Miscibility estimated by the volume change due to mixing of a polystyrene/poly(vinyl methyl ether) blend system

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The volume–temperature (V–T) relationship of polystyrene, poly(vinyl methyl ether) and their polymer blends in glassy and liquid states was measured at one atmospheric pressure from −25°C to 145°C. The expansion coefficient and volume change due to mixing in a liquid state were evaluated from the V–T relationship obtained experimentally. Using the equation of state derived by Sanchez and Lacombe and the above state parameters, the equation-of-state and molecular parameters of each homopolymer and polymer blend were estimated below phase transition temperature and the theoretical volume change due to mixing and heat of mixing were calculated. The experimental volume change due to mixing agreed roughly with the calculated value. The negative volume change due to mixing and heat of mixing calculated above indicated thermodynamic miscibility over the whole composition range. This polymer blend system was confirmed by measurement of the V–T relationship to be miscible in a thermodynamic sense.

(Keywords: polystyrene; poly(vinyl methyl ether); polymer blend; miscibility; volume change due to mixing; heat of mixing; equation-of-state parameter; molecular parameter)

INTRODUCTION

The miscibility and phase behaviour of polymer blends have been extensively studied by different methods. Miscibility has been estimated at a first stage by a simple and easy procedure, e.g. a turbidity of polymer blends, the presence of single glass transition temperature (T_g) measured by differential scanning calorimetry (d.s.c.), or dynamic mechanical or dielectric dispersions. Recently more quantitative discussion on miscibility has focused on the interaction between two or more components of polymer blends, which is a very important factor when discussing miscibility, i.e. thermodynamic miscibility and shift of the specific vibration band in infrared (i.r.) spectra.

Thermodynamic miscibility of polymer blends requires negative enthalpy of mixing, although there are few studies on the enthalpy of mixing (ΔH_m) because of its difficulty in measurement[1–8]. ΔH_m can be measured precisely at ambient temperature; however, the measurement of ΔH_m at high temperatures where polymer blend systems are in equilibrium may produce much more experimental error and has not been carried out. In practice it is at present evaluated by the correction of ΔH_m at an ambient temperature using the difference of heat capacity between liquid and glassy states (ΔC_p) usually measured by d.s.c., which contains some error. It is necessary to evaluate precise ΔH_m or other thermodynamic quantities on mixing at any temperature to investigate thermodynamic miscibility.

Sanchez and Lacombe[9,10] pointed out the important state quantity of the volume change due to mixing (ΔV_m) as well as ΔH_m for the thermodynamic miscibility in a liquid state. ΔV_m can be evaluated at any temperature by dilatometry, irrespective of glassy or liquid states, while the measurement of ΔH_m is more difficult at higher temperatures as mentioned above. Therefore the measurement of the P–V–T (pressure–specific volume–temperature) relation of polymer blend and homopolymers which provides ΔV_m is very accessible for an estimation of thermodynamic miscibility in the equilibrium liquid state. The equation-of-state parameter and molecular parameter are able to be determined using the P–V–T relation obtained experimentally and the lattice fluid theory by Sanchez and Lacombe.

In the present article we measured the P–V–T relation of a well-known polystyrene/poly(vinyl methyl ether) (PS/PVME) blend of lower critical solution temperature (LCST) type and each component homopolymer in both glassy and liquid states, and evaluated ΔV_m using the P–V–T relation obtained experimentally. One can then determine the equation-of-state parameter and molecular parameter of the PS/PVME blend system which can predict thermodynamic miscibility, e.g. ΔH_m. Negative ΔH_m was predicted at 90°C over an entire composition range. It was found to be miscible for the PS/PVME blend system.

EXPERIMENTAL

Materials

PS with a weight-average molecular weight (M_w) of 1.0×10^5 and molecular weight dispersity (M_w/M_n) of 1.06 was supplied from Pressure Chemical Co. PVME (Tokyo Kasei Inc.) was roughly fractionated by gel

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permeation chromatography (g.p.c.). Fractionated PVME was estimated to be $M_w = 6.8 \times 10^4$ and $M_w/M_n = 2.2$ from g.p.c.

