Mixing Enthalpy and Phase Behavior of PEO/PVAc Blends

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ABSTRACT: Phase behaviors and heats of mixing of the miscible blends of poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc) with different molecular weights were investigated by DSC. A method proposed by Natasohn and Ebert et al. was adopted to estimate the binodal temperatures and the enthalpies of mixing from onset temperatures and values of areas of a series of endothermic peaks (corresponding to heats of demixing), respectively, in their heating scanning thermograms obtained with different heating rates. Phase diagrams and heats of mixing of this blending system were also predicted by using Sanchez−Lacombe lattice fluid theory. A very good agreement was obtained for both phase behaviors and heats of mixing obtained with two different methods.

Introduction

Sanchez[1] had predicted that poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc) blends should be compatible, which is due to the fact that the solubility parameters of the two components are quite close, with a difference of only 0.02 cal$^{1/2}$/cm$^{3/2}$. PEO can act as a proton acceptor and form miscible blends with many proton-donating polymers,[2] since there is a partial negative charge on the oxygen atom.[3] On the other hand there is a partial positive charge on the carbonyl carbon atom of PVAc. Therefore, one can expect that PVAc may interact favorably with PEO, and they form a miscible couple.

In the last 2 decades, research groups have studied the miscibility of PEO/PVAc blends[4−10] from various aspects including morphology, dynamic mechanical properties, rheological properties, thermal behavior, crystallization, and viscosity in dilute solution. Kalfoglou et al.[4,5] investigated the morphology, thermal properties and dynamic mechanical properties of PEO/PVAc blends. It was indicated that this couple is probably miscible in the melting state over the complete composition range or in the solid state with PVAc content $\geq$40 wt %. Furthermore, Munoz et al.[6] obtained a negative interaction parameter (χ_{12}) from decreasing of the melting point of PEO in PEO/PVAc blends. This also suggested that PEO can form thermodynamically a stable single-phase system with PVAc.

Martuscelli and Silvestre et al.[7−9] examined the morphology, crystallization, and thermal behavior of the systems PEO/PVAc by SAXS, optical microscopy, and DSC. The addition of PVAc to PEO caused depression of the spherulite growth rate (G) and the overall kinetic rate constant (K_n). During the isothermal crystallization process, PVAc was incorporated into the interlamellar regions of PEO spherulites. At a given crystallization temperature, the thickness of amorphous and interphase layers increased with increasing the content of PVAc, but the average lamella thickness was independent of the blending composition. Therefore, it could be concluded that amorphous PVAc existed in the interlamellar of PEO spherulites. On the other hand, the only value of the glass transition temperature of PEO/PVAc blends indicated that the amorphous phases of two components are miscible. The measured glass transition temperatures of blends with different compositions were always less than the value of linear addition. This behavior was very likely due to the specific interaction of the two components in the amorphous phase.

In our previous paper,[10] the miscibility of PEO/PVAc blends was verified by means of the dilute solution viscometry method. It was found that the miscible extent of the systems PEO/PVAc increased with increasing the content of PEO together with decreasing the molecular weights of components. However, the above data do not allow one to draw quantitative conclusion on miscibility of PEO with PVAc. For polymer−polymer blends, the total free energy can be expressed as $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$. A polymer mixture is miscible only if the value of ΔG_{mix} is negative and the second derivative of ΔG_{mix} with respect to composition is positive. Since the combinatorial entropy terms are very small for high molecular weight polymers, the enthalpic contribution plays a dominant role in the sign of ΔG_{mix}. In other words, a mixture should be miscible if ΔH_{mix} approaches zero or is negative. Weak dispersive forces or van der Waals interactions between repeat units of two polymers usually lead to zero or positive value of heat of mixing. If specific interactions such as hydrogen bonds or dipole−dipole interactions are established, a negative enthalpy of mixing (or heat of mixing) can be obtained. Therefore, the evaluation of heat of mixing is of prime relevance to judge polymer−polymer miscibility.

