Macromolecules **1992,** *25,* 721–728

Miscibility and Phase Separation in Poly(methyl methacrylate)/Poly(vinyl chloride) Blends: Study of Thermodynamics by Thermal Analysis

Sunny Shen[†] **and John M. Torkelson**[*,†,‡]

Departments of Chemical Engineering and Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3120

Received May 7, 1990; Revised Manuscript Received November 2, 1990

ABSTRACT: Amorphous blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) were prepared via solution precipitation. From the study of T_g composition behavior, the blends were found to show large positive deviations from volume additivity and to be miscible over the entire composition range at temperatures below 180 °C. An endothermic heat of demixing and its concentration and temperature dependences have been measured by DSC. Spinodal and "cloud point" curves were extrapolated from these measurements. The results have been interpreted in terms of the modified Flory's equation-of-state theory by Hamada et al.[1] and compared with predictions of the directional specific interaction model proposed by ten Brinke and Karasz.[2] The modified equation-of-state theory can almost quantitatively reproduce the concentration dependence of the heat of mixing but failed to predict the positive excess heat capacity for this blend system, whereas the ten Brinke–Karasz model can describe qualitatively both the concentration and temperature dependence of the heat of mixing of homopolymer blends.

Introduction

It is well-known that mixtures of high molecular weight polymers are characterized by a nearly negligible value of the combinatorial entropy of mixing. A stable one-phase system can be obtained only if the mixing is exothermic. ten Brinke and Karasz[2] recently pointed out that there are two ways of fulfilling this requirement. For a blend of two homopolymers, miscibility will generally result from specific intermolecular interactions. For random copolymer–homopolymer mixtures, miscibility can arise from the so-called "repulsion effect". This refers to a situation for which the value of the exchange interaction parameter between the monomers that make up the copolymer is larger than the values of both of the other interaction parameters involved. In this extreme case, all these interaction parameters are positive, and yet miscibility occurs.

The lower critical solution temperature (LCST) behavior in the two classes of systems can be of an entirely different origin. For homopolymer blends in which the favorable directional specific interactions exist in addition to the unfavorable London dispersion forces, an increase in temperature increases Brownian motion which, in turn, reduces the number of specific interactions. On the other hand, in a random copolymer–homopolymer blend with mainly London dispersion forces, phase separation is due to unfavorable compressibility contributions.

Various theories have been developed to describe and predict the thermodynamics of polymer mixtures. The best-known examples are Flory's equation of state and the lattice fluid theory.[3,4] Flory's equation of state uses a random mixing assumption, which neglects any local densification which might result from strong specific interactions. However, Hamada et al.[1] have shown that Flory's equation of state can be improved by modifying the combining rules on mixing assumed by Flory. More recently, ten Brinke and Karasz[2] constructed an incompressible model emphasizing the importance of the directional specific interactions. They also claimed that there is a simple way to determine whether the phase behavior in a polymer mixture at a certain temperature is dominated by the directional specific nature of the interaction or by the compressible nature of the system. In the former case the excess heat capacity (ΔC_p) is positive and decreasing with increasing temperature, while in the latter ΔC_p is negative.

Barnum et al.[5] measured the excess heat capacities for two random copolymer–homopolymer systems and found that the ΔC_p's are positive, which cannot be explained by modern equation-of-state theories. A second group, Uriarte et al.,[6] also obtained a positive ΔC_p for another random copolymer–polymer system. However, their calculations of the temperature dependence of the heat of mixing from the modified Flory's equation-of-state theory by Hamada et al.[1] show positive excess heat capacity which increases with increasing temperature. Up to the present, no experimental information has been obtained in terms of the temperature behavior of the excess heat capacity.

Very recently, Coleman, Painter, and co-workers[7,8] cast doubt on the repulsion model for random copolymer–homopolymer blends. The model they proposed adds one more term to the Flory–Higgins relationship for the free energy of mixing to account for the presence of favorable intermolecular interactions.

Obviously, there is a need for theories of polymer blends which focus on specific interactions. The concentration and temperature dependences of the heat of mixing and the excess heat capacity could be very useful information for evaluating various theories. To demonstrate this idea, we have investigated the phase behavior and the heat of mixing of an amorphous homopolymer blend which involves specific intermolecular interactions. Blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) provide a good model as these blends meet the requirements of our study and as there have been other studies on the PMMA/PVC system. The experimental parameters for theoretical calculations are also available.

The first study on PVC and PMMA was done by Schurer et al.,[9] who concluded that PMMA/PVC is miscible only in blends having PVC contents greater than 60% w/w. Jager et al.[10] showed that the lower critical solution temperature (LCST) behavior causes partial phase separation

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[*] To whom correspondence should be addressed.

[†] Department of Chemical Engineering.

[‡] Department of Materials Science and Engineering.

0024-9297/92/2225-0721$03.00/0

of PMMA/PVC blends above a certain temperature. Razinskaya et al.[11] found no miscibility when blends are made by solvent casting from tetrahydrofuran solution, whereas Walsh and McKeown[12] stated that PMMA and PVC are miscible in all compositions when methyl ethyl ketone is the casting solvent. Other factors that influence the miscibility, such as tacticity and molecular weight, can be equally as important for this system, as demonstrated recently.[13-15] Moreover, the definition of the distance scale over which a blend is deemed to be miscible or immiscible is very important. Albert et al.[16] used nonradiative energy transfer and pulsed NMR techniques to study PMMA/PVC miscibility on a 5-nm scale. Parmer et al.[17] employed a solid-state CP-MAS NMR technique which apparently confirmed an upper limit to immiscibility on a 4.0 nm distance scale.

