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Relationship among Polymer–Polymer Interaction Energy Densities and the Deuterium Isotope Effect

Jen-Lien Lin and Ryong-Joon Roe*

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012. *Received February 25, 1987*

ABSTRACT: Cloud points for mixtures of polystyrene and poly(α-methylstyrene) and of polybutadiene and poly(α-methylstyrene) were measured, and the data were analyzed to determine the interaction energy densities Λ for these two pairs of polymers. In conjunction with the value of Λ for the pair polystyrene–polybutadiene previously determined, it is shown that the relationship $\Lambda_{12} = (\Lambda_{23}^{1/2} \pm \Lambda_{31}^{1/2})^2$ is obeyed fairly well. To study the deuterium isotope effect on polymer miscibility, a matching pair of deuteriated and hydrogeneous polystyrenes of closely similar structure were prepared by reacting a preformed polystyrene with either deuteriated benzene or ordinary benzene. It was found that the cloud points for the mixtures of polystyrene and poly(α-methylstyrene) were not affected by the deuteriation of polystyrene but the mixtures of polystyrene and poly(vinyl methyl ether) showed an appreciable deuterium isotope effect. The above-cited relationship linking Λ_{12} to Λ_{23} and Λ_{31} thus fails to predict the deuterium isotope effect on miscibility of polystyrene and poly(α-methylstyrene) if one accepts the literature value for the interaction parameter between hydrogenated and deuteriated polystyrene.

Introduction

The miscibility and phase-separation behavior of polymer blends can be described adequately in terms of mean-field theories. This is in contrast to the behavior of dilute polymer solutions in which the fluctuation effect plays a critical role. Among the mean-field theories, the most widely utilized for discussion of polymer blends are the Flory–Huggins free energy of mixing and the expressions derived by the random phase approximation method. In both these theories the characteristics of the particular polymer pair being considered are embodied in a single constant, the polymer–polymer interaction parameter χ. Prediction of the total thermodynamic behavior of the blend requires only the knowledge of the numerical value of χ for the pair and its possible dependence on temperature, pressure, composition, etc. Despite its practical importance, reliable values of the interaction parameter are available in the literature only for a very limited number of polymer pairs.

We have previously evaluated[1] the interaction parameter between polystyrene and polybutadiene through measurement of cloud points of blends containing these two homopolymers or their random copolymers. The average value of the parameter resulting from these evaluations was utilized to describe the scattering of X-rays[2] from styrene–butadiene block copolymers and their blends with polystyrene and was found to give good agreement with predictions based on the random phase approximation theory. The viability of the evaluation of the χ parameter from cloud points thus established, we now undertake in this work the study of polystyrene–poly(α-methylstyrene) and polybutadiene–poly(α-methylstyrene) pairs. At the same time we reexamine the question of isotope effect[3] on the interaction parameter that could arise when one of the polymers is substituted by its deuteriated equivalent.

The Flory–Huggins free energy of mixing, per unit volume of mixture, can be written[1,4] as

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln \phi_1 + (1/V_2)\phi_2 \ln \phi_2] + \Lambda\phi_1\phi_2 \tag{1}$$

where V_1 and V_2 are the molar volumes of polymer 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the mixture. The last term involving Λ is considered formally to include all the free energy of mixing that is not accounted for by the combinatory entropy of mixing, represented by the first term. The quantity Λ thus defined has the dimension of energy per unit volume and can be called polymer–polymer interaction energy density. More traditionally, the Flory–Huggins free energy of mixing is written in the form

$$\Delta G_M'/RT = (1/N_1)\phi_1 \ln \phi_1 + (1/N_2)\phi_2 \ln \phi_2 + \chi\phi_1\phi_2 \tag{2}$$

where $\Delta G_M'$ is the free energy of mixing per lattice volume (or per segment) and N_1 and N_2 are the numbers of segments in polymers 1 and 2. If V_{ref} is the volume of a lattice (or a segment), ΔG_M is equal to $\Delta G_M'/V_{\text{ref}}$, and it is seen that

$$\chi = \Lambda V_{\text{ref}}/RT \tag{3}$$

There are certain advantages[1,4] in using eq 1 based on Λ rather than the more traditional expression based on χ. (i) In the former, the characteristics of component polymers are expressed in terms of the molecular volume and the radius of gyration which are both well-defined experimentally, whereas the latter involves the concept of a lattice which has no experimental basis. (ii) The numerical value of Λ can be determined unambiguously in terms of a physical unit such as joule per centimeter cubed. The value of χ depends on the assumption of V_{ref}, which is often not specified explicitly. The common practice of equating V_{ref} to the volume of a repeat unit is unsatisfactory because the repeat units of the two polymers involved can be very different from each other. The use of χ, as a dimensionless quantity, has advantages for theoretical development, but Λ is the preferred choice for describing experimental results. (iii) For most polymer pairs lacking specific interactions and thus exhibiting the UCST behavior, the temperature dependence of Λ is very moderate, and the interaction energy density can be regarded as a constant in any qualitative or semiquantitative considerations. (iv) The interaction energy density provides a direct link to the familiar concept of solubility parameter through the approximate relationship[1]

