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Neutron Scattering Studies of Dimensions and of Interactions between Components in Polystyrene/Poly(vinyl methyl ether) and Poly(vinylidene fluoride)/Poly(methyl methacrylate) Amorphous Blends[†]

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ABSTRACT: A theory for analyzing the small-angle neutron scattering data from polymer blends over the entire phase diagram is developed. This type of analysis has been applied to polystyrene/poly(vinyl methyl ether) and poly(vinylidene fluoride)/poly(methyl methacrylate) amorphous blends, leading to the molecular weight, M_w, and radius of gyration, R_g, for the labeled molecules and the χ interaction parameter between the components of the polymer blend. The values of M_w and R_g together with the interaction parameter χ suggest that the two polymer blend systems studied in this work are miscible.

Introduction

Polymer blends have received considerable attention recently because of the current emphasis on modifying existing synthetic polymers rather than synthesizing new ones. This increased interest is evidenced by the number of recently published review on the compatibility and phase separation behavior of polymer blends.[1–5]

Several techniques have been developed in the past for studying polymer mixtures.[4] Over the last decade small-angle neutron scattering has been predominantly used for investigating homopolymers. Recently, this technique has been extended to polymer blends in order to quantitatively determine thermodynamic parameters.[6–12] The experiments consist of mixing a deuterated polymer with a second protonated one and studying this solid solution in a manner analogous to the classical light scattering of polymer solutions. The familiar Zimm analysis gives information about the weight-average molecular weight, M_w, the radius of gyration, R_g, and the virial coefficient, A_2, which is related to the Flory χ interaction parameter per monomer unit. These three values provide an understanding of the thermodynamics governing the miscibility of polymer mixtures.

The applicability of Zimm analysis to polymer mixtures has been limited, however, to the dilute regime. Thus, the investigation of the polymer mixtures has been limited to the edges of the phase diagram. In the present work we introduce an analysis for the evaluation of neutron scattering data which allows us to investigate dilute as well as concentrated solid solution polymer mixtures. The theoretical analysis[40] has been tested with results obtained from two polymer blend systems at different compositions and temperatures.

Scattering Theory

Over the past few years several theoretical treatments have been developed for the small-angle neutron scattering data obtained from concentrated solutions for homogeneous multicomponent[13–17] and for multiphase systems.[18,22] Here we present a new version and combine existing theories in a way to provide us with an analytical tool for the study of polymer blends.

We consider a homogeneous mixture of two polymers, A and S. The A polymer chains consist of hydrogen-containing chains, designated H, but will be partially replaced by the corresponding deuterated species, D. The H, D, and S components have a degree of polymerization Z_H, Z_D, and Z_S, respectively.

The elastically scattered intensity from such a mixture that has been corrected for contributions due to incoherent scattering is generally expressed in terms of the Rayleigh factor[45] and is related to the Fourier transformation of the monomer density correlation function as follows:

$$R(\vec{q}) = \sum\sum a_k a_j S_{kj}(\vec{q}) \tag{1}$$

where the subscripts k and j represent the three species present (here $k, j = \mathrm{H, D, S}$), and a_k and a_j are the coherent scattering lengths assuming that all subunits have the same volume, and q the amplitude of the scattering vector, is given by $(4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident beam and θ the angle between the incident and the scattered beam. The scattering function, $S_{kj}(\vec{q})$, is determined by the relation

$$S_{kj}(\vec{q}) = \left\langle \int [n_k(\vec{r}) - \langle n_k\rangle][n_j(0) - \langle n_j\rangle] \exp(-i\vec{q}\vec{r})\, \mathrm{d}r \right\rangle \tag{2}$$

The $n_k(\vec{r})$ is equal to unity if there is a monomer unit of species k in the volume element $\mathrm{d}\vec{r}$ and zero otherwise. $\langle n_k\rangle$ and $\langle n_j\rangle$ are the values of n_k and n_j averaged over the entire sample. We define

$$\delta n_k(\vec{r}) = n_k(\vec{r}) - \langle n_k\rangle \tag{3}$$

By using eq 3, which represents the local density fluctuations, we write eq 2 as

$$\begin{aligned} S_{kj}(\vec{q}) &= \left\langle \int \delta n_k(\vec{r})\cdot\delta n_k(0) \exp(-i\vec{q}\vec{r})\, \mathrm{d}^3\vec{r} \right\rangle \\ &= \langle \delta\tilde{n}_k(\vec{q})\cdot\delta\tilde{n}_j(0)\rangle \end{aligned} \tag{4}$$

For an incompressible system

$$\delta n_{\mathrm{H}}(\vec{q}) + \delta n_{\mathrm{D}}(\vec{q}) + \delta n_{\mathrm{S}}(\vec{q}) = 0 \tag{5}$$

By combination of eq 5 and 4 we get

$$S_{\mathrm{SS}}(\vec{q}) = S_{\mathrm{HH}}(\vec{q}) + S_{\mathrm{DD}}(\vec{q}) + 2S_{\mathrm{HD}}(\vec{q}) \tag{6}$$

$$S_{\mathrm{HS}}(\vec{q}) = -S_{\mathrm{HH}}(\vec{q}) - S_{\mathrm{HD}}(\vec{q}) \tag{7}$$

$$S_{\mathrm{DS}}(\vec{q}) = -S_{\mathrm{DD}}(\vec{q}) - S_{\mathrm{HD}}(\vec{q}) \tag{8}$$

From eq 1, 6, 7, and 8 we obtain

[†] We dedicate this paper to our esteemed colleague, Walter Stockmayer, whose pioneering work in the physical chemistry of polymer solutions and in the theory of scattering has been an inspiration for our studies.

