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PHASE BEHAVIORS IN BLENDS OF POLY(VINYL METHYL ETHER) AND POLY(STYRENE-CO-BUTADIENE)

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Abstract—The dependence of miscibility on temperature for blends of poly(vinyl methyl ether) (PVME) and styrene–butadiene random copolymer (SBR) was studied. The binary interaction energy densities of the blends could be evaluated from the observed cloud point curves. With a simple approach based on the mean-field theory for blends of a homopolymer with a random copolymer, the miscibility boundary could be determined as a function of composition of the copolymer. The predicted miscibility region for the given polymer pairs was compatible with the experimental results. © 1997 Elsevier Science Ltd

INTRODUCTION

The thermodynamic principles governing miscibility are often explained by the Flory–Huggins free energy of mixing. The Flory–Huggins free energy of mixing per unit volume of the mixture can be written as,

$$\Delta G_M = RT[(1/V_1)\Phi_1 \ln \Phi_1 + (1/V_2)\Phi_2 \ln \Phi_2] + \Lambda_{12}\Phi_1\Phi_2 \quad (1)$$

where V_1 and V_2 are the molar volumes of polymers 1 and 2, and Φ_1 and Φ_2 are the volume fraction of the two polymers in the blend. The first term in equation (1) is the combinatorial entropy of mixing and the second term involving Λ_{12} includes all contributions of the free energy of mixing not accounted for by the combinatorial term. The interaction energy density, Λ_{12}, is related to the Flory–Huggins interaction parameter χ_{12} by $\Lambda_{12} = RT\chi_{12}/V_r$, where V_r is a reference volume.

In binary mixtures of a homopolymer (A) with a random copolymer (CD), the dependence of miscibility on the copolymer composition has been studied extensively [1–5]. It is well known that the polymer–polymer interaction energy density, Λ_{12}, is described by the following binary interaction model which is a function of copolymer composition

$$\Lambda_{A/CD} = y\Lambda_{AC} + (1-y)\Lambda_{AC} - y(1-y)\Lambda_{CD} \quad (2)$$

where y denotes the composition of C units in the copolymer. This model can satisfactorily explain "repulsion effect" of the comonomer units, which may give rise to so-called "miscibility window" that is a typical phase behavior of copolymer blends [1].

Many previous investigations have given information about the temperature dependence of Λ_{12}, and it has been concluded that Λ_{12} has two kinds of temperature dependence: one is for the phase behavior of UCST (upper critical solution temperature) type and the other is LCST (lower critical solution temperature) type. It is interesting to examine the temperature dependence of Λ_{12} with respect to copolymer composition in A/CD blends, where the A/C blend has LCST-type phase behavior, whereas A/D has UCST-type. In this paper, we will evaluate the temperature dependence of the interaction energy density Λ_{12} for blends of poly(vinyl methyl ether) (PVME) and poly(styrene-co-butadiene) (SBR) from the measurement of the cloud points. We will also confirm the applicability of equation (2) to this blend system and provide the miscibility boundary with respect to the copolymer composition.

EXPERIMENTAL

Materials

The characteristics of the samples studied are given in Table 1. PS was obtained from Pressure Chem. Co. PVMEs are commercially available materials. (VM81 obtained from Aldrich Co, VM180 obtained from Tokyo chemical industry.) They were dissolved in toluene, purified by activated carbon powder, and precipitated twice by a large excess of *n*-hexane. The weight average molar masses in THF were determined by low-angle laser light-scattering (LDC Analytical Co., chromatrix KMX-6). Two of the copolymer samples, SBR50 and SBR60, were anionically polymerized and provided by Dr H. L. Hsieh of Phillips Petroleum Co. and Dr D. I. Yoon of Kumho Petrochemical Co., respectively. SBR68 is an emulsion polymerized commercial material supplied by Kumho Petrochemical Co. and they were purified several times in order to remove the emulsifier. The weight average molar mass of the copolymers in THF were determined by static light scattering [6]. The composition ratio of copolymer was measured by ^{1}H NMR. The polydispersities of samples were measured by gel permeation chromatography (Waters Co., Ultrastyragel linear column). Blends were prepared by casting from toluene solution and were dried for 48 h in

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vacuum at 10 K below the phase separation temperature of each mixtures.

Cloud point measurement

The cloud temperature was determined by monitoring the intensity of scattered light at 40° angle through the blend film located on a hot stage. A He–Ne laser (4 mW) was used as a light source. The scattered intensity was measured by a photo diode detector (Newport corporation 835 optical power meter).