$$\Lambda_{12} = (\delta_1 - \delta_2)^2 \tag{4}$$

The corollary of eq 4 is that among three polymers 1, 2, and 3, the Λ values for the three pairs which can be formed should be related approximately among themselves by

$$\Lambda_{12} = (\Lambda_{23}^{1/2} \pm \Lambda_{31}^{1/2})^2 \tag{5}$$

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Table I
Characterization Data of Polymer Samples

designation	polymer	M_n	M_w	remarks
2KPBD	polybutadiene	2 470	2 620	M_n by VPO, M_w/M_n by GPC
3KPBD	polybutadiene	3 430	3 600	M_n by VPO, M_w/M_n by GPC
5KPMS	poly(α-methylstyrene)	4 440	5 330	M_n by VPO, M_w/M_n by GPC
56KPMS	poly(α-methylstyrene)	53 200	56 400	M_w by light scattering, M_w/M_n by GPC
PVME	poly(vinyl methyl ether)	46 500	99 000	from Scientific Polymer Products
18KPS	polystyrene	17 900	18 700	from Pressure Chemicals
49KPS	polystyrene	46 000	49 000	from Pressure Chemicals
100KPS	polystyrene	95 400	101 700	from Pressure Chemicals
18KPSH	polystyrene	18 000	18 700	M_n and M_w by GPC, hydrogen exchanged
18KPSD	polystyrene	17 700	18 400	M_n and M_w by GPC, 93.4% deuteriation
49KPSH	polystyrene	45 400	48 500	M_n and M_w by GPC, hydrogen exchanged
49KPSD	polystyrene	44 200	47 600	M_n and M_w by GPC, 94.3% deuteriation
100KPSH	polystyrene	72 700	91 400	M_n and M_w by GPC, hydrogen exchanged
100KPSD	polystyrene	79 200	91 200	M_n and M_w by GPC, 93.8% deuteriation

Testing the validity of eq 5 is one of the objectives of the present study.

Experimental Section

Materials. Characterization data for all the samples employed are summarized in Table I. Poly(vinyl methyl ether) and three samples of polystyrene were purchased from commercial sources indicated there, and the characterization data for these samples are those furnished by the suppliers. Polybutadienes and poly(α-methylstyrenes) were synthesized in our laboratory by anionic polymerization under vacuum. Butadiene was polymerized in benzene solution at room temperature for 24 h with *n*-butyllithium as the initiator. α-Methylstyrene was polymerized in tetrahydrofuran solution at −78 °C (dry ice temperature) for 14 h with *n*-butyllithium also as the initiator.

The two polystyrenes designated 18KPSH and 18KPSD were prepared by chemical modification of the starting material, 18KPS, by the procedure of hydrogen and deuterium exchange reactions, respectively, as described previously.[3] Thus, 18KPSD was prepared by reacting the polystyrene 18KPS with excess deuteriated benzene in the presence of an organometallic catalyst and thereby allowing the aromatic hydrogens in the original polystyrene to be exchanged to deuteriums. Sample 18KPSH was prepared by exactly the same procedure as above, except that ordinary benzene instead of deuteriated benzene was used. Since the two samples, 18KPSD and 18KPSH, were obtained from the same starting material by the same procedure, their structures are expected to be closely similar to each other except for the difference in the aromatic deuterium and hydrogen atoms. Samples 49KPSH and 49KPSD were similarly prepared from 49KPS as the starting material, and samples 100KPSH and 100KPSD were prepared from 100KPS. The latter two samples are the same materials as were used in our previous work.[3] The degrees of deuteriation of aromatic hydrogens in 18KPSD, 49KPSD, and 100KPSD, determined by NMR, are given in Table I.

The cloud points of the mixtures were determined by light scattering in a manner described in an earlier publication.[1] The pairs of polymers studied are 2KPBD–5KPMS, 3KPBD–5KPMS, 56KPMS–49KPS, 56KPMS–49KPSH, 56KPMS–49KPSD, PVME–18KPS, PVME–18KPSH, PVME–18KPSD, PVME–100KPS, PVME–100KPSH, and PVME–100KPSD. These mixtures, except the ones involving 56KPMS, were prepared by mixing the component polymers without the aid of solvent. Thus, the appropriate amounts of the two polymers were weighed into a glass tube, which was then evacuated and sealed, and the content of the tube was stirred by means of a magnetically activated stirrer at some higher temperature at which the pair was miscible and sufficiently fluid.