The PMMA and PVC blend is a well-known system in which a hydrogen-bonding type of specific interaction involving the α-hydrogen of PVC and the carbonyl group of PMMA is expected.[18] The involvement of the carbonyl group is well established from a shift in the carbonyl infrared absorption frequency. The thermal degradation problem of PVC can be resolved by adding stabilizer, and the experimental temperature can be raised to about 250 °C.[13]

The direct measurement of the heats of mixing of two polymers is not possible since mixing of polymers in their viscoelastic molten state requires strong mechanical agitation. This gives rise to energy dissipation and thus to a strong increase of the temperature of the sample, independent of the magnitude and sign of the heat of mixing. Indirect methods, including measurements of the heats of mixing in the presence of a solvent, use Hess's law to extract the heat of mixing of the polymers.[19] This technique is judged to be confined to rubber samples since glasses are not at equilibrium and results depend on the history of the glassy sample.[20,21] In practice, it has not been particularly successful, possibly due to accumulation of errors in the series of experiments involved. Another well-known indirect method involves the calorimetric determination of the heats of mixing for low molecular weight or oligomeric model systems.[22,24] This may not always give reliable results due to differences between the high polymers and the analogues used. These differences could arise from chain effects, steric differences, or density differences. More recently, Natansohn[25] and Ebert et al.[26] proposed a direct measurement of heats of demixing using DSC and scanning in the range of the phase separation temperature. Ebert et al.[26] argued that for blends the endothermic heat of demixing should roughly correspond to the total heat of mixing, provided that the two phases mainly contain the pure components. This can be achieved by choosing appropriately the final scanning temperature.

In this work, we have studied the glass transition behavior, miscibility, and phase separation of PMMA/PVC blends. Although there have been other studies on this system, it is important to compare our results with those of the others which have been chosen as references for selecting model parameters in theoretical calculations. Our major effort concerned obtaining experimental information about the concentration and temperature dependences of the heat of mixing and the excess heat capacity of the homopolymer blends by using DSC thermal analysis. These results have been interpreted and compared with the theoretical predictions of the modern equation-of-state theory[1] and the ten Brinke and Karasz model.[2]

Experimental Section

Materials. Commercially available PMMA and PVC samples were used without further purification. PMMA was obtained from Scientific Polymer Products with M_w approximately 75 000 as reported by Scientific Polymer Products. PVC was purchased from Aldrich Chemical Co. with M_w = 83 500 and M_n = 37 400 as reported by Aldrich.

Preparation of Blends. Blends of PMMA and PVC were prepared by coprecipitation for DSC analysis. Appropriate amounts of each polymer were dissolved in tetrahydrofuran and stirred for a minimum of 24 h, followed by precipitation into a large excess of methanol. The resulting powders were then repeatedly washed and subsequently dried in a vacuum oven at room temperature until the weight was constant. To counteract degradation to PVC, 1 wt % stabilizer (based on PVC), di-*n*-octylin-*S*,*S*′-bis(isooctyl mercaptoacetate), obtained from Ciba-Geigy, was added to all blends. Some additional blend film samples for FTIR analysis were prepared by solent casting from acetone (1 wt %) onto potassium bromide (KBr) windows. The solvent was then completely removed by vacuum desiccation at room temperature. The low concentration of the solutions was essential to ensure that films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed.[27] All blend films were clear in appearance.

Calorimetric Measurements. Glass transition temperatures and heats of demixing were determined by using a Perkin-Elmer DSC-2C scanning calorimeter. All samples were heated at a rate of 40 °C/min to 147 °C and held there for 15 min, followed by quenching to −10 °C, using a liquid N_2 cooling device. Glass transition temperatures (T_g) were measured by using a heating rate of 10 °C/min. The onset of the heat capacity jump was taken as the glass transition temperature, T_g.

Heats of demixing were measured with samples of about 18–21 mg. The furnace atmosphere was made as identical as possible for each measurement by having exactly the same N_2 gas pressure. Before and after each measurement, the sample holder was carefully examined to make sure that the cover was tightly sealed. The range was set at 5 mcal/s for scanning rates of 80 °C/min, at 2 mcal/s for rates of 40 °C/min, and at 1 mcal/s for rates of 20 °C/min.[28] Areas under the peaks were converted into heats of demixing by reference to measurements on indium carried out at 20 °C/min.

Results and Discussion

T_g Composition Behavior. Parmer et al.[17] have reported the glass transition temperature measured as a function of blend composition for PMMA/PVC blends, showing a slightly sigmoidal deviation from the simple weight proportionality function. They also showed the effect of blend composition on the width of the glass transition. There is a sharp increase in the T_g width starting at about 50 wt % PMMA, with a maximum occurring at about 70 wt % PMMA. The T_g width remains constant for PMMA contents below 50 wt %, and the maximum transition width difference is about 15 °C. However, our results on T_g composition behavior given in Figure 1 show a large positive deviation. The transition width behavior (Figure 2) shows a trend similar to that of Parmer et al.'s: a sharp increase starting at about 60 wt % PMMA, with a maximum at about 85 wt % PMMA. The maximum T_g width difference is about 15 °C, also.[29]

Explanations for positive deviations from simple additivity have been proposed[30] which indicate that if the two polymers have strong exothermic or favorable specific interactions, a negative volume of mixing or densification may result in a higher T_g due to a reduction in free volume. The width of the transition may reflect the magnitude of local compositional fluctuations in polymer blends, giving a qualitative implication as to the relative homogeneity or miscibility of the system. The lower miscibility shown in Parmer et al.'s[17] system may be due to the slightly higher molecular weight materials they used.

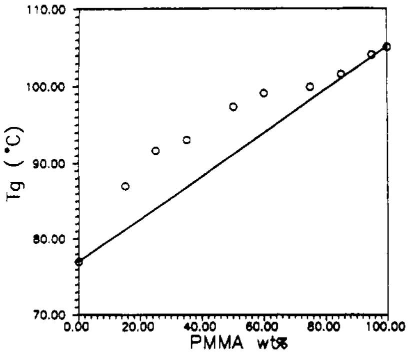

Figure 1. Glass transition temperature as a function of PMMA content in PMMA/PVC blends. The line represents the behavior based on the simple weight function $T_g = W_1T_{g1} + W_2T_{g2}$, where W_1 and W_2 are weight fractions of components 1 and 2, respectively.