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$$R(\vec{q}) = (a_H - a_S)^2 S_{HH}(\vec{q}) + (a_D - a_S)^2 S_{DD}(\vec{q}) + 2(a_H - a_S)(a_D - a_S) S_{HD}(\vec{q}) \quad (9)$$

Each pair correlation function can be divided into two parts. The first part, $P_{k \text{ or } j}(\vec{q})$, arises from interactions between monomer units within a polymer molecule and the second, $Q_{kj}(\vec{q})$, originates from intermolecular pair interactions. Therefore, we can write $S_{kj}(\vec{q})$ as

$$S_{HH}(\vec{q}) = N_H Z_H^2 [P_H(\vec{q}) + N_H Q_{HH}(\vec{q})] \quad (10)$$

$$S_{DD}(\vec{q}) = N_D Z_D^2 [P_D(\vec{q}) + N_D Q_{DD}(\vec{q})] \quad (11)$$

$$S_{HD}(\vec{q}) = N_H Z_H N_D Z_D Q_{HD}(\vec{q}) \quad (12)$$

where N_H and N_D are the total numbers of H and D macromolecules per unit volume, respectively. Assuming $Z = Z_H = Z_D$, the only difference between protonated and deuterated species is the coherent scattering lengthy density. They have the same single-chain scattering function; that is

$$P_H(\vec{q}) = P_D(\vec{q}) = P(\vec{q})$$

This implies that the interaction coefficients between H and S, χ_{HS}, and between D and S, χ_{DS}, are identical and that the interaction coefficient between H and D is zero so that the molecular conformation of the H and D polymers is identical. This is approximately but not exactly true as discussed later. The intermolecular correlation functions of deuterated and hydrogenated molecules are also assumed to be equivalent such that

$$Q_{HD}(\vec{q}) = Q_{DD}(\vec{q}) = Q_{HH}(\vec{q}) = Q(\vec{q})$$

Incorporating all of these results into eq 10–12 and finally combining them with eq 9, we obtain

$$R(\vec{q}) = Z^2\{[N_H(a_H - a_S)^2 + N_D(a_D - a_S)^2]P(\vec{q}) + [N_H(a_H - a_S) + N_D(a_D - a_S)]^2 Q(\vec{q})\} \quad (13)$$

For specifically symmetrical systems, the scattering intensity depends only upon the magnitude of $\vec{q}$. Since our experiments are performed at the relaxed state of the polymeric materials, we have a spherical symmetric system. Consequently, hereafter we will express our equations in scalar quantities of q. This equation can be rewritten in terms of the average length of the labeled component

$$\bar{a} = x a_D + (1 - x) a_H$$

where $x = N_D/(N_H + N_D)$. Thus

$$R(q) = x(1 - x)(a_D - a_H)^2 N Z^2 P(q) + (\bar{a} - a_S)^2 N Z^2 [P(q) + N Q(q)] \quad (14)$$

It is seen that Z_S, $P_S(q)$, and $Q_S(q)$ involving species S do not explicitly appear in the expression. This is a direct result of the incompressibility assumption. If there is no labeling ($x = 0$ or 1) or if radiation other than neutrons is used where the labeing procedure is not applicable, then only the second term remains and is not possible to separate $P(q)$ and $Q(q)$. In this case, interaction in terms of single molecular parameters is not possible except in dilute solution, where $P(q) \gg NQ(q)$.

A particular case of interest is that where only the labeled species is present; that is, $N_S = 0$. Then from the incompressibility assumption we have the following result: $P(q) = -NQ(q)$.[13-17] The second term of eq 14 vanishes, and the result is

$$R(q) = x(1 - x)(a_H - a_D)^2 N Z^2 P(q). \quad (15)$$

By this relation the weight-average molecular weight, M_w, and the radius of gyration, R_g, can be obtained by measuring the scattering intensity, which is maximized at $x = 0.5$. This is identical with a result previously proposed[13-17] and experimentally demonstrated.[14,15,17]

The second term of eq 14 also vanishes when $\bar{a} = a_S$. This condition may be achieved by proper selection of x, provided a_S is between a_H and a_D. Under these conditions of contrast matching, M_w and R_g may also be directly determined.

If interactions are independent of the deuteration (x), then measurements of $R(q)$ at several values of x permit the determination of $P(q)$ and $Q(q)$. By performing two neutron scattering experiments in which we change only the labeled composition x or one experiment with neutrons and another with X-rays on the same sample, provided we have enough electron density difference between A and S molecules, we can separate the two terms in eq 14.

The first term ($R_1(q)$) of eq 14 can be presented in the following form:

$$\frac{K_{\mathcal{N}} c(1 - c)}{R_1(q)} = \frac{1}{M_w} + \frac{R_g^2 q^2}{3M_w} \quad (16)$$

where $K_N = (\mathcal{N}/m^2)(a_H - a_D)^2$; m is the molecular weight of the monomer unit, $\mathcal{N}$ is the Avogadro number, c is the concentration in g/cm^3, M_w is the weight-average molecular weight, and R_g is the radius of gyration. It is obvious from eq 16 that by performing a Zimm-type analysis we are able to obtain R_g and M_w.