With the mixtures containing 56KPMS and a polystyrene, the cloud points could not be readily determined because of the relatively high molecular weights of the component polymers and the high T_g (around 170 °C for PMS). To get around this difficulty, a series of mixtures containing various amounts of dibutyl phthalate in addition to the two polymers were prepared, and their cloud points were first determined. The cloud point of the polymer mixture without the plasticizer was then evaluated by extrapolation of these cloud points to zero concentration of the plasticizer. The samples for the cloud-point measurement were prepared by dissolving weighed amounts of 56KPMS, the polystyrene (49KPS, 49KPSH or 49KPSD), and dibutyl phthalate in toluene and then removing the toluene slowly in a vacuum oven at 75 °C. To check the possibility that a small amount of dibutyl phthalate might also be lost during the removal of the toluene, the results given in Figure 1 were obtained. Here, cloud points obtained with mixtures containing equal weights of 56KPMS and 49KPS to which various amounts of dibutyl phthalate are added are plotted against the weight fraction of the latter. The circles refer to those data obtained with mixtures (containing relatively high concentration of dibutyl phthalate) that were prepared without the aid of toluene, and the squares refer to those results obtained with mixtures prepared with the aid of toluene. Where these two types of data overlap, it is seen that the mixtures prepared with the aid of toluene exhibit cloud points 3–5 °C higher than the mixtures prepared without toluene. As the concentration of dibutyl phthalate in the mixture is reduced, the amount of dibutyl phthalate which is lost during the removal of toluene is also likely to be reduced. The error, if any, in the extrapolated cloud point of the polymer mixture containing no dibutyl phthalate is therefore likely to be much smaller than the 3–5 °C difference apparent in Figure 1.

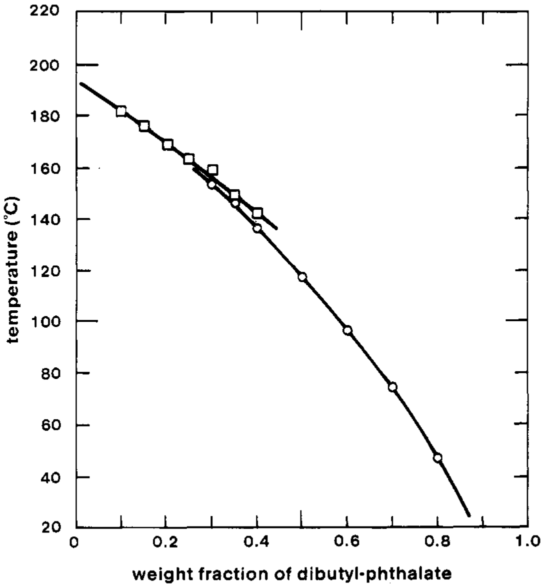

Figure 1. Cloud temperatures of ternary mixtures of polystyrene, poly(α-methylstyrene), and dibutyl phthalate are plotted against the weight fraction of dibutyl phthalate. All mixtures contain equal weights of the two polymers. The squares denote the results obtained with mixtures which were prepared by dissolving the components in toluene and then subsequently removing the toluene. The circles denote those obtained with mixtures prepared without the aid of toluene. The small difference between these two sets of data is probably due to the loss of some fraction of dibutyl phthalate during evaporation of toluene.

To analyze the data in terms of eq 1, the composition of the mixture was converted from weight fraction to volume fraction

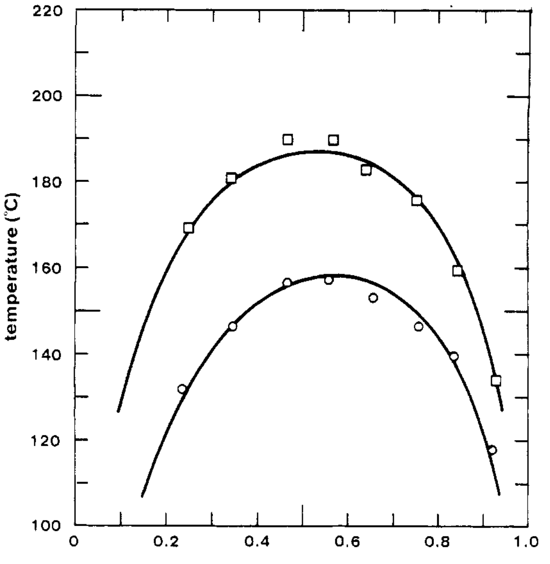

Figure 2. Cloud points of mixtures of polybutadiene and poly(α-methylstyrene). The squares were obtained with mixtures containing polybutadiene of M_w 3600 and the circles with mixtures containing polybutadiene of M_w 2620, the poly(α-methylstyrene) being of M_w 5330 in both cases.

by use of the following values of specific volume. For polybutadiene[5]

$$v_{sp} = 1.1138 + (8.24 \times 10^{-4})t \tag{6}$$

for polystyrene[6] (above T_g)

$$v_{sp} = 0.9217 + (5.412 \times 10^{-4})t + (1.687 \times 10^{-7})t^2 \tag{7}$$

and for poly(α-methylstyrene)[7] (above T_g)

$$v_{sp} = 0.87 + (5.08 \times 10^{-4})t \tag{8}$$

where t is in degree Celsius.