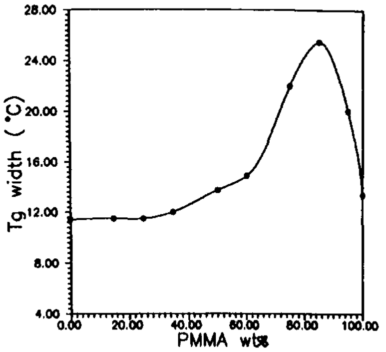

Figure 2. Glass transition width for PMMA/PVC blends plotted as a function of PMMA content.

The T_g composition results were analyzed further by using a third-power equation developed by Brekner et al.[31] Because of relatively small entropy contributions, interactions are considered essential for miscibility of polymer blends. The surface contacts between components will thus contribute most to both the conformational mobility and the "free volume" distribution and consequently to the value of the glass transition temperature of miscible polymer blends. On the basis of those observations, the third-power equation was developed by assuming that the binary contact interaction influences both conformation and free volume distribution in the polymer blend:

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)W_{2c} - (K_1 + K_2)W_{2c}^2 + K_2W_{2c}^3 \quad (1)$$

where $W_{2c} = KW_2/(W_1 + KW_2)$ represents the corrected weight fraction of component 2 (with the higher glass transition temperature being T_{g2} and the lower being T_{g1}), assuming volume additivity for the blend components, W_1 and W_2 are the weight fractions of components 1 and 2, respectively, and K is the parameter of the Gordon–Taylor equation,[32] defined as the ratio of the differences of the coefficients of expansion, $\Delta\alpha$, near T_g of the glassy (G1) and rubbery (L) states

$$K = \rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1 \quad (2)$$

where $\Delta\alpha_i = (\alpha_L - \alpha_{G1})_i$ for component i and ρ_i is the density for component i. Assuming the validity of the Simha–Boyer rule,[33] $\Delta\alpha T_g = 0.113$ (0.113 being a "universal" constant), then

$$K = \rho_1T_{g1}/\rho_2T_{g2} = K'T_{g1}/T_{g2} \quad (3)$$

If $K' = \rho_1/\rho_2$ is assumed to be unity (for our blend system $K' = 1.175$), the Gordon–Taylor equation can be considered an "ideal" volume additivity equation for the T_g of miscible polymer blends, and $K = T_{g1}/T_{g2}$.

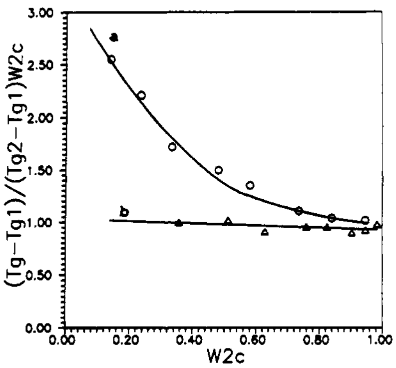

Figure 3. T_g composition behavior of PMMA/PVC blends according to the reformulated third-power equation (1a) using different values of the K parameter. $K = K'T_{g1}/T_{g2}$. (a) $K' = 1$; (b) $K' = 3.4$.

The parameter K_1 essentially accounts for deviations from additivity due to the difference between the contributions of the hetero– and the respective homomolecular contacts to the glass transition temperature of blends. In contrast, K_2 accounts for only the differences between the energetic perturbations in the molecular surroundings of the binary contacts.

To classify the T_g composition behavior of miscible polymer blends, the third-power equation (eq 1) was reformulated to the following manner:

$$(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c} = (1 + K_1) - (K_1 + K_2)W_{2c} + K_2W_{2c}^2 \quad (1a)$$

For volume additivity, both $K_1 = 0$ and $K_2 = 0$, and eq 1a reduces to the simple form

$$(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c} = 1 \quad (1b)$$

A straight horizontal line about unity will be obtained by plotting $(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c}$ vs W_{2c}. For deviations from volume additivity, straight lines of slope K_1 ($K_2 = 0$) or curved lines ($K_2 \neq 0$) are obtained.

Figure 3 shows the plot of $(T_g - T_{g1})/(T_{g2} - T_{g1})W_{2c}$ vs W_{2c} for PMMA/PVC blends. The glass transition behaviors of a number of polymer blend systems have been reviewed by Schneider.[34] Schneider and co-workers[35] assumed that segmental alignment by the directional specific interaction between the two different polymer chains contributes to a reduction of the available free volume and consequently to a decrease of the mobility in the polymer blend. This may explain the observed order for positive deviation for hydrogen bonding and charge-transfer interaction. At the same time, the stronger directional effect of the specific interactions will be accompanied by stronger perturbations of the conformational rearrangements in the neighborhood of the contacts. The deviation from additivity of PMMA/PVC blends falls in the range between PMMA/poly(vinylidene fluoride) (PVF_2) blends and blends of the polydonor poly[N-(2-hydroxyethyl)carbazolyl methacrylate] (PHECM) and the polyacceptor poly[ω-(hydroxyethyl)-3,5-dinitrobenzoyl methacrylate] (PDNBM-n).[36] It is evident that the PMMA/PVC system presents a large positive deviation from volume additivity, thus implying strong favorable specific interactions.