Polymer blends with weight fractions of 80/20, 55/45 and 25/75 (PS/PVME) were perfectly dissolved in 2 wt% toluene solution. The polymer blend films were prepared by casting from the blend solution at room temperature on the glass plate and allowed to dry under vacuum for several days to remove all the solvents.

The homopolymer and polymer blend samples have to be prepared very carefully for dilatometric measurements which have no air bubbles and are easy to close-pack in a dilatometer. The samples were compression moulded into a disc-like film in a vacuum press and were annealed between phase separation temperature and glass transition temperature under vacuum for several days to remove air bubbles in the film.

The density of the polymers and annealed polymer blends were measured at 23°C by a density gradient column comprising a diethylene glycol and 1,3-butanediol.

Dilatometry

The dry sample was sealed into a dilatometer composed of a capillary with a homogeneous inner diameter. The dilatometers of mercury itself, PS, PVME, and 80/20, 55/45 and 25/75 polymer blends were settled together in an oil bath and heated at a rate of 0.5°C min^{-1} from −35°C to 140°C. The meniscus height of mercury inserted in the capillary of the dilatometer, which was almost the same height, was measured using a precise cathetometer. Many methods have been described[11] to reduce the experimental error in the specific volume of each polymer and polymer blend.

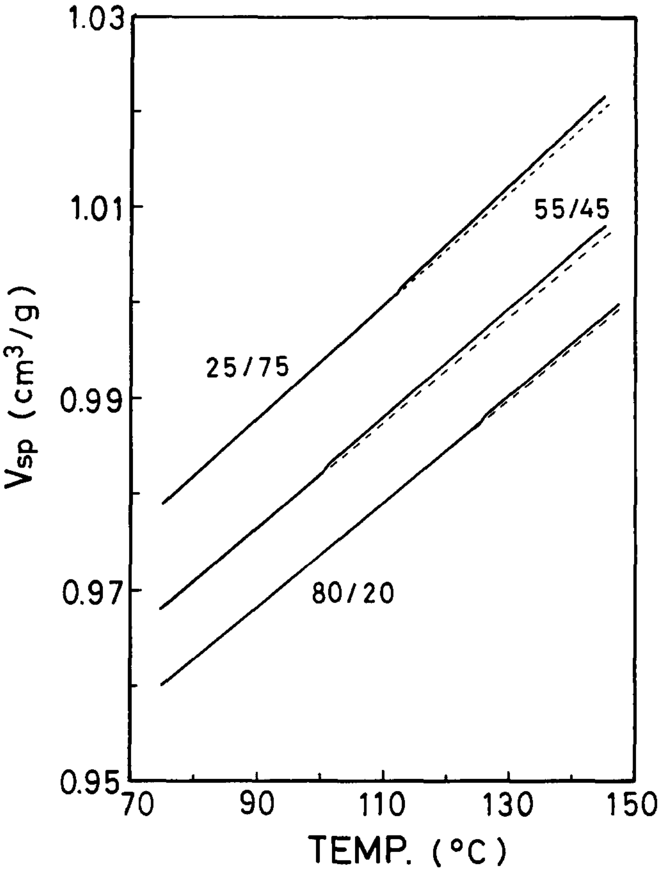

Figure 2 Specific volume–temperature relationship in a liquid region of 80/20, 55/45, and 25/75 polymer blends: the dotted lines represent linearly extrapolated specific volume–temperature relations to the higher temperature range

RESULTS AND DISCUSSION

One can obtain the specific volume–temperature (V–T) relation at one atmospheric pressure for each polymer and polymer blend by correction of the total volume change observed in the dilatometer[7]. *Figure 1* indicates the V–T relationship of PS, PVME, and 80/20, 55/45 and 25/75 polymer blends. The inflection point of the V–T curve corresponds to the glass transition temperature. All polymer blends, as well as homopolymers, have a single glass transition. Thus the PS/PVME blend is said to be miscible. V–T curves for polymer blends gave a broad glass transition region, similar to the appearance of the well known broad glass transition for other miscible polymer blends[12–14]. This suggests that PS/PVME blend is mixed in a rather micro-heterogeneous state due to composition fluctuation of the polymer blend.

