable for mixing and therefore must be associated with an increase of inter- or intramolecular conformational disorder on going from the homopolymer melts to the blends. The current measurements suggest that this is unlikely to arise from the PPGM component. The results in Figure 4 indicate that any change in molecular dimensions of the PPGM molecules is at the limits of detectability. Allen et al.[25] give values for the unperturbed dimensions of poly(propylene oxide) molecules of $R_g/M_w{}^{1/2} = 0.33$ Å determined over the range $4 \times 10^5 < M_w < 2 \times 10^6$. For the PPGM molecules discussed here a value of $R_g = 14.8$ Å would thus be predicted if this relationship holds at low M_w. The slightly smaller value actually observed could be accounted for by the low molecular weights and the consequent failure of the molecules to achieve a full random coil conformation. Ballard et al.[26] showed that for polystyrene in a Θ-solvent the dimensions begin to fall below those of random coils when the number of segments is less than about 40.

The possible slight reduction in $R_g{}^1$ at low concentrations is no more than would be expected for a molecule in a poor solvent below the Θ-temperature.[27] In this domain the coils are still essentially Gaussian and it is difficult to see that any small change from random coil statistics could produce a favorable entropic contribution. If the PPGM molecules seem unlikely to be at the origin of the noncombinatorial entropy, we must consider the PEGM component. Poly(ethylene oxide) crystallizes in a helical form with most of the OCCO groups in the gauche state. Raman scattering measurements[28] indicate that the helical structure breaks down in the melt as the trans to gauche ratio changes, but it is not possible to say if the value for random coil statistics is fully achieved. Small-angle neutron scattering measurements[29] give a higher value for the ratio $R_g/M_w{}^{1/2}$ (0.44 Å) for poly(ethylene oxide) in the melt than that obtained from light scattering and intrinsic viscosity measurements[30,31] in dilute solution under Θ-conditions ($R_g/M_w{}^{1/2} = 0.34$ Å). The SANS measurements confirm that over long ranges the molecules obey Gaussian statistics with $R_g \propto M_w{}^{1/2}$ but the difference in the $R_g/M_w{}^{1/2}$ ratio could indicate a local conformational structure, perhaps residual helical sequences which are lost in solution. Such a loss of local structure could be the source of the entropic contribution and would be larger at larger PEGM concentrations as the data indicate. Possibly careful Raman measurements on the blends would confirm the existence of such conformational changes.

5. Conclusions

We have shown that by careful analysis of neutron scattering data it is possible to obtain interaction parameters in polymer blends with good precision. Such measurements are potentially important for three reasons:

(1) They may be made directly on the blend under discussion whereas for high molecular weight blends, heat of mixing data can only be obtained by using oligomers or analogue molecules.

(2) They include both entropic and enthalpic contributions to the free energy.

(3) They may be made as a function of temperature whereas values obtained by fitting the cloud points or

spinodals are by definition confined to the temperature of those measurements.

We have also pointed out the possible pitfalls in such measurements in that manipulation of these data relies on invariance of the concentration fluctuations from sample to sample. This implies both good temperature equilibration and no effect of deuteration on the blend thermodynamics. This latter restriction is clearly a severe limitation since as discussed in the Introduction, many systems are already known to be affected. In a future paper we intend to tackle the problem of extracting interaction terms for a system where deuteration shifts the phase boundary (polystyrene with polybutadiene).

Finally, the data confirm that there is an extra (noncombinatorial) entropy of mixing for blends of PPGM with PEGM observed at low concentrations of PPGM and that this is favorable for mixing. Since no unusual conformational changes are observed for the PPGM molecules, this contribution may be associated with local conformational changes in the PEGM molecules.

Acknowledgment. We are grateful for the support of the scientific and technical staff at the Institut Laue-Langevin while carrying out these experiments. A.J.C. thanks SERC for support during the period of the work. Dr. Chai Zhikuan and Professor Shi Lianghe of the Chinese Academy of Science gave help with the initial experiments and Dr. M. Warner (SERC Rutherford) and Professor R. S. Stein (University of Massachusetts) have been involved in helpful discussion at the final stages of analysis.

Registry No. PEGM, 9004-74-4; PPGM, 37286-64-9; neutron, 12586-31-1.