For low concentrations of the labeled molecules in the A component, the relationship between $P(q)$ and $Q(q)$ is defined according to Zimm[39] by the relation

$$Q(q) = -2A_2 \frac{M_D^2}{\mathcal{N}} P^2(q) \quad (17)$$

where M_D is the molecular weight of the labeled molecules and A_2 is the second virial coefficient, which is related to the χ interaction parameter as follows:

$$A_2 = (\tfrac{1}{2} - Z_S \chi_{AS}) \rho_A^2 \bar{V}_S \quad (18)$$

where Z_S is the degree of polymerization of the S component having molal volume $\bar{V}_S$ and ρ_A is the mass density of the A component.

When $a_H = a_S$ relation 14 is reduced to

$$R(q) = (a_H - a_D)^2 N Z^2 [x P(q) + N x^2 Q(q)] \quad (19)$$

By substitution of N in the above equation with $\rho \mathcal{N}/M_w$ and substitution of the product ρx by c, where ρ is the mass density, we obtain

$$R(q) = K_{\mathcal{N}} c [M_w P(q) + \mathcal{N} c Q(q)] \quad (20)$$

On substitution of eq 17 into (20) we obtain

$$R(q) = K_{\mathcal{N}} c [M_w P(q) - 2A_2 c M_w^2 P^2(q)] \quad (21)$$

The above equation can be rearranged into a Zimm equation[43] as follows:

$$\frac{K_{\mathcal{N}} c}{R(q)} = \frac{1}{M_w P(q)} + 2A_2 c \quad (22)$$

From eq 22 we are able to obtain the molecular weight M_w, the radius of gyration, R_g, and the second virial coefficient, A_2. The above relationship is valid only for low compositions of labeled molecules in the labeled component and when the interactions between H and D are zero.

In the case of high concentrations of the labeled molecules in the A component we can obtain the information of the χ interaction parameter from the second term of eq 14, which describes the concentration fluctuations between a mean polymer [$\bar{a} = xD + (1 - x)H$] and a second one called S.

The scattering intensity of $q = 0$ may be related to the interaction parameter χ_{AS} between the polymers A and S. Through the Einstein relationship[23]

$$R_2(0) = (RTK_N c)/(\partial\pi/\partial c) \tag{23}$$

where $R_2(0)$ is the second term of eq 14 at $q = 0$, R is the gas constant, c is the concentration in g/cm^3 and π is the osmotic pressure, which is related to the chemical potential through the relation

$$\pi = -(\Delta\mu/V_A) \tag{24}$$

where V_A is the partial molar volume of component A and $\Delta\mu$ is the difference in chemical potential of the solution and solvent, given by

$$\Delta\mu = RT[\ln(1 - \varphi) + (1 - Z_S/Z_A)\varphi + Z_A\chi_{AS}\varphi^2] \tag{25}$$

where φ is the volume fraction of the protonated plus the deuterated polymer in the mixture and Z_S is the degree of polymerization of the component S. By using relations 23–25 and substituting $R_2(0)$ with the second term of eq 14 at $q = 0$, we obtain after the calculations

$$\{\varphi Z_A[P(0) + N_AQ(0)]\}^{-1} = (\varphi Z_A)^{-1} + ((1 - \varphi)Z_S)^{-1} - 2\chi_{AS} \tag{26}$$

From eq 26 we can calculate χ_{AS}

$$\chi_{AS} = \{[\varphi Z_A(P(0) + N_AQ(0))]^{-1} - (\varphi Z_A)^{-1} - ((1 - \varphi)Z_S)^{-1}\}/2 \tag{27}$$

The scattering intensity can be expressed in more general terms by using the results of the "random phase approximation" (RPA)[24] in terms of the intramolecular interaction function [$P^0(q)$ and $P_S{}^0(q)$] at Θ conditions and the interaction parameter χ_{AS}

$$\{\varphi Z_A[P(q) + N_AQ(q)]\}^{-1} = \frac{1}{\varphi Z_A P^0(q)} + \frac{1}{(1 - \varphi)Z_S P_S{}^0(q)} - 2\chi_{AS} \tag{28}$$

Thus, by using the second term of eq 14 and either relation 27 or 28, we can measure the χ_{AS} interaction parameter at zero scattering vector ($q = 0$), where $P^0(0)$ and $P_S{}^0(0)$ are equal to unity. By performing only two experiments and not four, as in a Zimm-type analysis, we can learn about the state of the miscibility in polymer mixtures over the entire phase diagram. This is illustrated by the results in the following sections on two different polymer mixtures.

Experimental Section

Materials. The polymers used in this study were protonated polystyrene (PSH), synthesized by anionic polymerization, deuterated polystyrene (PSD) (both from Polymer Laboratories), poly(vinyl methyl ether) (PVME) (Scientific Polymer Products), poly(vinylidene fluoride) (PVF$_2$), protonated atactic poly(methyl methacrylate) (PMMAH), and deuterated attactic poly(methyl methacrylate) (PMMAD) (supplied through the courtesy of E. I. du Pont de Nemours and Co). The molecular characteristics of a polymers are presented in Table I.

Specimen Preparation. Two series of mixtures were investigated: one with PS and PVME and another with PMMA and PVF$_2$. The PS/PVME mixtures were prepared by dissolution in benzene at low concentration (<2%) followed by freeze-drying. Disk-shaped specimens of 10-mm diameter and 1-mm thickness were obtained by molding the PS/PVME powder blend under vacuum at 100 °C.