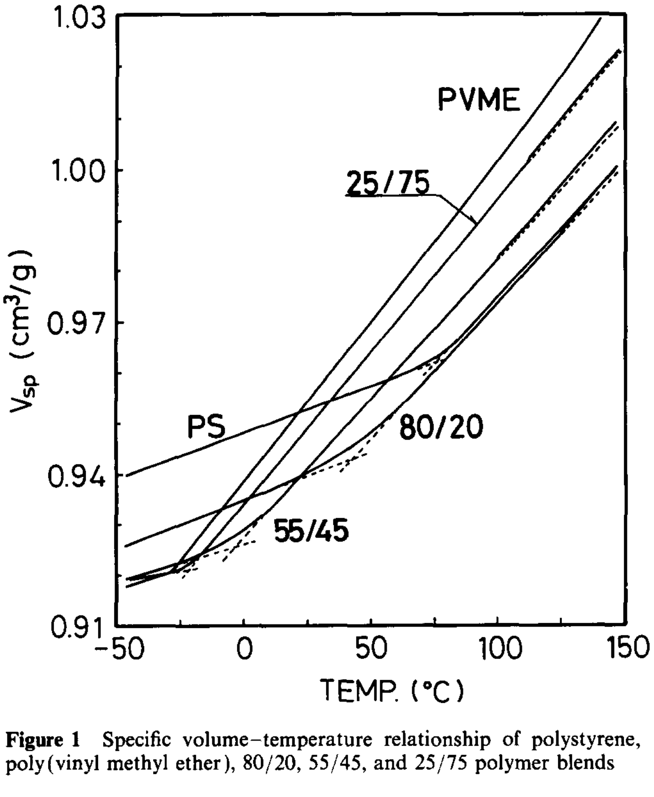

Figure 1 Specific volume–temperature relationship of polystyrene, poly(vinyl methyl ether), 80/20, 55/45, and 25/75 polymer blends

It is noted that the specific volume of polymer blends increases discontinuously at higher temperatures with increasing temperature. As shown in *Figure 2*, which demonstrates an enlarged V–T relationship of polymer blends in the liquid state, one can observe that the specific volume of 80/20, 55/45 and 25/75 polymer blends increases discontinuously around 125, 100 and 112°C, respectively, corresponding to the phase separation temperature. The dotted line in *Figure 2* indicates a linearly extrapolated liquid line to higher temperatures. The increase of the specific volume at phase separation suggests that the volume change due to mixing is negative and the miscible PS/PVME blend system is in a much more compact packing structure than the phase-separated blend system.

The glass transition temperature of a miscible PS/PVME blend observed by dilatometric measurement

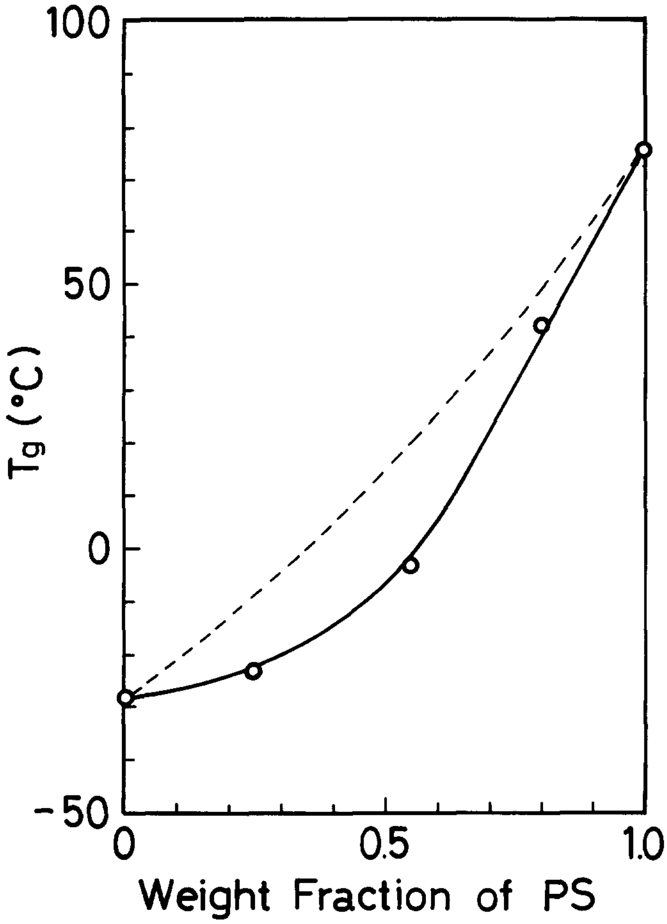

Figure 3 Glass transition temperature of miscible polystyrene/poly(vinyl methyl ether) *versus* weight fraction of polystyrene: the solid and dotted lines represent experimental and calculated lines by the Gordon–Taylor equation, respectively