To measure the enthalpy of mixing, ΔH_{mix}, directly is impossible.[11] This is due to the fact that the diffusion between components in solid state is so slow that the value of ΔH_{mix} cannot be measured by any sensitive calorimetry. Mixing of polymers in their melting state needs to import a large quantity of energy from the environment. At the same time, shear and friction happening during the mixing process would produce much energy. Therefore, it is impossible to measure ΔH_{mix} in the melting state. Several indirect methods were used to measure the heat of mixing.[12−16] One of

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them is to measure heats of solutions of components and their blends in a common solvent and to evaluate ΔH_{mix} by using a thermodynamic cycle based on Hess's law,[15,16] shown as follows:

$$\begin{array}{ccccc} \text{polymer 1} & + & \text{polymer 2} & \xrightarrow{\Delta H_{\mathrm{mix}}} & \text{mixture (1+2)} \\ + & & + & & + \\ \text{solvent} & & \text{solvent} & & \text{solvent} \\ \downarrow \Delta H_1 & & \downarrow \Delta H_2 & & \downarrow \Delta H_4 \\ \text{solution 1} & + & \text{solution 2} & \xrightarrow{\Delta H_3} & \text{solution (1+2)} \end{array}$$

Another indirect method to measure ΔH_{mix}[17−20] was proposed by Natansohn[17] and Ebert et al.[18] by using DSC. A series of endothermic (or exothermic) peaks and corresponding onset temperatures were obtained by scanning a blend sample with different heating rates in the range of the phase-separation temperature. Ebert et al.[18] argued that for miscible blend the endothermic peak of demixing should roughly corresponds to the total heat of demixing. Usually, values of heat of demixing and onset temperatures increase with heating rate and reach a plateau value when the heating rate is high enough. This is a common behavior for polymer blends. By extrapolating the onset temperature to zero heating rate, the "cloud point" temperature or binodal temperature could be estimated. In a similar manner, by extrapolating heats of demixing toward large heating rates a nearly constant value of heat of demixing was obtained. This value was taken as the heat of mixing with opposite sign.

In our previous communication,[21] heats of mixing of PEO/PVAc blends were determined by measuring their heats of solution and using Hess's thermodynamics. Negative values of mixing enthalpy were measured. A simplified Patterson theory[22] was adopted to evaluate the polymer−polymer interaction parameter. It indicated the presence of weak specific interactions between different repeat units.

In this paper, the enthalpy of mixing as a function of molecular weight of PVAc and composition and the phase diagrams in the systems PEO/PVAc were obtained by using DSC measurements. Sanchez−Lacombe lattice fluid (LF) theory[23,24] was applied to calculate spinodals and binodals and the enthalpy of mixing of this system. The main purpose of this work is to compare the values of enthalpy of mixing given by means of different indirect measuring methods with those calculated by LF theory and to find the preferred method to evaluate the enthalpy of mixing and phase behavior of miscible polymer blends.

Theoretical Background. In the lattice fluid theory, as formulated by Sanchez and Lacombe,[23,24] the Gibbs energy of mixing for polymer−polymer blends is related to the Gibbs energy per mer (indicated by the double bar) of the mixture (index m) and that of the pure components (index 1 or 2) by

$$\Delta G_{\mathrm{M}} = \mathrm{rN}[\bar{\bar{G}}_{\mathrm{M}} - (\phi_1\bar{\bar{G}}_1 + \phi_2\bar{\bar{G}}_2)] \tag{1}$$

where rN is the total number of lattice sites occupied in the mixture and $rN = r^0{}_1N_1 + r^0{}_2N_2 = r_1N_1 + r_2N_2$.

The Gibbs energy per mer of pure component reads

$$\bar{\bar{G}}_i = \epsilon^*{}_{ii}\left\{-\tilde{\rho}_i + \tilde{P}_i\tilde{v}_i + \tilde{T}_i\left[(\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i) + \frac{1}{r^0{}_i}\ln\left(\frac{\tilde{\rho}_i}{\omega^0{}_i}\right)\right]\right\} \quad i = 1 \text{ or } 2 \tag{2}$$

and that of the mixture is

$$\bar{\bar{G}}_{\mathrm{M}} = \epsilon^*\left\{-\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} + \frac{\phi_1}{r_1}\ln\left(\frac{\phi_1}{\omega_1}\right) + \frac{\phi_2}{r_2}\ln\left(\frac{\phi_2}{\omega_2}\right)\right]\right\} \tag{3}$$