Cast films of PVF$_2$/PMMA blends and PVF$_2$ were prepared from *N,N*-dimethylformamide solutions of the polymers according to a procedure described earlier.[25] The cast films were stacked together and melt pressed under vacuum at 225 °C for 10 min and then rapidly quenched in ice water. This procedure avoided crystallization of the PVF$_2$. Specimens that were discolored or that contained bubbles were discarded.

Table I
Molecular Weights and Polydispersities for the Polymers Used in This Study

	M_n	M_w	M_w/M_n
PSH	77 000	81 000	1.05
PSD	78 000	71 000	1.09
PVME	46 500	99 000	2.12
PMMAH	36 600	91 500	2.50
PMMAD	36 400	102 000	2.80
PVF$_2$	375 000	555 000	1.48

Scattering Techniques. The small-angle neutron scattering experiments were carried out at the National Center for Small Angle Scattering Research (NCSASR) located at Oak Ridge National Laboratory (ORNL). The 30-m SANS facility was used with a pinhole collimation, a wavelength of 4.75 Å, and a two-dimensional position-sensitive detector (64 × 64 cells) placed 15 m from the sample. Each experiment was carried out in four steps, three for the background measurements using the fully hydrogenated (H), deuterated (D), and S polymers separately, and a fourth for the polymer mixture, the sample, of the hydrogenated, deuterated, and third components (H/D/S). The coherent scattering intensity as given in eq 14 was obtained by subtracting the scattering obtained for the pure H, D, and S weighted by their respective mole fractions from the total scattering of the ternary mixture (H/D/S). The detector sensitivity was determined with pure water, where the scattering is incoherent and thus essentially independent of angle. The calibration of the instrument was performed by using a standard hydrogenated polystyrene M_n = 71 000 mixed with the homologous deuterated (18.3%) polystyrene.

The high-temperature experiments were performed by using a heating cell specially designed for the SANS instrument. The specimen was held between two quartz windows. Corrections due to the quartz scattering were performed.

Results and Discussion

The cloud point curve for PS/PVME was determined previously by Nishi et al.[4,26] and recently in our laboratory.[27] The PVF$_2$/PMMA cloud point curve in the melt has also been studied previously.[28-32] Both systems exhibit lower critical solution temperature (LCST) behavior. For the PS/PVME blend the minimum of the binodal was observed around 100 °C and was higher for lower molecular weights of the polystyrene component. In the PVF$_2$/PMMA blend the minimum in the cloud point curve occurred about 350 °C.

Polystyrene/Poly(vinyl methyl ether) (PS/PVME) Blend. Previously scattering studies on this blend considered only the dilute regime of two components.[11] Using a three-component system (H, D, and S) from a scattering point of view, we studied two different compositions of PS/PVME, 75/25 (w/w) and 50/50 (w/w), in the concentrated regime. In Figure 1 we present typical scattering intensities as a function of q obtained for two different compositions of labeled polystyrene, maintaining the same total composition of PS/PVME, namely, 75/25 (w/w). All intensities have been corrected for the empty beam, background, and incoherent scattering. In Figures 2 and 3 we present the $NZ^2P(q)$ and $N^2Z^2Q(q)$ intra- and intermolecular interference functions, respectively, obtained for the 75/25 (w/w) PS/PVME blend as a function of q, eq 13. From the slope and the intercept of the plot $[NZ^2P(q)]^{-1}$ vs. q^2 (Figure 4) we obtain the radius of gyration of the labeled molecules and from the intercept, the molecular weight. The interaction parameter χ was obtained from the second term of eq 14 at $q = 0$ using relation 27. The results are presented in Table II for the total compositions of 75/25 (w/w) and 50/50 (w/w).

The molecular weights and radii of gyration of PSD in the blend are relatively independent of the composition and approximately equal to the values obtained in the

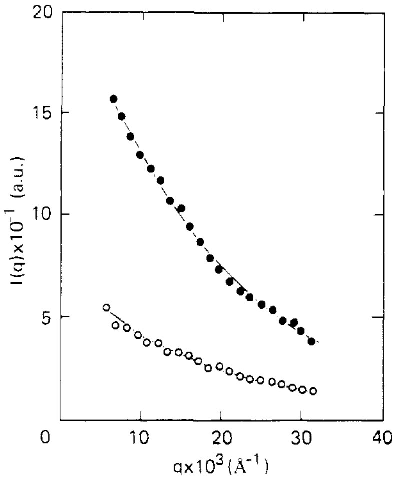

Figure 1. Scattering intensity vs. scattering q for the PS/PVME blend with 75/25 (w/w) composition in which 5% (○) and 20% (●) by weight of the PSH has been replaced with PSD.

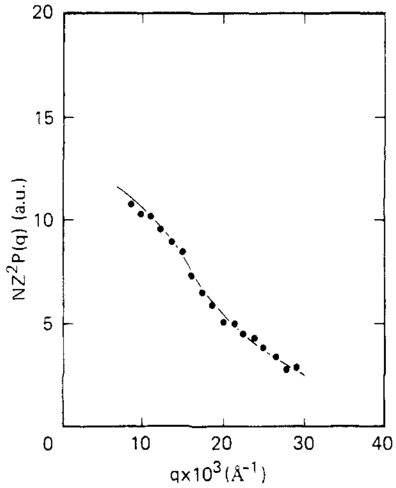

Figure 2. Intramolecular interference function $NZ^2P(q)$ is presented as obtained from the scattering data on the PS/PVME blend with 75/25 (w/w) composition (Figure 1) and eq 13.