Results and Discussion

A. Polybutadiene–Poly(α-methylstyrene). The observed cloud points of mixtures of 5KPMS with either 2KPBD or 3KPBD are plotted in Figure 2. The data were fitted to the binodal curve calculated on the basis of the Flory–Huggins eq 1, with Λ regarded as an adjustable parameter. To allow for the dependence of Λ on temperature and composition, Λ was represented by

$$\Lambda = \lambda_0 + \lambda_1\phi + \lambda_T T \tag{9}$$

and the best-fitting values of λ_0, λ_1, and λ_T were determined by means of a nonlinear least-squares algorithm. A single set of parameters represented by

$$\Lambda = 1.276 - 0.021\phi - 0.00183T \tag{10}$$

was used to fit both sets of cloud-point data in Figure 2. In eq 10, Λ is in calories per centimeter cubed, ϕ is the volume fraction of polybutadiene, and T is in Kelvin. The solid curves shown in Figure 2 are the binodals calculated by means of eq 1 and 10.

B. Polystyrene–Poly(α-methylstyrene). As described in the Experimental Section, the cloud points of the mixtures of polystyrene and poly(α-methylstyrene) could not be determined directly by the usual method because of their high T_g's. Instead, the cloud points of the ternary mixtures containing various amounts of dibutyl phthalate in addition were determined, and the results are shown in Figure 3. The cloud points of the binary mixtures of the polymers were then obtained by extrapolation to zero concentration of dibutyl phthalate. Figure 4 shows the cloud points thus determined, and the solid curve drawn there was calculated by use of the value of Λ represented by

$$\Lambda = 0.0608 + 0.0018\phi - 0.000056T \tag{11}$$

where ϕ is the volume fraction of poly(α-methylstyrene). Because of the similarity in the chemical structure between polystyrene and poly(α-methylstyrene), the Λ value for the pair is much smaller than that for the polybutadiene–poly(α-methylstyrene) pair. Figure 4 also demonstrates clearly that the incompatibility observed[8-13] with mixtures of high molecular weight polystyrene and poly-α-methylstyrene arises from a UCST and not from an LCST behavior.

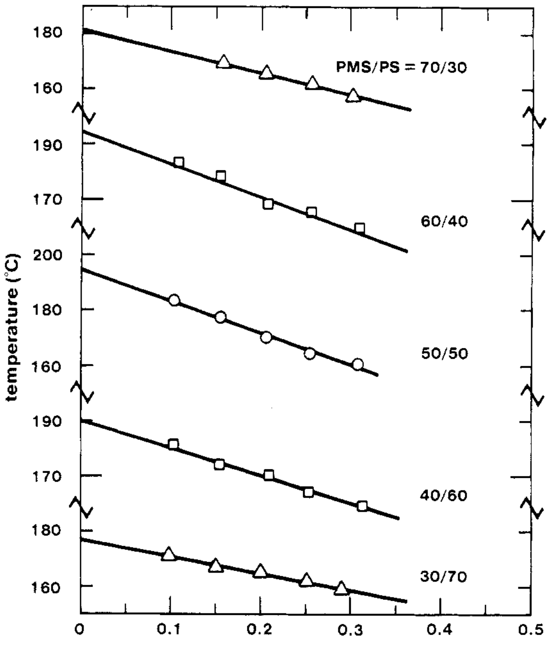

Figure 3. Cloud temperatures of ternary mixtures containing polystyrene (M_w 49 000), poly(α-methylstyrene) (M_w 56 400), and dibutyl phthalate. Each set of data refers to the mixture in which the relative composition of the two polymers (indicated by the weight percents of the two polymers) is fixed and only the amount of the diluent is varied. Linear extrapolation of each set to zero concentration of the latter gives the cloud point of binary mixture of the two polymers.