is shown in *Figure 3* as a function of composition. The dotted line in the figure indicates the theoretical curve estimated from the Gordon–Taylor equation. The difference between the theoretical and observed curves appears to stem from the assumption of simple additivity of specific volume in this theory. Thus it is suggested that the specific volume change due to mixing ($\Delta V_{\mathrm{m,sp}}$) is not zero but either positive or negative for the PS/PVME blend system.

It is certain that the miscible polymer blend has a single glass transition temperature and the immiscible polymer blend has two glass transition temperatures for each phase-separated phase. The V–T curve of the as-cast 55/45 polymer blend has a glass transition temperature, while the curve of the blend heated up to 140°C has two glass transition temperatures, indicative of the phase-separation by heating up to 140°C. The phase-separated polymer blend became miscible again by annealing at 90°C for about 142 h, where the polymer blend exhibits a one-phase (miscible) region.

Next we evaluate the equation-of-state parameter and molecular parameter of homopolymer and polymer blends using the V–T relationship and $\Delta V_{\mathrm{m,sp}}$ for the polymer blend. Thermodynamic quantities such as specific volume, temperature and expansion coefficient of homopolymer and polymer blends are the important state parameters. Equation-of-state parameters are obtained using an equation of state derived from fluid theory by Sanchez and Lacombe[9,10]. This theory is also useful to obtain the molecular parameter from the equation of state parameter. Using Sanchez and Lacombe's fluid theory, we estimated the molecular parameters in addition to the state parameters.

The equation of state at atmospheric pressure is represented for homopolymer and polymer blend in a liquid state as follows:

$$\tilde{\rho}^2 + \tilde{T}[\ln(1-\tilde{\rho}) + \tilde{\rho}] = 0 \qquad (1)$$

$$\tilde{\rho} = \rho/\rho^* = 1/\tilde{V} \qquad (2)$$

$$\tilde{T} = T/T^*, \qquad T^* = \varepsilon^*/k \qquad (3)$$

where $\tilde{\rho}$ and $\tilde{V}$ are the reduced density and the reduced volume, respectively. T, $\tilde{T}$, T^*, ρ, ρ^*, ε^* and k are the temperature, reduced temperature, characteristic temperature, density, characteristic density, characteristic energy, and Boltzmann constant, respectively. Equation (1) can be differentiated by temperature or pressure.

$$T\alpha = \frac{1}{\tilde{T}/(1-\tilde{\rho}) - 2} \qquad (4)$$

$$V^* = \frac{\beta k A}{\alpha \tilde{T} \tilde{V}^2} \qquad (5)$$

where α, V^*, β and A are the expansion coefficient, characteristic volume, isothermal compressibility, and Avogadro number, respectively. The expansion coefficient experimentally obtained at a given temperature for each homopolymer and polymer blend makes it possible to obtain the values of $\tilde{\rho}$ and $\tilde{T}$ by equations (1) and (4). The compressibility of the homopolymer only is evaluated by the empirical equation:

$$\beta^{-1/6} = \frac{21P}{MV_{\mathrm{sp}}} \qquad (6)$$

where P, M and V_{sp} are parachor, molecular weight of the repeating unit, and specific volume, respectively. The V^* of the molecular parameter for each homopolymer can be evaluated using equations (5) and (6). However, the V^* of polymer blends is impossible to evaluate because the parachor of polymer blends cannot be determined. The V^* of polymer blends can be determined using ΔV_{m} as mentioned later. ΔV_{m} is defined by equation (7):

$$\Delta V_{\mathrm{m}} = \gamma N(\tilde{V}V^* - \phi_1\tilde{V}_1V_1^* - \phi_2\tilde{V}_2V_2^*) \qquad (7)$$

where ϕ is the volume fraction ($\phi_1 = w_1/(w_1 + Qw_2) = 1 - \phi_2$, $Q = \rho_1^*V_1^*/\rho_2^*V_2^*$), γN is the total number of 'mer' in the polymer blend system, and the subscripts 1 and 2 represent PS and PVME, respectively. The specific volume change due to mixing ($\Delta V_{\mathrm{m,sp}}$) can be described using equation (7).