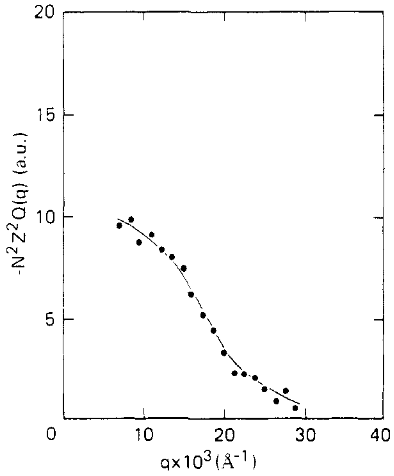

Figure 3. Intermolecular interference function $N^2Z^2Q(q)$ is presented for the PS molecules in the PS/PVME blend with 75/25 (w/w) composition.

PSH/PSD mixture. The interaction parameter χ is concentration dependent and negative. In view of the negative χ, one should expect that R_g in the blend is larger than in the bulk state. That values of the molecular weight and radius of gyration of the PSD in the blend are comparable with those of the PSD in the PSH in the bulk state together with the fact that the interaction parameter χ is negative indicate that we have a miscible blend of PS and PVME. We emphasize at this point te fact that M_w, R_g, and the χ interaction parameter are all necessary for deciding the state of miscibility.

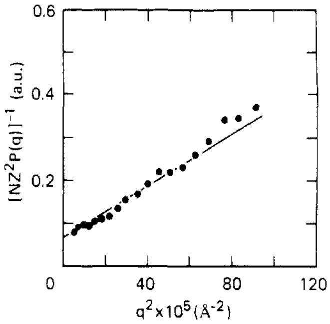

Figure 4. Value of $[NZ^2P(q)]^{-1}$ vs. q^2 is presented as in a single Zimm plot. The intercept is related to the molecular weight of PS molecules, and the combination of the slope and the intercept is related to the radius of gyration of PS.

Table II
Values of M_w, R_g, and χ for PVME/PS Blends Measured by SANS

	composition, w/w	R_g, Å ±5%	M_w ±10%	χ ±25%
PVME/PS	25/75	80	80 000	-4.1×10^{-4}
PVME/PS	50/50	82	74 000	-3.2×10^{-4}
PSH/PSD	82/18	79	78 000	

Table III
Values of χ for PVME/PS Blends

	composition, w/w	SANS this work	vapor sorption [a]	SANS Zimm plot [b]
PVME/PS	25/75	-4.1×10^{-4}	-1.7×10^{-3}	
PVME/PS	50/50	-3.2×10^{-4}	-1.5×10^{-3}	
PVME/PS	95/5			-4.0×10^{-2}

[a] Reference 34. [b] Reference 11.

A preliminary study of the temperature effect on the PS/PVME mixture showed us that as we increased the temperature, R_g was slightly decreasing, M_w was constant to the error limit, and the χ interaction parameter increased, approaching zero from negative values. These preliminary data indicate that as we increase the temperature, we approach the binodal. More detailed experiments are under way for several blend compositions and temperatures as close as possible to the binodal.

Previous work using vapor sorption measurements[34] and SANS in a two-component dilute blend system[11] has shown, also by studying the χ interaction parameter, that a miscible blend has been obtained. In Table III we present values of χ obtained by us, Kirste et al.[11] by analyzing the SANS data through the Zimm plot technique, and Kwei et al.[34] using the vapor sorption technique. We conclude from these values (Table III) that the different techniques show a composition dependence of the interaction parameter χ as well. The values of χ measured by other investigators do not compare directly with ours due to the different molecular weights of the PVME used for the blends and the different conditions of the preparation. Recently, Schelten[44] studied the temperature dependence of the χ's of the concentrated solutions of the PSD with PVME using SANS. The values of χ's obtained are in good agreement with ours considering that the amorphous polymer blend system has been prepared above the glass transition (T_g) and then cooled rapidly to below room

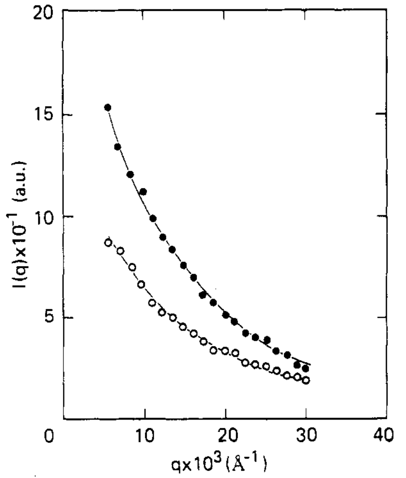

Figure 5. Scattering intensity vs. q for the PVF$_2$/PMMA blend with 50/50 (v/v) composition in which 8.2% (○) and 20.7% (●) by weight of the PMMAH has been replaced with PMMAD.

Table IV
Values of M_w, R_g, and χ for PVF$_2$/PMMA Blends Measured by SANS

	composition, w/w	R_g, Å ±5%	M_w ±10%	χ ±25%
PVF$_2$/PMMA	25/75	119	45 000	-6.3×10^{-4}
PVF$_2$/PMMA	50/50	110	50 000	-1.7×10^{-4}
PMMAH/PMMAD	80/20	115	54 000	

temperature. If the T_g is above room temperature, then the structure of the blend will be frozen upon passing through T_g. Thus in this case the measured χ will correspond to a temperature near T_g (which will depend upon the composition of the blend).