where ϕ_i stands for the close-packed volume fraction of component i. $\tilde{\rho}_i$, $\tilde{P}_i$, $\tilde{v}_i$, $\tilde{T}_i$ and $\tilde{\rho}$, $\tilde{P}$, $\tilde{v}$, $\tilde{T}$ are the reduced parameters of density, pressure, volume, and temperature of the pure components and those of the mixtures, respectively. They are defined by their actual pressure (P), volume (V), and temperature (T) and scaling parameters (denoted with asterisks) as follows:

$$\tilde{P}_i = P/P^*{}_i \quad \tilde{P} = P/P^* \tag{4}$$

$$\tilde{T}_i = T/T^*{}_i \quad \tilde{T} = T/T^* \tag{5}$$

$$\tilde{v}_i = V_i/V^*{}_i \quad \tilde{v} = V/V^* \tag{6}$$

$$\tilde{\rho}_i = 1/\tilde{v}_i \quad \tilde{\rho} = 1/\tilde{v} \tag{7}$$

$$V^*{}_i = r^0{}_i\mathrm{N}_i v^*{}_i \quad V^* = (r_1\mathrm{N}_1 + r_2\mathrm{N}_2)v^* \tag{8}$$

The close-packed volume of a mer, v^*, and the average number of mers for a molecule, r, in the mixture are given by

$$1/v^* = \phi_1/v^*{}_1 + \phi_2/v^*{}_2 \tag{9}$$

$$1/\mathrm{r} = \phi_1/r_1 + \phi_2/r_2 \tag{10}$$

Because the close-packed volume of one chain molecule is conserved in the mixture and in the pure state,[24] the size of one lattice site in the mixture, v^*, and that in the pure component i, $v^*{}_i$, must fulfill the following condition:

$$r_i v^* = r^0{}_i v^*{}_i \tag{11}$$

where $r^0{}_i$ and r_i are the number of lattice sites occupied by a molecule of component i in the pure fluid and that in the fluid mixture, respectively. For the pure component, $r^0{}_i$ can be calculated from the following relationship:

$$r^0{}_i = \mathrm{M}_i P^*{}_i/kT^*{}_i\,\rho^*{}_i \tag{12}$$

Here M_i is the molecular weight of component i, $\rho^*{}_i$, the close-packed density of component i, and k, the Boltzmann constant.

In the close-packed state, ω_i and $\omega^0{}_i$ are number of configurations available to a r_i-mer and $r^0{}_i$-mer[23,25] and

$$\omega_i = \delta_i \mathrm{r}_i/\sigma_i \mathrm{e}^{r_i - 1} \tag{13}$$

$$\omega^0{}_i = \delta^0{}_i\, r^0{}_i/\sigma^0{}_i \mathrm{e}^{r^0{}_i - 1} \tag{14}$$

where δ_i, $\delta^0{}_i$ and σ_i, $\sigma^0{}_i$ are the flexibility parameters and the symmetry numbers of an r_i-mer and of an r^0_i-mer, respectively. In the present case, $\sigma_i = \sigma_i^0 = 1$ and

$$\delta_i = z(z-1)^{r_i-2} \tag{15}$$

$$\delta^0_i = z(z-1)^{r_i^0-2} \tag{16}$$

where z is the coordination number of the lattice ($z = 12$).

Scaling parameters can also be expressed in terms of the interaction energies ϵ^*_{ii} for pure component and ϵ^* for mixtures

$$P^*_i = \epsilon^*_{ii}/v^*_i \quad P^* = \epsilon^*/v^* \tag{17}$$

$$T^*_i = \epsilon^*_{ii}/k \quad T^* = \epsilon^*/k \tag{18}$$

where P^*_i, T^*_i, and ρ^*_i can be obtained by fitting the following equation of state to PVT data for pure components:

$$\tilde\rho_i^2 + \tilde P_i + \tilde T_i\left[\ln(1-\tilde\rho_i) + \left(1 - \frac{1}{r^0_i}\right)\tilde\rho_i\right] = 0 \tag{19a}$$

The equation of state for the mixtures is formally identical with eq 19a for pure component and can be written as

$$\tilde\rho^2 + \tilde P + \tilde T\left[\ln(1-\tilde\rho) + \left(1 - \frac{1}{r}\right)\tilde\rho\right] = 0 \tag{19b}$$