Figure 3 also shows that the observed deviations of the T_g composition data characterized by $K = K'T_{g1}/T_{g2}$ ($K' = 1$) can be compensated for by an appropriate change in the K' coefficient. This indicates that possible specific

Table I
Carbonyl Band Absorption Maxima for PMMA and PMMA/PVC Blends

polymer	carbonyl band position ν, cm^{-1}	$\Delta\nu$, cm^{-1}
pure PMMA	1734	2
PMMA/PVC = 60/40 (wt %)	1732	

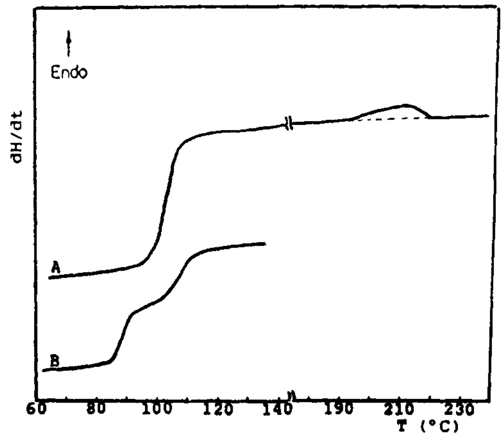

Figure 4. DSC curves for a 60:40 (wt %) PMMA/PVC blend. (A) Single T_g before phase separation and the endothermic peak of phase separation; (B) second run at 10 °C/min, after phase separation.

interactions can be included in an arbitrary fitting parameter K of the Gordon–Taylor equation, as has been suggested by Walsh and McKeown.[12]

Supplemental FTIR Data. FTIR spectroscopic studies were performed on thin films of pure PMMA and PMMA/PVC mixtures on KBr windows. Shifts to lower frequency of the carbonyl band of the PMMA may be indicative of specific interactions with the PVC, with the magnitude of the band shift being proportional to the strength of the interaction.[37] The results are provided in Table I. Blends with greater than 40 wt % PVC content show the same approximately 2 cm^{-1} band shift. Thus, while FTIR spectroscopy provides information consistent with specific interactions between the two polymers, it is not sensitive enough to provide more detailed information such as how the strength of the interaction may vary as a function of blend composition.

Phase Diagram Determination. The endothermic peak shown in Figure 4 was observed during a LCST phase separation which occurred upon heating a 60:40 (wt %) PMMA/PVC blend in a DSC. After a rapid quench, the blend behaved as a two-component system which gives two separate T_g's. Various types of information can be obtained by the analysis of endothermic peaks such as that in Figure 4. Following the notation of Ebert et al.,[26] the onset temperature of the peak was assigned as T_e. T_e increases with increasing heating rates and levels off at higher heating rates, as shown in Figure 5. The extrapolation of the onset temperature to the zero heating rate may be expected to yield a "cloud point" temperature since there is no well-defined binodal temperature curve for a polydispersed blend system on a pseudo-two-component phase diagram.[38] The endothermic peaks could not be observed at heating rates under 20 °C/min. Although the extrapolations are somewhat arbitrary, they are our best estimations based on the data that we have. The errors brought in by the extrapolations will not affect our following experimental results. In a similar manner, the extrapolation to large heating rates should yield the spinodal temperature, since spinodal decomposition is instantaneous. The plateau value was taken as the spinodal temperature. The error bars in Figure 5 represent the standard deviations from a minimum of four measurements. Some supplemental experiments (see ref 39) have been done, giving information about the lower limits of the error bars on the cloud points. These experiments also provide further substantiation for the reasonableness of the estimated spinodal temperatures. The corresponding spinodal and cloud point curves are thus shown in Figure 6.

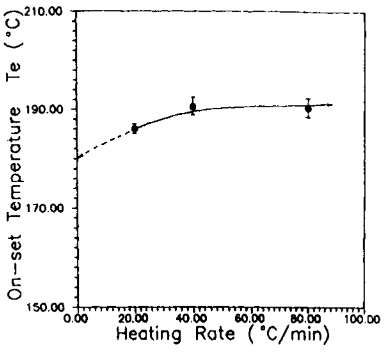

Figure 5. Dependence of the onset temperature T_e on the heating rate for a 60:40 (wt %) PMMA/PVC blend.

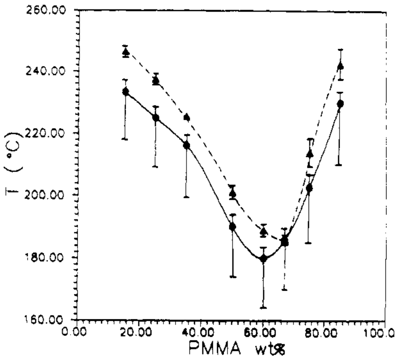

Figure 6. Extrapolated spinodal and cloud point curves of PMMA/PVC blends. (▲) Spinodal; () cloud point.

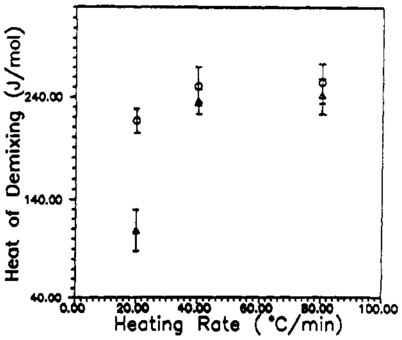

Figure 7. Dependence of the endothermic peak area on the heating rate. (○) 60:40 (wt %) PMMA/PVC; (△) 75:25 (wt %) PMMA/PVC.

Concentration Dependence of Heats of Demixing/Mixing. Heats of demixing have been determined from the area under the endotherm peaks. This area also increases with increasing heating rates, reaching a plateau when the heating rate is higher than 40 °C/min (Figure 7). Cifra et al.[40] recently studied the short-range fluctuations in the spinodal decomposition of binary polymer mixtures. They found that at the very early stage of decomposition phase separation is controlled mainly by short-range interaction and not by diffusion processes. In other words, demixing at the very early stages is controlled by thermodynamics rather than kinetics. This conclusion coincides with Natansohn's argument[25] that at high heating