Poly(vinylidene fluoride)/Poly(methyl methacrylate) (PVF$_2$/PMMA) Blends. This type of mixture has been extensively studied in the past.[25,28-33,35-38] Here we present the results obtained from the neutron scattering experiments performed with specimens having two different total compositions, 25/75 (v/v) and 50/50 (v/v) (PVF$_2$/PMMA). In Figure 5 we present the scattering intensities for a 50/50 (v/v) PVF$_2$/PMMA mixture in which we vary the labeled PMMA composition. Analyzing these scattering intensities with eq 13, we obtain the scattering functions $NZ^2P(q)$ and $N^2Z^2Q(q)$ presented in Figures 6 and 7, respectively. The values of M_w and R_g measured by using a Zimm-type plot (Figure 8)[39] and the interaction parameter χ obtained from the experimental data using the analysis described in the theoretical section are presented in Table IV.

The molecular weights and the radii of gyration of PMMAD in the blend are independent of the comparison and approximately equal to the values measured in PMMAH/PMMAD in the bulk. These molecular dimensions together with the negative interaction parameter χ demonstrate that the PVF$_2$/PMMA blend in the amorphous state is miscible.

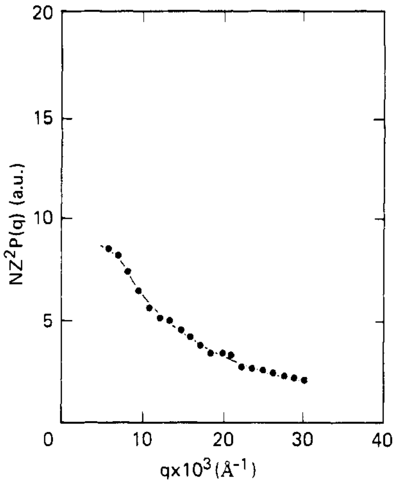

Figure 6. Intramolecular interference function $NZ^2P(q)$ is presented as obtained from the scattering data of the PVF$_2$/PMMA blend with 50/50 (v/v) composition (Figure 5) and eq 13.

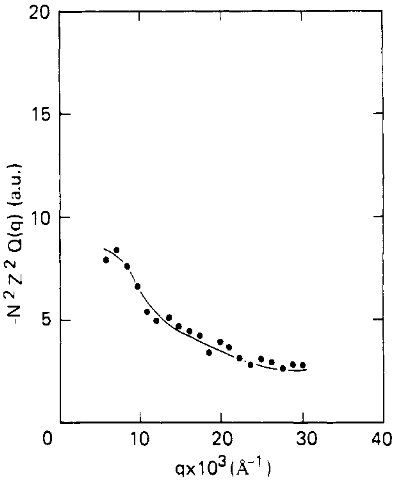

Figure 7. Intermolecular interference function $N^2Z^2Q(q)$ is presented for the PMMA molecules in the PVF$_2$/PMMA blend with 50/50 (v/v) composition.

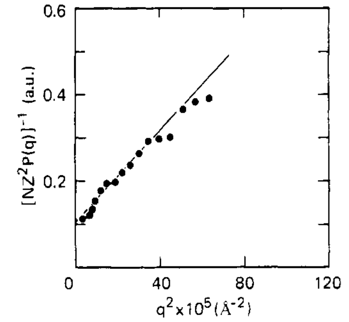

Figure 8. Value of $[NZ^2P(q)]^{-1}$ vs. q^2 is presented as in a single Zimm plot. The intercept is related to the molecular weight of PMMA molecules, and the combination of the slope and intercept is related to the radius of gyration of PMMA.

Table V
Values of χ for PVF$_2$/PMMA Blends

		$\chi \times 10^4$					
			melting point depression				
	composition, v/v	SANS this work	ref 35	ref 38	ref 25 and 37	SAXS[a]	inverse gas chrom[b]
PVF$_2$/PMMA	25/75	-6.28	-8.19	-2.50	-6.56	-1.99	-4.09
PVF$_2$/PMMA	50/50	-1.64	-8.19	-1.67	-2.46	-4.99	+1.91

[a] Reference 38. [b] Reference 41.

The values of the interaction parameter χ are also composition dependent and compare well with the values (Table V) obtained from the melting point depression technique,[25,35,37,38] SAXS,[38] SANS, and inverse gas chromatography.[41] We observe a good agreement of the χ values obtained from different techniques. It is noted that one set of melting point depression values of χ[35] does not show concentration dependence. However, the Hoffman–Weeks technique for obtaining equilibrium melting points was not used in this case, so these values may reflect a melting point change arising from differences in crystal thickness or perfection as well as those related to the chemical potential of the amorphous phase.

Conclusions

A method for studying blends over the entire phase diagram with neutron scattering and its application to two particular amorphous polymer blends (PVME/PS and PVF_2/PMMA) has been presented.

This method proved to be useful for studying polymer blends. However, improvements need to be made in order to take into account the polydispersity, the differences in molecular weights, and the nonequal interaction parameters between the protonated polymer and the third polymer (H/S) and the deuterated polymer and the third polymer (D/S). Recently, we found a surprising difference of 40 °C in the lower critical solution temperature (LCST) between PVME/PSD and PVME/PSH.[27] Obviously, this difference is due to the nonequality of the interaction parameters between χ_{DS} and χ_{HS} and the nonzero value of χ_{HD}.