In a binary mixture there are three possible contacts with the nonzero interaction energy: 1−1, 2−2, and 1−2. Therefore, ϵ^* consists of the three interaction energies according to the relationship

$$\epsilon^* = \phi_1^2\,\epsilon^*_{11} + 2\phi_1\phi_2\epsilon^*_{12} + \phi_2^2\,\epsilon^*_{22} \tag{20}$$

where ϵ^*_{12} is the interaction energy of a mer of component 1 (or 2) when it is surrounded by z-mers component 2 (or 1). The spinodals and binodals are calculated by a method[26,27] not requiring the derivatives of the Gibbs energy. The only adjustable parameter is ϵ^*_{12} in our calculation. As we know, the Gibbs energy of mixing can be split into its enthalpic part and entropic part. Then the enthalpy of mixing per mer reads in the LF theory:

$$\Delta\bar{\bar{H}} = \bar{\bar{H}}_{\mathrm{M}} - (\phi_1\bar{\bar{H}}_1 + \phi_2\bar{\bar{H}}_2) \tag{21}$$

$$\Delta\bar{H}_{\mathrm{M}} = \frac{\Delta H^{\mathrm{M}}}{rN} = \epsilon^*(-\rho + \tilde P\tilde v) - [\phi_1\epsilon^*_{11}(-\tilde\rho_1 + \tilde P_1\tilde v_1) + \phi_2\epsilon^*_{22}(-\tilde\rho_2 + \tilde P_2\tilde v_2)] \tag{22}$$

Experimental Section

Samples. PEO was purchased from Fluka AG without further purification. PVAc was obtained from Aldrich-Chemie. To have PVAc samples with narrow molecular weight distribution, a step precipitation method was used to fractionate the commercial PVAc. Acetone and petroleum ether were used as a solvent and a precipitating agent, respectively. The molecular weight of PEO and PVAc samples were characterized by GPC and listed in Table 1.

Preparation of Blends. PEO/PVAc blends with different compositions of PEO/PVAc (80/20, 70/30, 60/40, 50/50, 40/60, and 20/80 by weight) were prepared by the solution casting method. Chloroform was used as the solvent. After over 24 h of stirring, the solutions were cast on a Teflon plate. To remove the residual solvent in blends, the casting films were vacuum desiccated at 80 °C for 24 h. Since PEO easily absorbs water, the samples prepared were kept in a desiccator.

Table 1. Average Molecular Weight of PEO and PVAc Measured by GPC

	M_n (×10^{-4})	M_w (×10^{-4})	M_w/M_n
PEO46	4.00	4.62	1.15
PVAc17	0.89	1.68	1.89
PVAc50	3.81	4.95	1.30
PVAc126	8.47	12.6	1.50

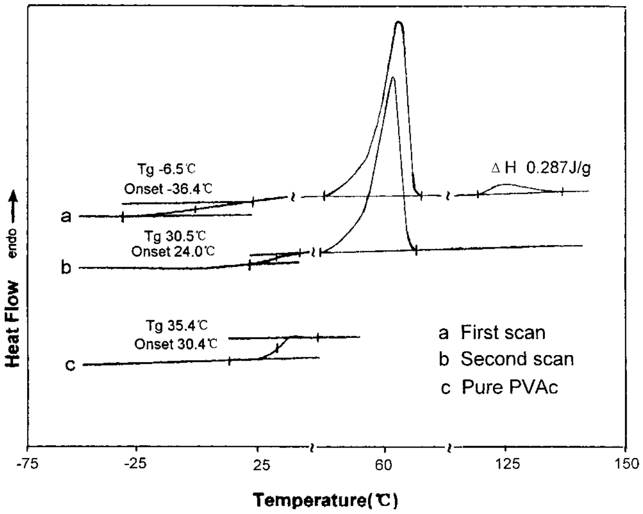

Figure 1. DSC curves for a 60/40 (by weight) PEO46/PVAc50 blend. Curve a: first scan for PEO46/PVAc50. Curve b: second scan for PEO46/PVAc50. Curve c: scan for pure PVAc50.