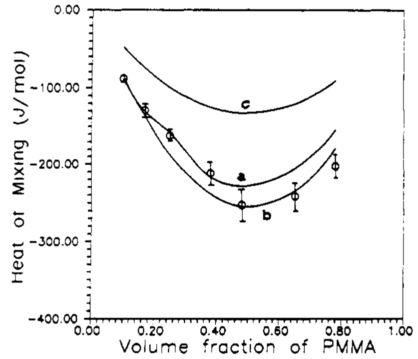

Figure 8. Concentration dependence of the heat of mixing (○) Experimental data. (a) Calculations of modified Flory's equation of state by Hamada et al.[1] $X_{12} = -6.27$ J/cm^3; $c_{12} = 0.15$; $Q_{12} = 0$; $s_1/s_2 = 0.8$. (b) Calculations of modified Flory's equation of state by Hamada et al.[1] $X_{12} = -12.54$ J/cm^3; $c_{12} = 0.112$; $Q_{12} = 0$; $s_1/s_2 = 0.8$. (c) Calculations of the directional specific interaction model by ten Brinke and Karasz.[2]

rates the blend is forced to transform from a single-phase to a two-phase system, giving an endotherm or an exotherm which is a measure of the two components' interaction. At lower heating rates the peak cannot be distinguished. On the other hand, Flory's definition of the heat of mixing is in terms of the difference between the total interaction energy in the mixture as compared with that for the pure liquid components. Therefore, the plateau values were taken as the heat of demixing and identified as a rough approximation of the heat of mixing with an opposite sign. This approximation becomes more realistic when the two phases mainly contain the pure components. This can be achieved by choosing the final scanning temperature appropriately, according to the phase diagram obtained. One should be aware that after the rapid heating to the final scanning temperature, the difference between the total interaction energy in the mixture as compared with that of the pure components is fully measured. However, within such a short period of time, the mixture will not be able to achieve complete physical separation through chain diffusion. If the sample is kept at that final scanning temperature for a long enough time, the blend will eventually separate into phases of final composition containing largely either PMMA or PVC. One should also be aware of the possibility that the temperature dependence of the heat of mixing would limit the accuracy of this approach. The experimental data of the concentration dependence of the heat of mixing is thus given in Figure 8, where the error bars again represent the standard deviations. The values obtained from this approach are within the same range as the values of the heat of mixing obtained by calorimetric studies on oligomeric and low molecular weight analogue systems.[22,41] Data have been converted from calories per gram to joules per mole to be consistent with SI units in the theoretical calculations.

Figure 8 also shows the theoretical calculations of the concentration dependence of the heat of mixing from both the modified Flory's equation-of-state theory by Hamada et al.[1] and the directional specific interaction model by ten Brinke and Karasz.[2] Flory's equation-of-state theory[42,43] is based on the assumption of Prigogine[44] that the degree of freedom of a polymer fragment can be separated into internal and external components. The external component of the degree of freedom is denoted by $3c$, with $c < 1$. Each pure polymer mixture component is then characterized by characteristic temperature, pressure, and volume, T_i^*, P_i^*, and v_i^*, respectively, and the reduced magnitudes $\tilde{T}_i$, $\tilde{P}_i$, and $\tilde{V}_i$, which may be evaluated from the pure component data: specific volume v_i, thermal expansion coefficient α_i, and thermal pressure coefficient ν_i. For a system of identical molecules the equation of state is

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}(\tilde{v}^{1/3} - 1) - 1/(\tilde{v}\tilde{T}) \qquad (4)$$

where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{v} = v/v^*$. Assuming low pressure (or atmospheric pressure), $\tilde{v}_i$ is normally obtained from the thermal expansion coefficient of component i:

$$\tilde{v}_i = \{1 + \alpha_i T/[3(1 + \alpha_i T)]\}^3 \qquad (5)$$

$\tilde{T}_i$ is obtained from $\tilde{v}_i$:

$$\tilde{T}_i = (\tilde{v}_i^{1/3} - 1)/\tilde{v}_i^{4/3} \qquad (6)$$

P_i^* is obtained from the thermal pressure coefficient, ν_i:

$$P_i^* = \nu_i T \tilde{v}_i^2 \qquad (7)$$

Extension to mixtures requires a set of combining rules. Mixing is assumed to be random between segments of equal hard-core volume. The interactions are assumed to take place between the surfaces of adjoining segments, and the number of interacting contacts of chain segments is proportional to their specific surface area.[45] An interaction parameter, X_{12}, associated with a difference in chemical nature between the components is introduced to calculate the properties of the mixture. In addition, a noncombinatorial entropy correction factor Q_{12} is used as an adjustable parameter to obtain better quantitative agreement with experimental observations.[46] In this study Q_{12} is not included.

The equation of state for mixtures is identical to eq 4, provided that the characteristic quantities of a mixture are defined as

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \theta_2 X_{12} \qquad (8)$$

$$\tilde{T} = T/T^* = (\Phi_1 \tilde{T}_1 P_1^* + \Phi_2 \tilde{T}_2 P_2^*)/P^* \qquad (9)$$

where

$$\Phi_i = m_i v_i^*/(m_1 v_1^* + m_2 v_2^*) \qquad (10)$$

$$\theta_2 = (s_2/s_1)\Phi_2/[\Phi_1 + (s_2/s_1)\Phi_2] \qquad (11)$$

and Φ_i, θ_i, and m_i are volume, surface, and weight fractions of component i. s_2/s_1 is the surface ratio of the segments. Since Flory's equation of state is based on the random mixing assumption, which neglects any local densification resulting from specific interactions, we used Hamada et al.'s modification[1] of the combining rule by using the number of external degrees of freedom for the mixture as

$$c = c_1\Phi_1 + c_2\Phi_2 - c_{12}\Phi_1\Phi_2 \qquad (12)$$

where c_{12} is the parameter characterizing the deviation from additivity. Also

$$v^* = v_1^*\Phi_1 + v_2^*\Phi_2 + 2v_{12}^*\Phi_1\Phi_2 \qquad (13)$$

where

$$v_{12}^* = \{(v_1^{1/3} + v_2^{1/3})/2\}^3 \qquad (14)$$

Equation 10 then becomes

$$\tilde{T} = T/T^* = (1/P^*)[\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2 - (c_{12}\Phi_1\Phi_2 kT/v^*)] \qquad (15)$$