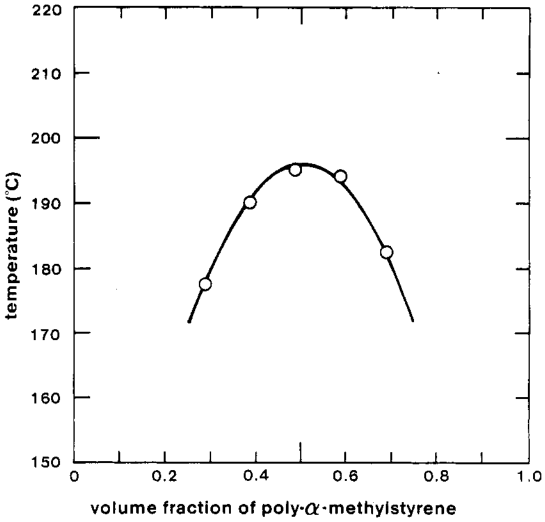

Figure 4. Cloud points of the mixtures of polystyrene and poly(α-methylstyrene), determined by the method illustrated in Figure 3.

Table II
Comparison of Observed and Calculated Values of Λ^a

	150 °C			250 °C		
polymer pair	obsd	calcd^b	error	obsd	calcd^b	error
polystyrene–polybutadiene	0.730	0.803	+10%	0.520	0.541	+4%
polybutadiene–poly(α-methylstyrene)	0.491	0.435	−12%	0.308	0.293	−5%
polystyrene–poly(α-methylstyrene)	0.0380	0.0235	−38%	0.0324	0.0274	−15%

[a] Λ in cal/cm^3. [b] Calculated according to eq 5.

C. Validity of Equation 5. The Λ value for the pair polystyrene–polybutadiene was previously evaluated[1] from the observed cloud points. The average of the values evaluated for five sets of mixtures containing only homopolymers of styrene and butadiene can be given by

$$\Lambda = 1.573 + 0.09\phi - 0.0021T \qquad (12)$$

where ϕ refers to the volume fraction of polystyrene.

Equation 5, giving the relationship among the Λ values for the three pairs that can be formed from three polymers, can now be tested. In Table II, the "observed" values are those evaluated by means of eq 10–12 for ϕ = 0.5 and at two temperatures, 150 and 250 °C. The "calculated" values were then obtained by means of eq 5. For example, the value for the polystyrene–polybutadiene pair was calculated by means of eq 5 from the knowledge of the observed Λ values for polybutadiene–poly(α-methylstyrene) and for polystyrene–poly(α-methylstyrene). The choice between a + and − sign in eq 5 was made by comparison with the observed value, but the choice would have been obvious, in any case, from the consideration of the similarities and differences in the chemical structure among the three polymers. The temperature 150 and 250 °C were chosen because most of our cloud point data lie between these two temperature limits. In Table II, the agreement between the observed and calculated values of Λ is good. The relative error for the polystyrene–poly(α-methylstyrene) pair is fairly large, but on the absolute scale the discrepancy is still small. The result thus demonstrates the useefulness of eq 5 as a semiquantitative tool to estimate the interaction energy density Λ. Equation 5 probably would hold, in general, for polymer pairs interacting with nonpolar forces, such as those studied in this work. Its applicability to polymer pairs interacting with other types of forces as well, such as polar or hydrogen-bond forces, remains to be studied.

In view of the apparent success of eq 5, one might wonder whether eq 4, from which eq 5 is originally derived, can be utilized to estimate Λ values in the first place. The answer, however, is "no" at present, because of the difficulty of obtaining reliable values of the solubility parameters for polymers. The solubility parameters for polymers available in the literature vary in most cases over too wide a range to be useful for this purpose. If we use the group additivity method proposed, for example, by van Krevelen,[14] the δ values for polystyrene, poly(α-methylstyrene), and polybutadiene at 25 °C are calculated to be 8.98, 8.67, and 8.12, respectively. Use of these values in eq 4 then leads to the Λ value of 0.740 for polystyrene–polybutadiene, 0.303 for polybutadiene–poly(α-methylstyrene), and 0.0961 for polystyrene–poly(α-methylstyrene). These values agree in their orders of magnitude with our observed values (see Table II), but the agreement is not close enough to allow their use for the prediction of binodals.

D. Deuterium Isotope Effect. Matching pairs of deuteriated and hydrogenated polystyrenes having similar molecular weight and chemical structure were prepared, as described in the Experimental Section, by starting with a sample of polystyrene and subjecting it alternatively to deuterium-exchange and hydrogen-exchange reactions.