Measurement of Cloud Points and Heats of Mixing. Cloud points and heats of demixing for PEO/PVAc blends were determined by using a Perkin-Elmer DSC7 scanning calorimeter. The weight of samples was about 8−9 mg for any analysis. All samples were heated at a rate of 20 °C/min from room temperature to 80 °C and held there for 15 min, followed by cooling at a rate of 1.3 °C/min to room temperature. This process was made to eliminate the influence of heating history on the measurement of heat of demixing. Afterward, these samples were heated again from room temperature to 200 °C at different heating rates ranging from 20 to 60 °C/min. A series of endothermic peaks which correspond to each heating rate were given by thermograms. The extrapolation of a curve of the onset temperature of each endothermic peak vs the corresponding heating rate to zero heating rate yielded the "cloud point" temperature of the blend. In a similar manner, by extrapolation of the curve of heat of demixing vs corresponding heating rate toward increasing heating rates, a nearly constant value was obtained. This value was taken as the heat of mixing of this blend with opposite sign.

Results and Discussion

Figure 1 shows thermograms of the blend with PEO46/PVAc50 = 60/40 (curves a and b) and of the pure PVAc50 (curve c). In the first scan, a single glass transition temperature (T_g = −6.5 °C), which is between T_g of pure PEO (−73 °C[5]) and T_g of pure PVAc50 (35.4 °C), and a phase-separation temperature occurring at 112.3 °C could be found. According to the explanation[17−19] the endothermic peak around 112.3 °C corresponds to the heat of demixing of this blend. In the second scan, the glass transition temperature of the blend moved to 30.5 °C, which is close to T_g of pure PVAc50 (curve c). It meant that this T_g was almost the contribution of pure PVAc50. At the same time, the endothermic peak disappeared. Therefore, we can conclude that the phase

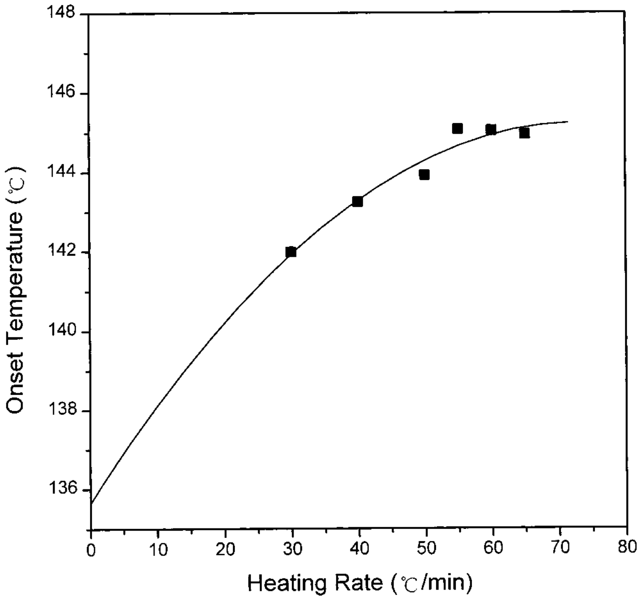

Figure 2. Dependence of the onset temperature on the heating rate for the PEO46/PVAc126 blend (80/20, by weight). The solid line is the extrapolation of the onset temperature to zero heating rate.