The heat of mixing per segment at low pressure is

$$\begin{aligned}\Delta H_{\mathrm{m}}/\tilde{r}N &= -RT[c/\tilde{v}\tilde{T} - \Phi_1 c_1/\tilde{v}_1\tilde{T}_1 - \Phi_2 c_2/\tilde{v}_2\tilde{T}_2] - 3/2RTc_{12}\Phi_1\Theta_2 \\ &= v^*[\Phi_1 P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \Phi_2 P_2^*(1/\tilde{v}_2 - \\ &\qquad 1/\tilde{v}) + \Phi_1\Phi_2 X_{12}/\tilde{v}] - 3/2RTc_{12}\Phi_1\Theta_2 \quad (16)\end{aligned}$$

where $\tilde{r}N$ is the number of the total segments of N_1 r_1-mers and N_2 r_2-mers.

As mentioned before, application of the equation-of-state theory requires experimental data for the specific volumes v, the thermal expansion coefficient α, and the thermal pressure coefficient ν. We borrowed the data from Vorenkamp et al.'s study[12] in which they simulated the spinodal curves for PVC blends with both isotactic PMMA and atactic PMMA. This would be reasonable since we have materials with similar molecular weights and phase diagrams. Reasonable values for v, α, and ν at 120 °C are presented in Table II, and the experimental data are temperature independent at temperatures beyond 120 °C.[47,49] In the calculation we have used c_{12}, X_{12}, and s_1/s_2 as adjustable parameters but with logical physical meaning of the magnitudes. Given the fact that we have specific interactions in the mixture and an exothermic heat of mixing, X_{12} must be a negative value. In a most recent study of the thermodynamics of polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends,[49] X_{12} was reported as −9.00 J/cm^3. According to our study on the T_g composition behavior of PMMA/PVC blends discussed previously and the literature review for PS/PVME blends,[34] the deviation from additivity of the PMMA/PVC blend is stronger than that of the PS/PVME blend with similar molecular weights, indicating a stronger specific interaction. Hence, $X_{12} = -12.54$ J/cm^3 was taken for our PMMA/PVC blend system, which fits closely for the blends with higher PMMA volume fraction. Calculations were also done by using $X_{12} = -6.27$ J/cm^3, showing a better fit to experimental results for the blends with lower PMMA volume fraction. The combination of the two values provides a quantitative fitting range for the experimental data.

ten Brinke et al.[50] argued that specific interactions cause volume contraction on mixing. Therefore, the molecules come closer together in the mixture and the number of external degrees of freedom will be smaller than that obtained by a linear combination of the pure components.[1,50] Hence c_{12} should be larger than zero. Hamada et al.[49] used $c_{12} = 0.02$ for the PS/PVME system. $c_{12} = 0.150$ or 0.112 was needed to fit the experimental results quantitatively in our case. Calculations made on the basis of Bondi radii[51] and Sanchez's suggestion[52] about s_1/s_2 both give values close to 1. Chai et al.[53] reported an s_1/s_2 value of 0.94 for PMMA blend with chlorinated polyethylene with a content of 51.6 wt % chlorine. We chose 0.8, which is the value used in Vorenkamp et al.'s work.[13] All the experimental data and sets of parameters used to fit the experimental results are listed in Table II.

Figure 8 illustrates that the calculated ΔH_{m} (expressed in joules per mole) curves from the modified Flory equation-of-state theory can reasonably reproduce the concentration dependence. This figure also shows the calculation of the directional specific interaction model developed by ten Brinke and Karasz,[2] who adapted the incompressible lattice–gas model.[54,55] In ten Brinke and Karasz's model, there are basically three parameters: U_1, U_2, and q. U_1 represents the energy associated with attractive or favorable specific interactions, whereas U_2 represents the energy associated with London dispersion forces. Ln q reflects the loss of entropy due to the formation of a favorable interaction. The enthalpy of mixing is then given by

Table II
Experimental Data of Each Blend Component and the Fitting Parameters for the Mixtures

polymer	$\alpha \times 10^3$, °C^{-1}	ν, J cm^{-3} °C^{-1}	v, cm^3 g^{-1}	
PVC	0.500	1.137	0.740	
PMMA	0.580	1.116	0.870	
	s_1/s_2	X_{12}, J/cm^3	C_{12}	Q_{12}
mixture	0.8	−6.27	0.150	0
	0.8	−12.54	0.112	0

$$\Delta H_{\mathrm{m}} = RT\chi_{\mathrm{H}}(T)\Phi_1\Phi_2 = z[\lambda U_1 + (1-\lambda)U_2]\Phi_1\Phi_2 \quad (17)$$

where z is the coordination number of the lattice minus 2. λ is given by

$$\lambda = [1 + qe^{\beta(U_1-U_2)}]^{-1} \quad (18)$$

where $\beta = 1/kT$ with k being the Boltzmann constant. In ten Brinke and Karasz's demonstration,[2] the value of $U_1 = -2.59$ kJ/mol is chosen in such a way that a LCST occurs near 127 °C; the value for $U_2 = 0.148$ kJ/mol corresponds to a difference in solubility parameters at 200 °C of about 1.5; $q = 10$ is chosen somewhat arbitrarily, knowing that it should be much smaller than the value of about 500 proposed for certain complex low molecular weight mixtures.[55] A cubic lattice has been used so that $z = 1$. The LCST of our PMMA/PVC blend occurs at about 180 °C, and the difference in solubility parameters is about 0.4 at room temperature.[56] Assuming that U_1 and U_2 change proportionally with respect to the LCST temperature and the solubility parameter difference, the parameters for PMMA/PVC system are proposed as follows: $U_1 = -2.93$ kJ/mol, $U_2 = 0.063$ kJ/mol, $q = 10$ and $z = 1$.