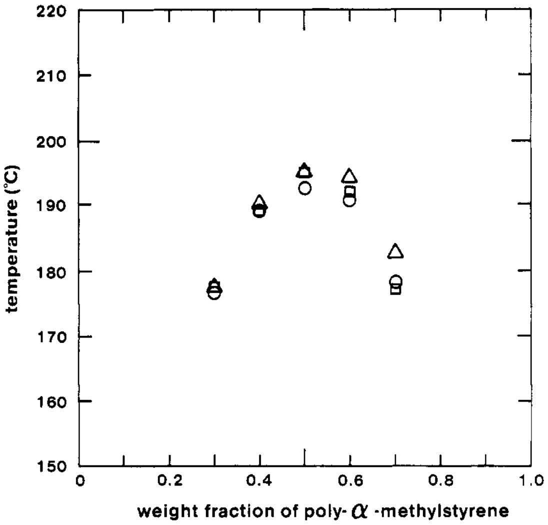

Figure 5. Cloud points of mixtures containing poly(α-methylstyrene) (M_w 56 400) and one of the polystyrenes, 49KPS (triangles), 49KPSH (squares), and 49KPSD (circles). The results show that no deuterium isotope effect is detectable for this pair of polymers.

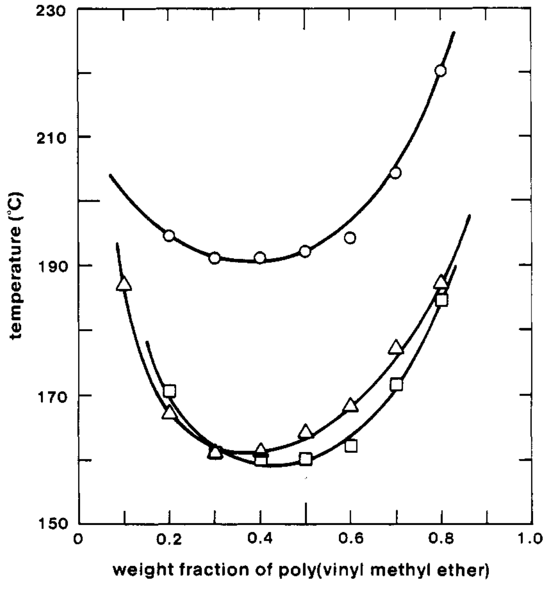

Figure 6. Cloud points of mixtures containing poly(vinyl methyl ether) and one of the polystyrenes, 18KPS (triangles), 18KPSH (squares), and 18KPSD (circles).

Figure 5 shows the cloud points of the mixtures of 56KPMS with either 49KPS, 49KPSH, or 49KPSD. The cloud points shown here were all obtained by extrapolation of those of ternary mixtures containing varying amounts of dibutyl phthalate. The result clearly shows that no deuterium isotope effect is detectable for the pair polystyrene–poly(α-methylstyrene).

Figure 6 shows the cloud points of the mixtures of poly(vinyl methyl ether) with either 18KPS, 18KPSH, or 18KPSD. In this case, there is a clear indication of the effect of deuteriation. Figure 7 shows the cloud points of

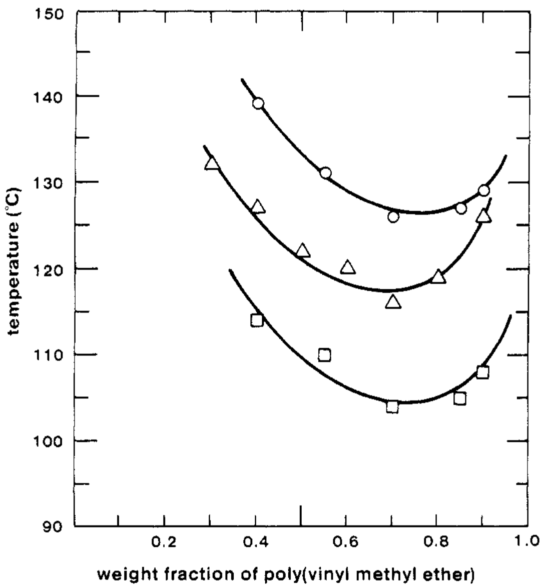

Figure 7. Cloud points of mixtures containing poly(vinyl methyl ether) and one of the polystyrenes, 100KPS (triangles), 100KPSH (squares), and 100KPSD (circles). Figures 6 and 7 indicate the presence of an appreciable deuterium isotope effect in the case of mixtures of polystyrene and poly(vinyl methyl ether).

the mixtures of poly(vinyl methyl ether) with either 100KPS, 100KPSH, or 100KPSD, again indicating the presence of an appreciable deuterium isotope effect. These results confirm the previous ones reported by Yang et al.[15] and Halary et al.[16] Deuteriated polystyrene is evidently more compatible with poly(vinyl methyl ether), and the cloud points of mixtures containing PSD are shifted upward by about 30 °C in Figure 6 and by more than 20 °C in Figure 7.