By calculating the interaction parameters χ from the solubility parameters (δ) of PSH, PSD, and PVME, which are 9.10, 9.06 and 8.10 $(cal/cm^3)^{1/2}$, respectively, we found that the difference between $\chi_{PSH/PVME}$ and $\chi_{PSD/PVME}$ is of the order of 0.02. According to the calculations of McMaster[42] using equation-of-state theory, this small difference is enough to cause a shift of the LCST as much as we observed ($\sim$40 °C). Also this small difference between χ_{HS} and χ_{DS} cannot be distinguished with the SANS technique due to the error limits. The interaction parameter between the protonated and deuterated polystyrene is very small, justifying our assumption in the theoretical treatment for the analysis of the neutron scattering experiments.

The characteristic ratio for PMMA calculated from the SANS measurements is not in good agreement with the conventionally accepted value, probably due, in part, to the fact that the polymer was of broad molecular weight distribution. In this case, the values of M_w determined by solution characterization and by SANS are also not in good agreement, possibly arising in part from calibration errors. It is noted that the SANS value is lower, so it is unlikely that the discrepency is related to aggregation in the blend.

While ideally, measurements on narrow molecular weight distribution polymers are desirable, this was not done in this study because narrow-distribution PMMAD was not readily available.

For the moment, our experiments in their design and analysis are valuable since the difference in χ parameters is small. But for future work one should measure the χ_{HS} and χ_{DS} separately by measuring the scattering intensity of the H/S and D/S blends separately and analyzing the data with eq 27. Evidently, this experiment can be performed as a function of composition so that we can find the composition dependence of χ.

The method which we developed for studying polymer blends was used for the investigation of two systems, PS/PVME and PVF_2/PMMA. The conclusion is that both blends are miscible under the conditions of preparation. This conclusion is supported by the fact that the measured interaction parameters were negative, indicating strong specific interactions which ensure the miscibility of the two polymers.

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Registry No. PS, 9003-53-6; PVME, 9003-09-2; PVF_2, 24937-79-9; PMMA, 9011-14-7; neutron, 12586-31-1.

References and Notes

(1) Paul, D. R.; Altamirano, J. O. *Adv. Chem. Ser.* **1975**, *No. 142*, 371.

(2) Manson, J. A.; Sperling, L. H. "Polymer Blends and Composites"; Plenum Press: New York, 1976.

(3) Klempner, D.; Frisch, K. C., Eds. "Polymer Alloys: Blends, Blocks, Grafts, and Interpenetrating Networks"; Plenum Press: New York, 1977.

(4) Polymer Blends, Paul, D. R.; Newman, S., Eds. "Polymer Blends"; Academic Press: New York, 1978; Vols. I, II.

(5) Paul, D. R.; Barlow, J. W. *Adv. Chem. Ser.* **1979**, *No. 176*, 315.

(6) Kirste, R. G.; Kruse, W. A.; Ibel, K. *Polymer* **1975**, *16*, 120.

(7) Ballard, D. G. H.; Rayner, M. G.; Schelten, J. *Polymer* **1976**, *17*, 640.

(8) Russell, T. P.; Stein, R. S. *J. Macromol. Sci. Chem.* **1980**, *B17*, 617.

(9) Wignall, G. D.; Child, H. R.; Li-Aravena, F. *Polymer* **1980**, *21*, 131.

(10) Walsh, D. J.; Higgins, J. S.; Doube, C. P.; McKeown, J. G. *Polymer* **1981**, *22*, 168.

(11) Jelenic, J.; Kirste, R. G.; Schmitt, B. J. private communication of results to be published in *Makromol. Chem.*

(12) Russell, T. P.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1593.

(13) Williams, C., et al. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 379.

(14) Akcasu, A. Z.; Summerfield, G. C.; Jahshan, S. N.; Han, C. C.; Kim, C. Y.; Yu, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 863.

(15) Wignall, G. D.; Hendricks, R. W.; Koehler, W. C.; Lin, J. S.; Wai, M. P.; Thomas, E. L.; Stein, R. S. *Polymer* **1981**, *22*, 886.

(16) Benoit, H.; Koberstein, J.; Leibler, L. *Makromol. Chem., Suppl.* **1981**, *4*, 85.

(17) Boué, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 29.

(18) Summerfield, G. C.; King, J. S.; Ullman, R. *Macromolecules* **1978**, *11*, 218.

(19) Jahshan, S. N.; Summerfield, G. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1859.

(20) Jahshan, S. N.; Summerfield, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2415.

(21) Koberstein, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 593.

(22) Picot, C. "Static and Dynamic Properties of the Polymeric Solid State"; Pethrick, R. A., Richards, R. W.; Eds.; Reidel: Dordrecht, Holland, 1982; pp 127–172.

(23) Einstein, A. *Ann. Phys.* **1910**, *33*.

(24) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; Chapter IV.

(25) Morra, B. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1980.

(26) Nishi, T.; Kwei, T. K. *Polymer* **1975**, *16*, 285.

(27) Yang, H.; Hadziioannou, G.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 159.

(28) Wahrmund, D. C.; Bernstein, R. E.; Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1978**, *18*, 677.

(29) Bernstein, R. E.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 683.