References and Notes

(1) Cooper, D. R.; Booth, C. *Polymer* **1977**, *18*, 164.
(2) Friday, A.; Cooper, D. R.; Booth, C. *Polymer* **1977**, *18*, 171.
(3) Allen, G.; Chai, Z.; Chong, C. L.; Higgins, J. S.; Tripathi, J. *Polymer* **1984**, *25*, 239.
(4) Eichinger, B.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *14*, 2035.
(5) Higgins, J. S.; Stein, R. S. *J. Appl. Crystallogr.* **1978**, *11*, 346.
(6) Einstein, A. *Ann. Phys.* **1910**, *33*, 1275.
(7) Debye, P.; Bueche, A. *J. Chem. Phys.* **1950**, *18*, 1423.
(8) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440.
(9) Huggins, M. L. *J. Phys. Chem.* **1942**, *46*, 151.
(10) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660 (1941); **1942**, *10*, 51.
(11) Warner, M.; Higgins, J. S.; Carter, A. J. *Macromolecules* **1983**, *16*, 1931.
(12) Hadziioannou, G.; Higgins, J. S.; Stein, R. S. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1983**, *24* (2), 213.
(13) Stein, R. S.; Hadziioannou, G. *Macromolecules*, accepted.
(14) Atkin, A. L.; Kleintjens, L. A.; Koningsveld, R.; Fetters, L. J. *Polym. Bull.* **1982**, *8*, 347.
(15) The effect of deuterating the polystyrene component has been observed by the present authors.
(16) Yang, H.; Hadziioannou, G.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 159.
(17) Higgins, J. S.; Ma, K.; Hall, R. H. *J. Phys. C* 1981, *14*, 4995.
(18) ILL, Grenoble, France.
(19) Ibel, K. *J. Appl. Crystallogr.* **1976**, *9*, 296.
(20) Jacrot, B. *Rep. Prog. Phys.* **1976**, *39*, 911.
(21) May, R. P.; Ibel, K.; Haas, J. *J. Appl. Crystallogr.* **1982**, *15*, 15. Oberthur, R., private communication.
(22) See, for example, Chapter 2 in: Olabisi, O.; Robeson, L. M.; Shaw, M. T., Eds. "Polymer Miscibility"; Academic Press: New York, 1979.
(23) Maconnachie, A. *Polymer* **1984**, *25*, 1068.
(24) Chong, C. L. Ph.D. Thesis, Imperial College, 1981.
(25) Allen, G.; Booth, C.; Price, C. *Polymer* **1967**, *8*, 397.
(26) Ballard, D. G. H.; Rayner, M. G.; Schelten, J. *Polymer* **1976**, *17*, 349.
(27) Perzynski, R.; Adam, M.; Delsanti, M. *J. Phys.* (*Paris*) **1982**, *43*, 129.
(28) Maxfield, J.; Shepherd, I. W. *Polymer* **1975**, *16*, 507.
(29) Allen, G. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 381.
(30) Allen, G.; Booth, C.; Hurst, S. J.; Jones, M. N.; Price, C. *Polymer* **1967**, *8*, 391.
(31) Beech, D. R.; Booth, C. *J. Polym. Sci., Part A-2* **1969**, *7*, 575.

Notes

Poly(1,4-*trans*-cyclohexanediyldimethylene succinate): Electron Crystallographic Considerations

BARBARA MOSS

Electron Diffraction Department, Medical Foundation of Buffalo, Inc., Buffalo, New York 14203

FRANÇOIS BRISSE*

Département de Chimie, Université de Montréal, C.P. 6210, Succ. A, Montréal, Québec, H3C 3V1 Canada.
Received December 19, 1983

Introduction

Electron diffraction data can be used qualitatively for structural analysis. However, it is vitally important that the intrinsic differences from X-ray diffraction be considered in order to extract a reliable structural model. Dorset has noted that the principal phenomena that affect the electron diffraction data from thin organic crystals are n-beam dynamical scattering[1] and crystal bending.[2] The separate consideration of these effects has been justified for thin crystal with small bend deformations for the test structures of a paraffin and a linear polymer.[3] If either of these effects is large, a kinematic structure analysis may give erroneous results.[4-6] A structural model is required in order to determine their importance in a particular case. There is consequently no alternative to the standard structural refinement initially.

The microcrystals used for electron diffraction are often deformed on the microscope grid, as evidenced by bend contours. On the basis of Cowley's model,[7] it may be shown that projections down a long crystallographic axis are most sensitive to bend effects, which may affect both the intensity data and the observed symmetry of the zone. The general effect is to reduce coherence in the electron beam direction so that the observed diffraction pattern may appear to come from only a part of the unit cell.

Dynamical scattering is a well-known phenomenon in electron diffraction where the scattering cross-section for electrons is much larger than for X-rays. Diffracted beam amplitudes may be calculated as a function of crystal thickness from a perfect crystal, using, for example, the Cowley–Moodie multislice technique. (For practical guidelines, see ref 8–10.) Each zone must be analyzed

0024-9297/84/2217-2202$01.50/0