In our previous study[3] we investigated the effect of deuteration of polystyrene on its compatibility with polybutadiene, by a procedure very similar to that used in this work, and found that no deuterium isotope effect could be detected for this pair. On the basis of these results we may infer that the deuterium isotope effect on polymer compatibility is negligible when the polymer pair involved interacts by nonpolar forces and thus exhibits a UCST behavior. When the pair exhibits an LCST behavior, the specific interaction forces responsible for the compatibility might be more sensitively affected by the replacement of hydrogen with deuterium. In a recent work,[17] Monnerie et al. studied the compatability of poly(vinyl methyl ether) with polystyrenes deuterated selectively on the aromatic and aliphatic part of the polymer. They found that only the polystyrenes deuteriated on the aromatic part of the chain showed a pronounced deuterium isotope effect. It therefore appears that the specific interaction between polystyrene and poly(vinyl methyl ether), giving rise to their compatibility, resides on the phenyl group of the styrene monomer and, moreover, the nature of this interaction is such that it is sensitive to the effect of deuteriation.

Recently Bates and Wignall[18] measured the intensity of neutron scattering from a mixture of hydrogenated and deuteriated polystyrenes and deduced the value of the χ parameter between these two polymers to be $(1.7 \pm 0.4) \times 10^{-4}$ at 160 °C. With the use of eq 3 Λ is then calculated to be $(1.4 \pm 0.3) \times 10^{-3}$ cal/cm^3. Strazielle and Benoit[19] studied the solution properties of hydrogenated and deuteriated polystyrenes in cyclohexane near the Θ temperature and concluded that the differences in the thermodynamic properties exhibited by these two isotopic polystyrenes can be summarized by the difference $\Delta\delta$ in the solubility parameters between them amounting to 0.048 (cal/cm^3)$^{1/2}$ (after taking the excluded volume effect into account). Their results thus give the value of Λ between PSD and PSH equal to 2.3×10^{-3} cal/cm^3. Buckingham and Hentschel[20] made a theoretical study of deuterium isotope effect and their result, for long-chain polymers, can be represented by the value of Λ between the deuteriated and hydrogenated species given by

$$\Lambda = (1/2\kappa)(\Delta V/V)^2 \qquad (13)$$

where κ is the isothermal compressibility and $\Delta V/V$ is the relative change in volume on deuteriation. With the use of the values, $\kappa = 5.33 \times 10^{-5}$ bar^{-1} for polystyrene[21] above T_g and $\Delta V/V = 10^{-3}$–10^{-2} (quoted[19] to be valid for most organic molecules), Λ is estimated to be between 2.2×10^{-4} and 2.2×10^{-2} cal/cm^3. The values experimentally obtained by the above two groups of workers fall right between these two limits.

These values of Λ, although small in magnitude, are still substantial. When a value of 1.4×10^{-3} cal/cm^3 is substituted in eq 5, it suggests that the Λ value for deuteriated polystyrene against polybutadiene must differ from the corresponding value for hydrogenous polystyrene by about 9% at 150 °C. In the case of polystyrene–poly(α-methylstyrene), the deuteriation of polystyrene must, according to eq 5, change the Λ value at 150 °C form 0.0380 to either 0.0540 or 0.0248 cal/cm^3 (depending on whether the + or − sign is taken), which in a relative term is +42% and −35% change. Such a large change in Λ would have to be clearly reflected in the cloud-point curve. The upper critical solution temperature T_C, derivable from eq 1 (on the assumption of Λ being independent of composition), is given by

$$T_C = 2\Lambda V_1 V_2 / R(V_1^{1/2} + V_2^{1/2})^2 \qquad (14)$$

where V_1 and V_2 are the molar volumes of the polymers involved. Thus, when the molecular sizes of the polymers are kept approximately constant, the cloud-point curve has to be shifted in proportion to the change in Λ. In this study, the polystyrenes were deuteriated only on the aromatic positions and therefore the expected shift might be somewhat smaller, but still our results entirely contradict these expectations and show no change on deuteriation of polystyrene in its miscibility with either polybutadiene or poly(α-methylstyrene). It therefore appears that eq 5 is not applicable when the deuterium isotope effect is involved. This is surprising, since the isotope effect probably arises from the differences in the volume between the hydrogenated and deuteriated species and, if so, the consideration based on the cohesive energy density concept would be expected to apply well. A need for further study on the question of deuterium isotope effect is therefore indicated.

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Registry No. Polystyrene, 9003-53-6; poly(α-methylstyrene), 25014-31-7; polybutadiene, 9003-17-2; dibutyl phthalate, 84-74-2; poly(vinyl methyl ether), 9003-09-2.