Figure 1, as one of example, shows the scattered light intensities obtained with SBR60/VM81 (90:10, w/w) blend at a constant heating/cooling rate of 1 K/min. The point, indicated by an arrow, at which the intensity started to rise rapidly was taken as the cloud point. The mixing procedure on cooling occurred rather slower than the demixing procedure on heating, making the determination of the cloud temperature on heating more easy. When the cloudy sample was annealed just below the indicated temperature, it became clear. If the indicated temperature was spinodal at this mixture, the annealing could not induce the cloudy two phases to become one phase. This fact supported that the cloud point measured on heating was sufficiently close to the binodal one. The very slow heating rates were initially tried, and it was found that the effect of heating rate was usually within an experimental error. All the measurements were performed at 1 K/min.

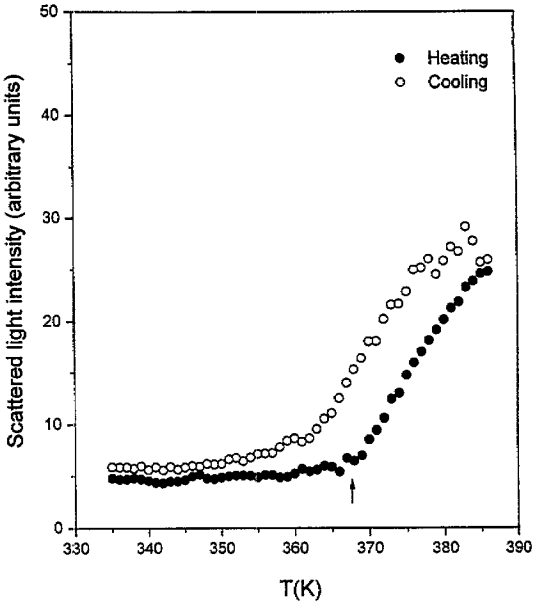

Fig. 1. Scattered light intensity as a function of temperature for 90 wt% SBR60 and 10 wt% VM81 blend at (●) heating and (○) cooling rate of 1 K/min. The point (indicated by arrow) at which the scattered light intensity on heating starts to increase rapidly is taken as the cloud point.

RESULTS AND DISCUSSION

Interaction energy density Λ_{12}

The critical temperature curves of these blends are shown in Fig. 2. The LCSTs increase as styrene content increases and the molecular weight of PVME decreases. VM81/SBR50 blends have been already phase separated at room temperature and no evidence of dissolution has been detected even above 470 K. Blends of PS with PVME have been extensively examined, and this system exhibits an LCST which is one of the characteristic phenomena in miscible blends [7–9]. The cloud temperature curves of PVME/PS in Fig. 2 is in good agreement with literature data when the molecular weights of samples used in this study are considered [8]. According to previous reviews for blends of PVME with other styrenic random copolymer, PVME is also miscible with the copolymers up to a certain composition limit [11–14]. The PVME/SBR blends are expected to show a similar phase behavior.

The observed cloud temperature is appreciably dependent on several experimental conditions such as heating and cooling rates. On the assumption that the cloud point is equivalent to the binodal temperature in thermodynamic equilibrium, the interaction energy density can be determined by the following approach. The resulting cloud point curve in Fig. 2 was fitted with a calculated curve based on equation (1). To

Table 1. Descriptions of polymer samples studied

Sample designation		Composition (wt%)			M_w	M_w/M_n
			% unsaturation			
		Styrene	Trans	Vinyl		
PS48	polystyrene	100	0	0	48,000	1.06
SBR50	random copolymer	48	55	27	24,000	1.04
SBR60	random copolymer	60	31	28	50,000	1.07
SBR68	random copolymer	68	38	28	150,000	1.21
VM81	PVME				81,000	1.69
VM180	PVME				180,000	1.81

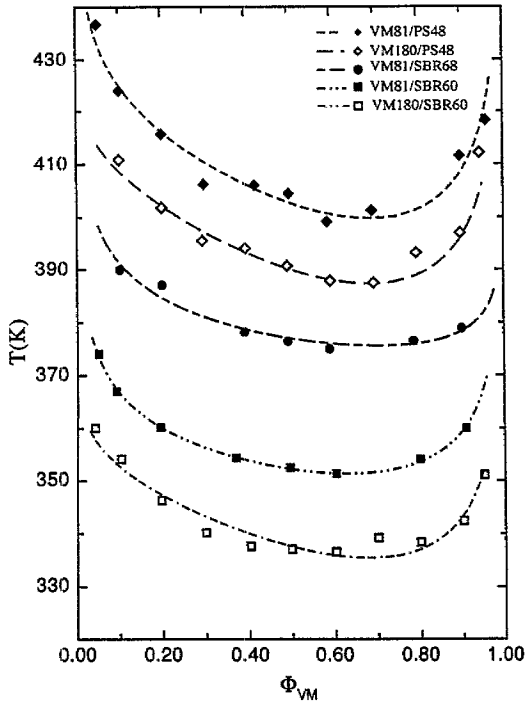

Fig. 2. Cloud points plotted against Φ_{VM} for the PVME/PS, PVME/SBR pairs. The curves represent the non-linear least-squares fit. (Φ_{VM} is the weight fraction of PVME in blends.)