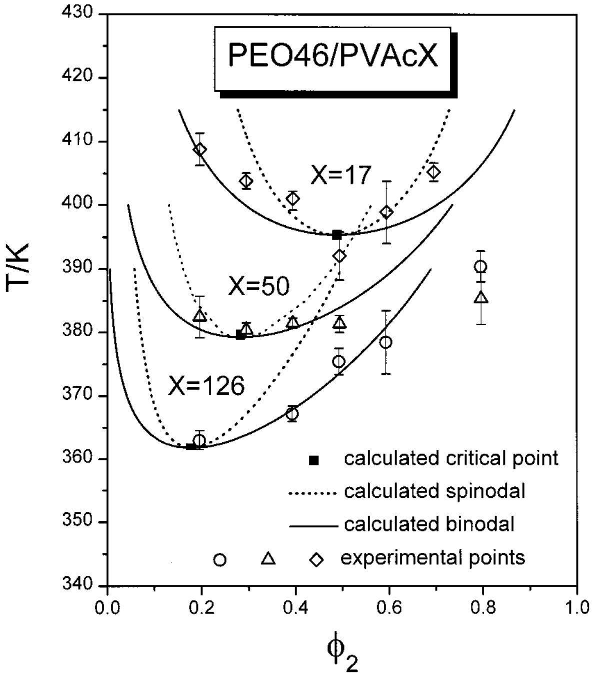

Figure 3. Comparison between the experimental cloud points and calculated binodal, where ϵ^*_{12} = 619.505 for PEO46/PVAc126, ϵ^*_{12} = 619.536 for PEO46/PVAc50, and ϵ^*_{12} = 619.596 for PEO46 /PVAc17.

Table 2. Scaling Parameters of PEO and PVAc

	P^* (atm)	ρ^* (g/cm^3)	T^* (K)
PEO	6245.00	1.223	589.30
PVAc	5021.25	1.253	649.01

separation has occurred in the amorphous part of the blend after the first scan. According to the literature,[5] PEO is very easy to crystallize and the content of the amorphous phase is very low; thus, it is very difficult to measure the T_g of PEO in general. We did not get the experimental value of T_g for the pure PEO46 by using DSC. So it was not shown in Figure 1.

As shown in Figure 1, the system PEO46/PVAc50 (60/40) is miscible below the starting phase-separation temperature, 112.3 °C. Therefore, it can be suggested that PEO/PVAc blends should exhibit what are known as lower critical solution temperatures (LCST). A similar conclusion was obtained in our previous paper.[21] We found out that the interaction parameter χ_{12}/V_1^* of this blending system increased with temperature.[21] It can be tentatively explained as the miscible extent of PEO/PVAc blends decreasing with increasing temperature.

Figure 2 shows the typical relationship of heating rates vs the onset temperature (phase-separation temperatures) of the blend PEO46/PVAc17 (80/20). The phase-separation temperature increases with the heating rate in the beginning and reaches nearly a constant value when the heating rate is higher than 50 °C/min. By extrapolation of the curve of the phase-separation temperatures vs heating rates to zero heating rate, the equilibrium phase-separation temperature (binodal) or "cloud point" temperature could be obtained for the corresponding blend. The equilibrium phase-separation temperatures of blends of PEO46 and PVAc with different molecular weight in different weight fractions are shown in Figure 3.

For the binary polymer mixture, de Gennes[28b] gave the dependence of the critical Flory–Huggins interaction parameter on molecular weight of components as

$$\chi_c \propto N_1^{-1/2} N_2^{-1/2} \tag{23a}$$

where χ_c is the critical value of the Flory–Huggins interaction parameter and N_1 and N_2 are the numbers of repeat units of components 1 and 2, respectively. If N_2 is changeable while N_1 is fixed, we can rewrite eq 23a as

$$\chi_c \propto N_2^{-1/2} \tag{23b}$$

Because both χ_c in Flory–Huggins theory and ϵ^*_{12} in LF theory represent the interaction of asymmetry segments between components, we can give a similar equation for ϵ^*_{12}[29]

$$\epsilon^*_{12} = A + BM_2^{-1/2} \tag{24}$$

where M_2 is the molecular weight of component 2 (PVAc).

For the blends of PEO46 and PVAc with different molecular weight, we obtained A = 619.45 and B = 18.72 by fitting the experimental "cloud points". According to eq 24, the interaction energy parameter ϵ^*_{12} can be calculated as ϵ^*_{12} = 619.505 for PEO46 /PVAc126, ϵ^*_{12} = 619.536 for PEO46 /PVAc50, and ϵ^*_{12} = 619.596 for PEO46 /PVAc17. According to the above ϵ^*_{12}, the spinodals and binodals can be calculated by means of a new method not requiring the derivatives of free energy developed by Horst and Wolf.[26,27] The equation-of-state parameters, P^*, T^*, and ρ^*, used in our work are given in Table 2. They have been used to calculate phase diagrams (spinodal and binodal) of polymer mixtures on the basis of the Gibbs free energy of mixing, ΔG. No derivatives of ΔG with respect to the composition variables are required. The calculation procedure of the spinodal line in binary systems is demonstrated below where ΔG is written as a function of the volume fraction. For the calculation the volume fraction is divided into *n* points. For each of these points it is checked whether the system is unstable or not. If the overall value of ΔG for the demixed system ($\Delta G^{\text{o.a.}}$) is less than ΔG of the homogeneous system, the overall composition lies within the unstable area, because here the beginning of the demixing process leads to a decrease in ΔG (no energy barrier). Otherwise the overall composition lies in stable or the metastable range. Checking all points yields the entire unstable area, and thus the spinodal line, as its boundary. For the overall composition, set of volume fractions is found for which $\Delta G^{\text{o.a.}}$ has its minimum value. Connecting these volume fractions yields the binodal line.