$$\Delta V_{\mathrm{m,sp}} = \frac{1}{\rho_1^*V_1^*} \times \{(w_1 + Qw_2)\tilde{V}V^* - w_1\tilde{V}_1V_1^* - Qw_2\tilde{V}_2V_2^*\} \qquad (8)$$

where w is the weight fraction. Equation (8) is transformed as follows:

$$V^* = \frac{\left(\Delta V_{\mathrm{m,sp}} + \dfrac{w_1\tilde{V}_1}{\rho_1^*} + \dfrac{w_2\tilde{V}_2}{\rho_2^*}\right)\tilde{\rho}}{\dfrac{w_1}{\rho_1^*V_1^*} + \dfrac{w_2}{\rho_2^*V_2^*}} \qquad (9)$$

Substituting $\Delta V_{\mathrm{m,sp}}$ for a certain experimentally obtained

Table 1 Thermodynamic state parameters and molecular parameters of PS, PVME and PS/PVME polymer blends, and pair molecular parameters of PS/PVME polymer blends

	PS	80/20	55/45	25/75	PVME
$\alpha \times 10^4$ (K^{-1})	5.408	5.561	5.609	5.880	6.245
ρ ($g\,cm^{-3}$)	1.031	1.033	1.024	1.012	1.005
$\tilde{v}$	1.076	1.079	1.080	1.085	1.092
$\tilde{p}$	0.929	0.927	0.926	0.922	0.916
$\tilde{T}$	0.502	0.509	0.511	0.522	0.537
T^* (K)	723	714	711	696	677
$\varepsilon^* \times 10^{14}$ (erg)	9.979	9.852	9.813	9.606	9.337
ρ^* ($g\,cm^{-3}$)	1.110	1.114	1.106	1.098	1.097
V^* ($cm^3\,mol^{-1}$)	12.61	12.76	13.11	13.55	13.84
$\Delta V_{m,sp}$ ($cm^3\,g^{-1}$)		−0.00653	−0.00461	−0.00105	
V^*_{12} ($cm^3\,mol^{-1}$)			13.18		
ε^*_{12} (erg)			9.889×10^{-14}		

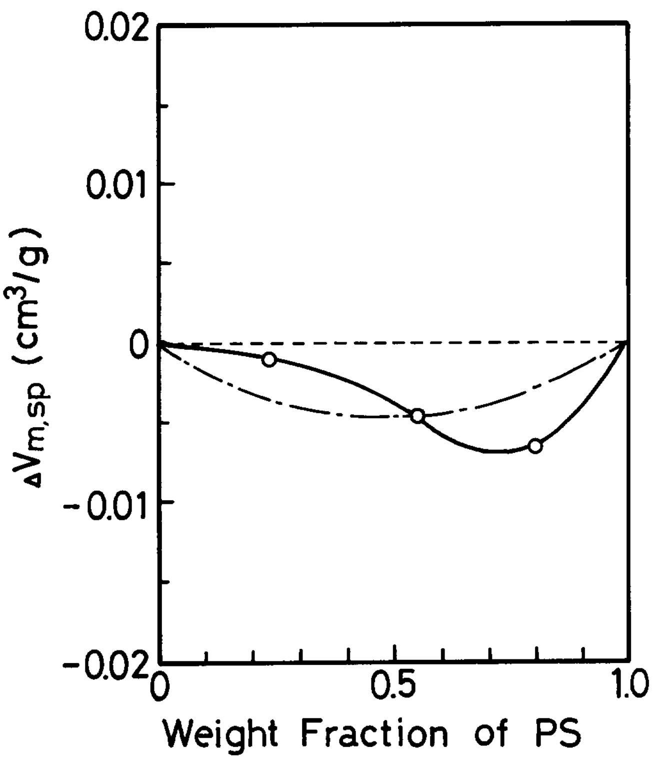

Figure 4 Specific volume change of mixing at 90°C of a miscible polystyrene/poly(vinyl methyl ether) blend system: the solid and dotted lines represent experimental and calculated lines, respectively

blend composition into equation (9), V^* for its composition of polymer blends is determined. Thus all the molecular parameters such as V^* and ε^* and the equation-of-state parameters were estimated for pure polymers and polymer blends.