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Light Scattering from Polymer Blend Solutions. 5. Characterization of Systems of Relatively High Incompatibility

Minoru Nagata, Takeshi Fukuda,* and Hiroshi Inagaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.
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ABSTRACT: Solutions of polymer blends polystyrene/poly(ethylene oxide), polystyrene/polyisoprene, and polystyrene/polyisobutylene were studied by the "optical Θ" light-scattering method. The interaction parameter χ_{12} between unlike polymers in dilute solution was determined for each system, with which the segment–segment interaction parameter $\chi_{12}{}^{\circ}$ was estimated by the aid of dilute solution excluded volume theories. These $\chi_{12}{}^{\circ}$ values are closely related with those estimated by the solubility parameter method and, moreover, seem compatible with the available experimental data on the solvent-free systems composed of much shorter chains or relevant copolymers. Several ternary solutions were studied up to concentrations near the spinodal points, indicating that at least in limited cases with highly incompatible (i.e., large $\chi_{12}{}^{\circ}$) systems, demixing can occur even in the "dilute" solution which is characterized by a concentration-independent and blend-ratio-independent value of χ_{12}. The molecular weight exponent of the spinodal concentration is roughly similar in all examined systems (about −0.6).

Introduction

Light scattering from a dilute ternary solution of the type polymer (1)/polymer (2)/solvent (0) is represented by eq 1, if the condition in eq 2 is met.[1] In eq 1 and 2,

$$K\phi/R_0 = (m_1x_1)^{-1} + (m_2x_2)^{-1} - 2\chi_{12}\phi + ... \qquad (1)$$

$$\psi_1m_1x_1 + \psi_2m_2x_2 = 0 \qquad (2)$$

R_0 is the scattering intensity at zero angle, ϕ is the sum of the volume fractions ϕ_1 and ϕ_2 of the polymers, $x_i = \phi_i/\phi$ is the blend composition, m_i is the *weight-average* degree of chain length, $\psi_i = \partial n/\partial\phi_i$ is the refractive index increment, and K is the optical constant proportional to $(\psi_1 - \psi_2)^2$. This "optical Θ" method permits determination of the polymer–polymer interaction parameter χ_{12} without knowing the solvent–polymer interactions χ_{01} and χ_{02}, hence with the highest possible precision[2,3] (see ref 4 for the definition of the χ parameters). The method has been successfully applied to some blend systems.[1,3,5,6]

The formal similarity of eq 1 to the scattering equation for dry blends[7] may be clear, the latter being obtained by setting $\phi = 1$ in eq 1 and neglecting higher terms in ϕ. Owing to this dilution factor ϕ, experimental approaches are feasible even to those systems which are difficult to characterize in the dry state due to large χ_{12}, viz., immiscibility. However, introduction of a solvent brings about complexities, too, arising from solvent–polymer interactions, rendering the solution χ_{12} usually very different in value from the bulk χ_{12}.[1] The main cause for the difference is considered to be the excluded volume effect between unlike polymers. This problem was the subject of a previous paper,[8] wherein we have proposed a simple method for analyzing dilute solution data for the "net" or "segment–segment" interaction parameter, $\chi_{12}{}^{\circ}$.[4] This parameter should be independent of chain length and, at least to a first approximation, of solvent, too. It is an important but still unanswered problem to examine to which extent parameter $\chi_{12}{}^{\circ}$ is related with the relevant parameter for the solvent-free system. This is the main subject of this paper. We will study by the mentioned light-scattering method some polymer blends which are rather highly incompatible in bulk, showing virtually for the first time that dilute ternary solution data are, in many cases, closely related with those for the bulk blends.

Experimental Section

The molecular characteristics of the polymer samples are listed in Table I. The samples of polystyrene (PS), poly(ethylene oxide) (PEO), and polyisoprene (PIP) have a narrow distribution in molecular weight and were used as received from the manufacturers, while those of polyisobutylene (PIB) are fractions of a commercial polymer, the fractionation being made with a cyclohexane/methanol system at 30 °C (for the sample sources, see Table I). The volume fraction ϕ_i and the degree of chain length were calculated with

$$\phi_i = w_iv_i/(w_0v_0 + w_1v_1 + w_2v_2) \qquad (3)$$

$$m_i = M_{i,\mathrm{w}}v_i/V_0 \qquad (4)$$

where w_i is the weight fraction, v_i is the specific volume in the pure state, $M_{i,\mathrm{w}}$ is the weight-average molecular weight, and V_0 is the molar volume of the solvent (i = 0, 1, or 2; thus $m_0 = 1$). The v_i values of the polymers were assumed to be given by the following relations determined for the liquid polymers:

$$v_1 = 0.9199 + (5.08 + 2.354 \times 10^{-3}t)10^{-4}t \quad (\mathrm{PS})^{9}$$

$$v_2 = 0.8726 + 6.9 \times 10^{-4}t \quad (\mathrm{PEO})^{10}$$

$$v_2 = 1.080 + 6.89 \times 10^{-4}t \quad (\mathrm{PIP})^{11}$$

$$v_2 = 1.077 + 6.45 \times 10^{-4}t \quad (\mathrm{PIB})^{12}$$

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