Table 2. Polymer–polymer interaction energy densities[a] determined from the best fit to cloud point measurements

Component 1	Component 2	λ_0 (cal/cm^3)	λ_1 (cal/cm^3)	λ_2 ($\times 10^3$) (cal/cm^3 K)	Λ^b (cal/cm^3)
PS48	VM81	−0.423	0.027	1.074	−0.089
PS48	VM180	−0.375	0.028	0.970	−0.072
SBR68	VM81	−0.338	0.007	0.920	−0.061
SBR60	VM81	−0.299	0.012	0.894	−0.027
SBR60	VM180	−0.283	0.019	0.852	−0.019

[a] $\Lambda_{12} = \lambda_0 + \lambda_1\Phi + \lambda_2 T$.
[b] at $\Phi = 0.5$, $T = 298$ K.

allow for the dependence of Λ_{12} on temperature and composition, Λ_{12} was represented by [4, 15]

$$\Lambda_{12} = \lambda_0 + \lambda_1\Phi + \lambda_2 T \quad (3)$$

The best fitting values of the constants λ_0, λ_1, and λ_2 were evaluated by the means of nonlinear least squares method and weight average molecular weights were used for the calculation of the molar volume. The coefficients thus obtained are listed in Table 2. There are scattered data for the value of $\Lambda_{PVME/PS}$ obtained by different techniques [9, 10]. It is found that the values of $\Lambda_{PVME/PS}$ obtained in this study are not beyond the bounds of the published experimental data. In trying to examine the applicability of equation (2), one has to estimate all of the Λ values. The values of PVME/PS and PVME/SBR can be calculated from the measured cloud points. However, the value for PVME/PBd should be estimated by using equation (2) with the known values for PVME/PS, PVME/SBR, and PBd/PS, since the cloud points for PVME/PBd are beyond the range of measuring temperature. In this study, the applicability of equation (2) will be examined by comparing the two calculated Λ values from the two blends pairs, PVME/SBR60 and PVME/SBR68.

The Λ values of PS blends with VM81 and VM180, and those of SBR60 blends in Table 2 should be theoretically equal, regardless of the molecular weight of PVME. The results of this study are, however, puzzling even though the difference between the two values is relatively small. For further analysis, the averaged values are used. To estimate the temperature dependence of the Λ values with convenience, the ratio of the weight content of the styrene monomer unit to that of PVME in blend was fixed to 1:1. Also, the Λ parameters (λ_0, λ_1, λ_2) in Table 2 were averaged. The averaged values are listed in Table 3. The Λ value for the blends of PS and PBd was previously estimated by a curve fitting procedure which was analogous to the present method [15]. The average value for PBd/PS pairs evaluated from the five sets of blends can be given by

$$\Lambda_{PBd/PS} = 1.620 - 1.95 \times 10^{-3}T \quad (4)$$

The Λ value of PVME/PBd, evaluated by equation (2) with those of PVME/PS, PBd/PS, and PVME/SBR68, is represented by

$$\Lambda_{PVME/PBd} = 0.872 - 0.73 \times 10^{-3}T \quad (5)$$

The Λ value of PVME/PBd, evaluated from PVME/SBR60, is given by

$$\Lambda_{PVME/PBd} = 0.837 - 0.60 \times 10^{-3}T \quad (6)$$

The two Λ values from equations (5) and (6), are 0.654 and 0.658 (cal/cm^3), respectively, at 298 K. The agreement between the two values is good. By using the solubility parameters of PVME and PBd, which are 9.35 ± 0.15 and 8.40 ± 0.10 [(cal/cm^3)$^{1/2}$], respectively, the value of Λ for PVME/PBd is also calculated at 0.72 ± 0.49 (cal/cm^3). Here, it should be noted that the Λ values evaluated from equation (5) and (6) are in the range of the values calculated by solubility parameters. The result thus demonstrates that equation (2) may be applicable to this blend system.

Miscibility boundary for PVME/SBR blends

The averaged value of equations (5) and (6) is

$$\Lambda_{PVME/PBd} = 0.855 - 0.67 \times 10^{-3}T \quad (7)$$

Applying equations (4) and (7) to equation (2), we can calculate the copolymer composition dependence of the temperature–Λ curve over all the copolymer compositions for PVME/SBR blends. Using the obtained values for Λ, the binodal curves for PVME/SBR blends having various copolymer composition are calculated.