The combining rules of polymer blend system were assumed:

$$V^* = \phi_1^2 V_1^* + 2\phi_1\phi_2 V_{12}^* + \phi_2^2 V_2^* \qquad (10)$$

$$\varepsilon^* V^* = \phi_1^2 V_1^* \varepsilon_{11}^* + 2\phi_1\phi_2 V_{12}^* \varepsilon_{12}^* + \phi_2^2 V_2^* \varepsilon_{22}^* \qquad (11)$$

where V_{12}^* and ε_{12}^* are the respective pair characteristic volume and the pair characteristic energy, which is an energy parameter characterizing the attractive and repulsive term for mer-mer interaction, respectively. Substituting the V^* and ε^* obtained experimentally for a certain blend composition into equations (10) and (11), V_{12}^* and ε_{12}^* characteristic of the polymer blend, independent of composition of the polymer blend, can be evaluated. Thermodynamic quantities and the molecular parameters of pure polymers and polymer blends are listed in *Table 1*. Once V_{12}^* and ε_{12}^* are determined, we can evaluate V^* and ε^* for any composition using equations (10) and (11). The specific volume change due to mixing at 90°C where the system is in equilibrium liquid state is shown in *Figure 4*, indicating that the solid and dotted lines, respectively, represent the experimental and theoretical symmetric curve estimated using equation (8). Both $\Delta V_{m,sp}$ gave a negative value over the whole composition range. It is suggested that a larger negative $\Delta V_{m,sp}$ obtained experimentally means much more closed packing when the weight fraction of PS is around 0.7. The asymmetric curve of the $\Delta V_{m,sp}$ *vs.* weight fraction also suggests a special interaction between PS and PVME. Lu *et al.*[15] also reported the interaction for this blend system. $\Delta V_{m,sp}$ of the other polymer blends is shown in *Figure 5* for comparison. One can also see an asymmetric $\Delta V_{m,sp}$ curve for the PS/poly(phenylene oxide) blend system[16] and a symmetric curve for the PS/poly(2-chlorostyrene) blend system[7], which also give a negative $\Delta V_{m,sp}$. Further consideration is necessary to describe the combining rule with an asymmetric nature.

Similarly to an evaluation of $\Delta V_{m,sp}$, the ΔH_m of various blend compositions is calculated by using ε^* obtained from equation (11) and the following equation:

$$\Delta H_m = \gamma N[-\tilde{\rho}\varepsilon^* + \phi_1 \tilde{\rho}_{11} \varepsilon_{11}^* + \phi_2 \tilde{\rho}_{22} \varepsilon_{22}^*] \qquad (12)$$

The predicted values of the heat of mixing (ΔH_m) at 90°C are shown in *Figure 6*. The heat of mixing gave a negative value over the whole composition range, indicating the PS/PVME blend is thermodynamically miscible in a liquid state and corresponding to the interaction parameter estimated from CO_2 sorption properties of the PS/PVME blend system[17]. The absolute value of the heat of mixing around a weight fraction of 0.5 is about half as large as that of the PS/poly(2-chlorostyrene) blend[7] and nearly equal to that of the PS/poly(phenylene oxide) blend[16]. It is noted that ε_{12}^* for the PS/PVME blend system is larger than ε^* for both homopolymers as well as the PS/poly(2-chlorostyrene) blend system, indicating the strong interaction between PS and PVME.