Semiempirical Temperature Dependence of Heats of Demixing/Mixing. On the basis of the analysis of Ebert et al.,[26] the heat of mixing is independent of the heating rate; hence, the shape of the DSC peak is predominantly determined by thermodynamic properties of the blend and is represented by the integrated heat of demixing ΔH_{d} as a function of the temperature difference ΔT_{d} between the actual temperature T and the onset temperature T_{e}. In our case, the heat of demixing is found to be heating rate dependent up to a plateau value. Above this value the heat of demixing is heating rate independent. On the basis of Natansohn's argument[25] that at high heating rates the exotherm or endotherm peak reflects the interaction between the two components, we are only interested in the DSC peak shape determined under sufficiently high heating rates, which also reflects mostly the thermodynamic properties of the blend.

The integrated heat of demixing ΔH_{d} as a function of the temperature difference ΔT_{d} between the actual temperature T and the onset temperature T_{e} for our PMMA/PVC system with 25 wt % PMMA is plotted in Figure 9. The 25 wt % PMMA blend was chosen because each phase separation temperature associated with the endothermic peak of this blend is high enough to ensure that each of the two phases obtained contains largely either PMMA or PVC. Therefore, the change of the heat of demixing over a certain temperature range could be approximately equated to the corresponding change of the heat of mixing over the same temperature range with an opposite trend of temperature dependence. In other words, the heat of mixing can be described as a function of the temperature difference ΔT_{m} between the corresponding mixing temperatures T' below T_{e} and the onset temperature T_{e}. Slopes

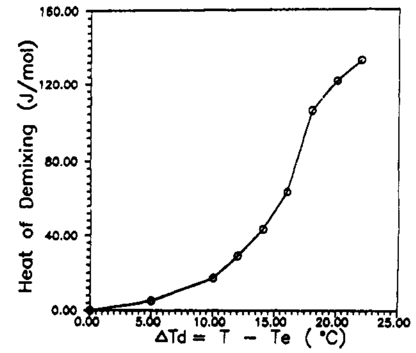

Figure 9. Integral heat of demixing ΔH_d as a function of the temperature difference ΔT_d between the actual temperature T and the onset temperature T_e for 25:75 (wt %) PMMA/PVC blend.

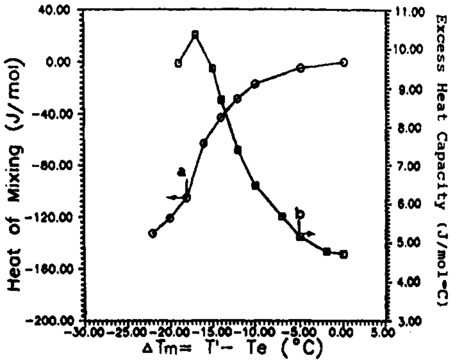

Figure 10. (a) Corresponding heat of mixing ΔH_m as a function of the temperature difference ΔT_m between the corresponding actual temperature T' and the onset temperature T_e for 25:75 (wt %) PMMA/PVC blend. (b) Excess heat capacity ΔC_p as a function of the temperature difference ΔT_m between the corresponding actual temperature T' and the onset temperature T_e for 25:75 (wt %) PMMA/PVC blend.

of this curve were also calculated as a function of the temperature difference ΔT_m between T' and T_e. These semiempirical temperature behaviors of heats of mixing and excess heat capacity ($\Delta C_p = \partial \Delta H_m / \partial T$) are shown in Figure 10. It is evident that the asymmetric peak shape is associated with the excess heat capacity, mostly decreasing with increasing temperature as predicted by the ten Brinke–Karasz theory.[2] Of course, this is an approximate and simplified approach within a very small temperature range. The temperature dependence of both the heat of mixing and the excess heat capacity can only represent the behaviors at the vicinity of the spinodal temperature, and the peak shape could be influenced by a number of experimental factors. However, this is the first experimental analysis which gives semiquantitative information about the temperature behaviors of the heat of mixing and the excess heat capacity of a polymer blend itself. It is hoped that more refined and sophisticated methods of experimental analysis may be developed in the near future.

The temperature dependence of the heat of mixing was also calculated for both the equation-of-state theory and the ten Brinke–Karasz model. As shown in Figure 11, the ten Brinke–Karasz model[2] gives a quantitative description of the LCST behavior, whereas the equation-of-state theory[1] cannot model the positive excess heat capacity. We also calculated the heat of mixing with $X_{12} = -9.00$ J/cm^3 and $c_{12} = 0.02$ (values taken from the PS/PVME study[49]), regardless of the quantitative fitting. This calculation still shows negative excess heat capacity. Moreover, we also noticed that when the heat of mixing is calculated over a smaller temperature range (about 20 °C), as shown in Figure 11, the change of the heat of mixing is actually not monotonic. This might reflect the nature of eq 16 in which the first three terms can be balanced out over a certain temperature range, making the heat of mixing fluctuate. Figure 12 shows the temperature dependence of the heat of mixing calculated over a larger temperature range for the modified equation of state. To make the predictions of the excess heat capacity from this theory would probably require the interaction parameter X_{12} to be temperature dependent.

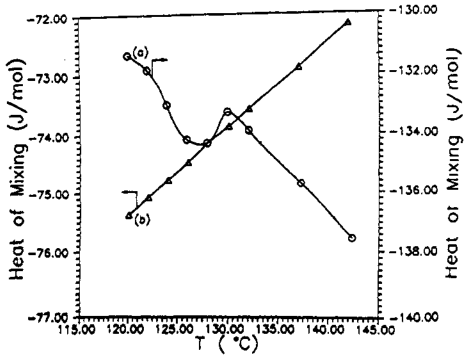

Figure 11. Calculations of the temperature dependence of the heat of mixing. (a) Modified Flory's equation-of-state theory by Hamada et al.[1] $s_1/s_2 = 0.8$; $X_{12} = -6.27$ J/cm^3; $c_{12} = 0.15$. (b) ten Brinke-Karasz model.[2] $U_1 = -2.93$ kJ/mol; $U_2 = 0.063$ kJ/mol; $q = 10$ and $z = 1$.