For blends of finite molecular weight polymers, a critical point occurs at a temperature for which Λ equals Λ_{crit} given by

$$\Lambda_{crit} = 0.5RT(V_1^{-0.5} + V_2^{-0.5})^2 \quad (8)$$

where V_1 and V_2 are the molar volumes of polymers 1 and 2. Because the miscibility corresponds to $\Lambda < \Lambda_{crit}$, the miscibility boundaries for the two pairs of VM81/SBR60 and VM180/SBR60 can be constructed as seen in Fig. 3. For the calculations, the molar volumes of SBR60, VM81, and VM180 are assumed to be 52,000, 77,000, and 171,000, respectively. In Fig. 3, it is shown that the predicted phase boundary is compatible with the results obtained from the cloud point experiments. Therefore, we can confirm the applicability of the binary interaction model to A/CD blends, where the A/C blend has LCST-type phase behavior whereas A/D has UCST-type.

Figure 3 shows a maximum in the miscibility boundary at a certain copolymer composition (i.e. $y = 0.85$). The existence of the maximum implies that equation (2) is a quadratic with a minimum. By differentiating with respect to y, one can obtain

$$y_0 = (\Lambda_{CD} - \Lambda_{AC} + \Lambda_{AD})/2\Lambda_{CD} \quad (9)$$

where y_0 is the weight fraction of D in the copolymer showing a maximum in the miscibility boundary. (Note that y_0 is dependent on temperature as Λ is a function of temperature.) Since y_0 is a composition in

Table 3. Interaction energy densities that the ratio of styrene in SBR to PVME was fixed to 1:1 and was averaged in order to eliminate the effect of molecular weight

Pair	λ^a (cal/cm^3)	λ_T ($\times 10^3$) (cal/cm^3 K)	Homopolymer	Φ_{Homo}
VM/PS	−0.385	1.02	VM	0.50
VM/SBR68	−0.335	0.92	VM	0.41
VM/SBR60	−0.285	0.87	VM	0.38
PBd/PS	1.620	−1.95	PBd	0.50

[a] $\lambda = \lambda_0 + \lambda_1 \times \Phi_{Homo}$.

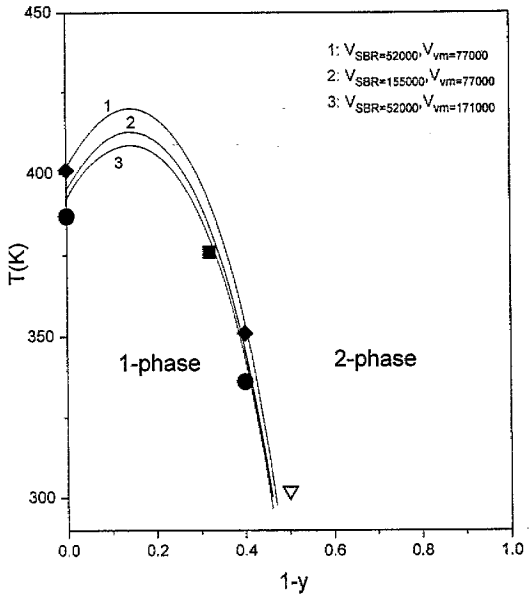

Fig. 3. Predicted miscibility boundaries as a function of copolymer composition for VM/SBR blends and experimental results (1: $V_{SBR60} = 52{,}000/V_{VM81} = 77{,}000$, 2: $V_{SBR68} = 155{,}000/V_{VM81} = 77{,}000$, 3: $V_{SBR60} = 52{,}000/V_{VM180} = 171{,}000$). The boundary lines are the locus of LCSTs, and they are obtained from the miscibility condition that $\Lambda = \Lambda_{crit}$. Λ_{crit} is calculated for each molar volume of blends. ◆ (VM81/SBR60), ■ (VM81/SBR68), ● (VM180/SBR60) are the minima in the observed cloud point curves for the miscible blends. ▽ indicates the immiscibility of VM81/SBR50 blends at 298 K. (y is the weight fraction of the styrene monomer unit in SBR.)

the range of $0 < y < 1$, equation (9) can now be written as

$$|(\Lambda_{AD} - \Lambda_{AC})/\Lambda_{CD}| < 1 \qquad (10)$$

Equation (10) is the condition for which the miscibility boundary has a maximum in a copolymer composition. For PVME/SBR blends, it was found that this condition could be satisfied at the maximum temperature of the miscibility boundary as shown in Fig. 3. This means that the repulsive interaction between the two monomer units of SBR may enhance the mutual miscibility for PVME/SBR blends.

We note that we did not obtain a perfect random SBR with the 85% styrene monomer unit.

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