(30) Bernstein, R. E.; Wahrmund, D. C.; Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1978**, *18*, 1220.

Macromolecules **1984,** *17,* 573–585

(31) Paul, D. R.; Barlow, J. W.; Bernstein, R. E.; Wahrmund, D. C. *Polym. Eng. Sci.* **1978**, *18*, 1225.
(32) Bernstein, R. E.; Cruz, C. A.; Paul, D. R.; and Barlow, J. W. *Macromolecules* **1977**, *10*, 681.
(33) Wang, T. T.; Nishi, T. *Macromolecules* **1977**, *10*, 421.
(34) Kwei, T. K.; Nishi, T.; Roberts, R. F. *Macromolecules* **1974**, *7*, 667.
(35) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(36) Patterson, G. D.; Nishi, T.; Wang, T. T. *Macromolecules* **1976**, *9*, 603.
(37) Morra, B. S.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(38) Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 439.
(39) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(40) Hadziioannou, G.; Gilmer, J.; Stein, R. S. *Polym. Bull.* **1983**, *9*, 563.
(41) Di Paola-Baranyi, G.; Fletcher, S. J.; Degre, P. *Macromolecules* **1982**, *15*, 885.
(42) McMaster, L. P. *Macromolecules* **1976**, *6*, 760.
(43) Stein, R. S.; Hadziioannou, G.; accepted for publication in *Macromolecules*.
(44) Herkt-Maetzky, C.; Schelten, J., private communication.
(45) The Rayleigh factor is defined as

$$R(\vec{q}) = I_s(\vec{q})d^2/I_0V_s$$

where d is the sample-to-detector distance, $I_s(\vec{q})$ is the scattered intensity, I_0 is the incident beam intensity, and V_s is the scattering volume. The $R(\vec{q})$ used in light scattering is equivalent to the differential scattering cross section $d\Sigma/d\Omega$ used in neutron scattering.

Multiphase Equilibria in Solutions of Polydisperse Homopolymers. 3. Multiple Critical Points[†,‡]

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ABSTRACT: The cloud-point curve equation is derived for a solution of a polydisperse polymer with a concentration-dependent interaction parameter $g(T,\phi)$, and a method for its numerical solution is devised. Also, a classification scheme is proposed for critical points based on their multiplicity, and the relationship between our and the previously devised categories is probed (particularly between our triple critical point and the tricritical point). Criteria for the existence of critical points of multiplicity $m = 2$–6 are given in terms of chain-length averages, concentration derivatives of $g(T,\phi)$, and the overall polymer concentration ϕ. The significance of multiple critical points lies in their close association with multiphase equilibria. Such points may arise because of the asymmetry of the chain-length distribution and/or because of a strong concentration dependence of $g(T,\phi)$. Two specific cases are analyzed: a polydisperse polymer solution with a concentration-independent parameter $g(T)$, and a monodisperse polymer solution with a concentration-dependent parameter $g(T,\phi)$. In the first instance, multiple critical points may appear even in systems with only a few components if their characteristics are properly chosen. At most, an s-component system at constant pressure may display a critical point of multiplicity $2s - 3$, and it may separate into s phases. In the latter case, double and triple critical points may appear if the concentration dependence of $g(T,\phi)$ is at least quadratic. The pattern of cloud-point curves for the two analyzed cases is distinctly different.

1. Introduction

The first to introduce the concept of a critical point of multiplicity higher than one was probably Korteweg.[2] Without much reference to any physical situation, he studied the characteristics of certain singular points (critical points, or plait points, among others) on a three-dimensional surface, as well as their behavior during a continuous transformation of this surface. His classification of critical points into points of the first and second kind (located on convex–convex and convex–concave parts of the surface, respectively) has been shown[3,4] to have a thermodynamic significance, as the phases around such points on the free energy ternary surface are (meta)stable and unstable, respectively. Furthermore, Korteweg noticed that upon transformation of the surface, two real critical points may approach each other, merge, forming a double plait point, and become imaginary (i.e., disappear from the surface). A homogeneous double critical point was defined as a confluence of two critical points of the first kind, while a heterogeneous double critical point designated merging of critical points of the first and second kind.

Extensive thermodynamic interpretation of the above singular points was given by van der Waals[3] and Schreinemakers,[4] although only in terms of mathematical criteria and general patterns of resulting phase diagrams. Meijering[5] with Hardy[6] then analyzed in detail the phase behavior of ternary and quaternary regular solutions and concluded that these systems may contain only homogeneous double critical points since all critical points in such solutions have to be stable or metastable. Tompa,[7] on the other hand, studied three-phase separation in solvent–polymer (1)–polymer (2) ternary systems where the two polymers differed merely by their chain lengths but did not interact with each other. Assuming simple Flory–Huggins thermodynamics (with a concentration-independent parameter χ),[8] he discovered that the phase separation proceeded via a heterogeneous double plait point mechanism. The validity of this claim was later proven conclusively by applying Korteweg's instability criterion to this case.[9] The same mechanism is in effect for three-phase separations in some solutions of ternary polymer mixtures[10] and of polydisperse polymers in general. The types of double critical points encountered and the manner in which multiphase separations proceed in

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[†] We take pleasure in dedicating this paper to our friend, Professor Walter H. Stockmayer, on the occasion of his 70th birthday.

[‡] Presented in part at the International Symposium on Phase Transitions in Polymers, June 11–13, 1980, Cleveland, Ohio (see ref 1).

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