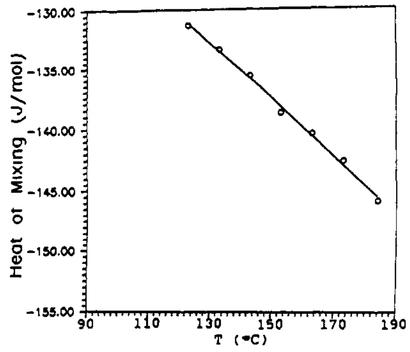

Figure 12. Calculations of the temperature dependence of the heat of mixing from modified Flory's equation-of-state theory by Hamada et al.[1] over a larger temperature range. $s_1/s_2 = 0.8$; $X_{12} = 6.27$ J/cm^3; $c_{12} = 0.15$.

Conclusions

The study of the T_g composition behavior of PMMA/PVC blends shows that the specific interaction between PMMA and PVC is almost as strong as hydrogen bonding. It is shown that DSC measurements of heat of demixing can provide information about spinodal and cloud point curves of polymer blends. Careful and appropriate treatment of these measurements can convert the endothermic heat of demixing to the exothermic heat of mixing. It is also shown that the DSC analysis is the first experimental approach giving semiquantitative temperature behavior of the heat of mixing and excess heat capacity at the temperature range of phase separation; this is based on the assumption that the peak shape represented by the integrated value of ΔH_d as a function of the temperature difference ΔT_d between the actual temperature T associated with the endothermic peak and the onset temperature T_e reflects mostly the thermodynamic properties of the blends. The directional specific interaction model proposed by ten Brinke and Karasz[2] can qualitatively describe both the temperature and concentration dependences of the heat of mixing, giving positive excess heat capacity. However, the modified Flory's equation-of-state theory by Hamada et al.[1] can fit the concentration dependence of the heat of mixing almost quantitatively, but it cannot predict the temperature dependence with a constant interaction parameter X_{12}. It is obvious that the specific interaction issue needs to be emphasized in new theories. More refined experimental approaches for obtaining the temperature dependence of the heat of mixing and the excess heat capacity of polymer blends need to be developed, as it has been shown that the temperature behavior of the heat of mixing and excess heat capacity can be useful in evaluating the applicability of various theories.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation in the form of a Presidential Young Investigator Award and the Materials Research Center at Northwestern University for use of its differential scanning calorimeter.

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(28) Note: (a) According to the theoretical treatment of the DSC curve given by Flynn (*Status of Thermal Analysis*; Meins, O., Ed.; NBS Special Publication 338; U.S. Government Printing Office; Washington, DC, 1970; p 119), the temperature difference between the sample and the holder is related to the steady slope of the curve. Assuming the holder's temperature is the observed temperature, we did some DSC scans to watch the baseline slope change upon increasing heating rate by setting all other scanning parameters the same. The slope of the baseline has no obvious change with the heating rate from 10 to 80 °C/min. In other words, the difference between the sample temperature and the observed temperature does not change significantly at higher heating rates. (b) According to Lohe (*Kolloid Z. Z. Polym.* **1965**, *203*, 105), the thermal conductivity κ of PMMA does not change much as a function of temperature up to 250 °C. This is also the situation for PVC up to 100 °C. (Steere, R. C. *J. Appl. Polym. Sci.* **1966**, *10*, 1673).

(29) Note: Reference 17 has not stated whether the T_g's were obtained by "inflection point" or by "half of ΔC_p". However, the difference between our observations and those of ref 17 does not depend on the method of T_g determination as we checked our DSC data using both methods. The changes in T_g width over the composition range were obtained in the same manner in both ref 17 and the present study.

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(39) Note: We know for a 60 wt % PMMA blend that the heat of demixing peak ends at about 220 °C (see Figure 4). After a 40 °C/min heating to 220 °C, the sample was kept at 220 °C for 1 min followed by a rapid quenching to −10 °C. Two T_g's (86 and 102 °C) appear on the second scan at 10 °C/min. From the T_g composition figure (Figure 1), these two T_g's correspond to the compositions of 17 wt % PMMA and 86 wt % PMMA, respectively. 50 wt % PMMA and 75 wt % PMMA blends have also been examined with the same approach, showing the same results. A 35 wt % PMMA blend was also set at 220 °C for 1 and 5 min, respectively, followed by the same quenching. Only one T_g can be observed on the second scan, which is consistent with the phase diagram showing that 220 °C is within the binodal region of the 35 wt % PMMA blend. A 75 wt % PMMA blend was again kept at 240 °C for 1 min followed by quick quenching and a second scan. The two T_g's observed (82 and 103 °C) correspond to the compositions of about 7 wt % PMMA and 90 wt % PMMA, respectively. Several conclusions can be drawn from these experiments: (A) Within a 1–2 min time frame, 80–90% phase separation (based on phase compositions) of this blend system can be achieved. However, the two T_g's do not change further after the sample is kept at 220 °C for another 1.5 h. (B) At about 220 °C, the two phases obtained from the cloud point curve of this PMMA/PVC blend may already contain largely either pure component. This gives lower temperature error bars on the cloud points, which could compensate for some of the uncertainty related with the extrapolations. (C) From the study of the 35 wt % PMMA blend, the estimated spinodal curve seems reasonable. Unfortunately, the 35 wt % PMMA blend is the only one we can use to check on the spinodal temperatures. The metastable region of the 35 wt % PMMA blend is at high enough temperature so that the corresponding compositions of the two phases obtained at such temperature would be far apart. Moreover, if the 35 wt % PMMA has phase separated, the difference in volume fractions of the rich and lean phases would not be too large. These are the two conditions that make the two T_g's observable.

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Registry No. PMMA, 9011-14-7; PVC, 9002-86-2.