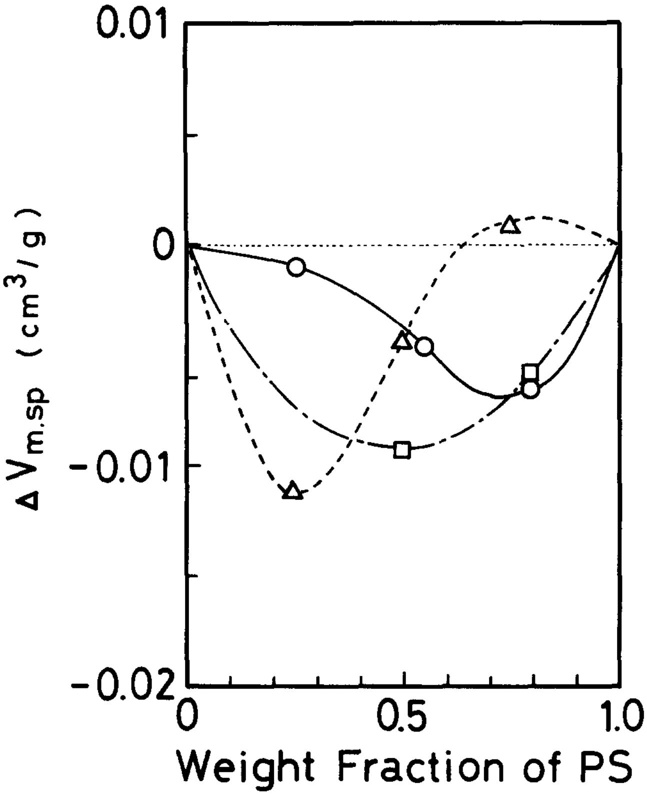

Figure 5 Specific volume change of mixing of polystyrene/poly(vinyl methyl ether) (○), polystyrene/poly(2-chlorostyrene) (□), and polystyrene/poly(phenylene oxide) (△) *versus* weight fraction of polystyrene

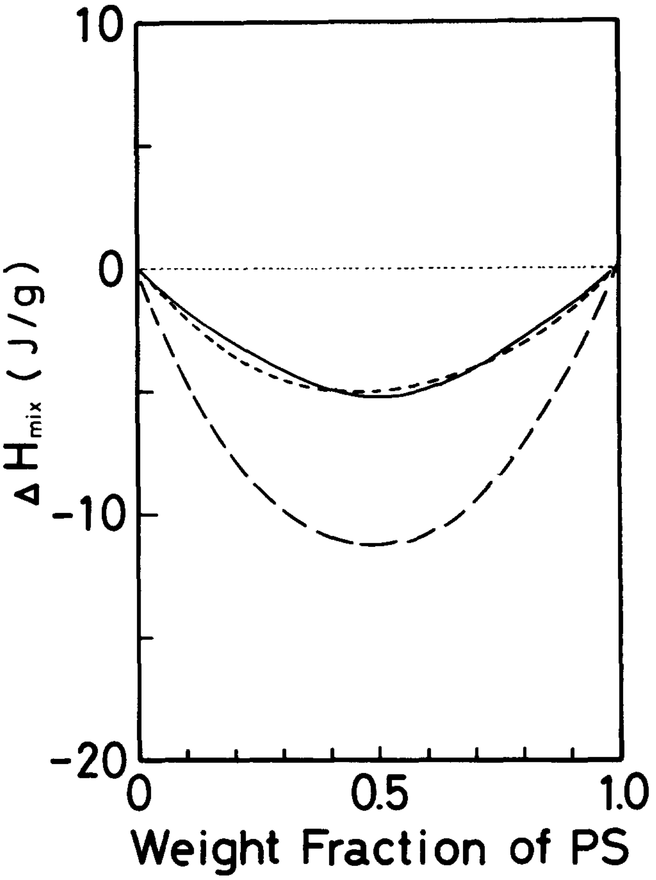

Figure 6 Heat of mixing of polystyrene/poly(vinyl methyl ether) (——), polystyrene/poly(2-chlorostyrene) (— — —), and polystyrene/poly(phenylene oxide) (– – – – –) *versus* weight fraction of polystyrene

In conclusion, the specific volume–temperature relationship obtained by dilatometry and the equation of state could predict the thermodynamic miscibility of a polymer blend in the liquid state. It was found that such a simple method is available to estimate thermodynamic miscibility. The relatively negative larger volume change due to mixing and heat of mixing suggest miscibility due to the special and/or strong interaction. It is necessary to consider further a combining rule representing the special interaction.

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