It is seen that there is only one adjustable parameter (ϵ^*_{12}) in this calculation on the basis of LF theory, and phase diagrams of the systems PEO46 and PVAc with different molecular weights can be obtained. Furthermore, the heats of mixing of this polymer pair can also be calculated by using the interaction energy parameter ϵ^*_{12}, which has been determined by eq 24. The phase diagrams of the systems PEO46/PVAc*X* ($X = 17$, 50, and 126) are shown in Figure 3, where ϕ_2 is the volume fraction of PVAc. The dotted and solid lines in Figure 3 represent the spinodal curves and binodal curves calculated by LF theory, respectively. The symbols are the "cloud points" measured by DSC. Obviously, a good fit between the binodals and the measured cloud points is obtained and the phase diagrams with LCSTs are seen for the systems PEO/PVAc as discussed in the above. Furthermore, the critical temperatures (T_c) and compositions (ϕ_{2c}) decrease with increasing of PVAc molecular weights (the detailed data are given as follows: $T_c = 395.35$ and $\phi_{2c} = 0.489$ for PEO46/PVAc17, $T_c = 379.63$ and $\phi_{2c} = 0.283$ for PEO46/PVAc50, and $T_c = 361.74$ and $\phi_{2c} = 0.178$ for PEO46/PVAc126). The conclusion is identical with that of Nishi et al.[30] by experimental results and of An et al.[31] by calculated data. To summary it is concluded that the miscibility and miscible extent decrease with increasing molecular weight of PVAc, and the critical points shift to high PEO concentration with an increase of the molecular weight of PVAc.

Both positive and negative heats of demixing detected by DSC have been reported for different blends.[17-20] For miscible polymer blends, the heat of demixing should be positive (endothermic) and the heat of mixing negative (exothermic).

Heats of demixing of PEO46/PVAc17 blends with PEO/PVAc = 80/20 (in weight) obtained by DSC with different heating rates are shown in Figure 4. It is observed that the values of heats of demixing are positive and increase with increasing of heating rate in the beginning and reach to a nearly constant at high heating rates (≥40 °C/min). To the heat of mixing defined by Flory,[32] it is the difference between the total interaction energy of the mixture and that of the pure liquid components. Torkelson[19] and Natansohn[17] argued that at the very high heating rate, the miscible blend was forced to transform from a single-phase system into a two-phase system. The thermal behavior (endothermic or exothermic) is a measure of the two components' interaction. So the area under the peak at the high heating rate should be heat of demixing especially when the two phases mainly contain the pure components.

Figure 5 and Figure 6 show the comparison between the enthalpies of mixing measured by DSC and those calculated by LF theory for the systems PEO 46/PVAc*X* ($X = 50$ and 126). All open points represent the heats of mixing, which are obtained by extrapolating heats of demixing to the high heating rate and all solid points the heats of mixing calculated by LF theory at the measured temperature. During a continuous heating process in the DSC measurement, we cannot obtain heats of mixing of different compositions at a fixed temperature. The phase-separation temperatures of the samples with different compositions were used to calculate the enthalpy of mixing by LF theory. In this calculation, the following temperatures, i.e., 382.4, 380.4, 381.4, and 381.3 K, for which the corresponding composition is $\phi_2 = 0.2$, 0.3, 0.4, and 0.5 for the system PEO46/PVAc50, and 362.96, 367.17, 375.38, 378.43, and 390.40,K, for which the corresponding composition is $\phi_2 = 0.2$, 0.4, 0.5, 0.6, and 0.8 for the system PEO46/PVAc126, were adopted.

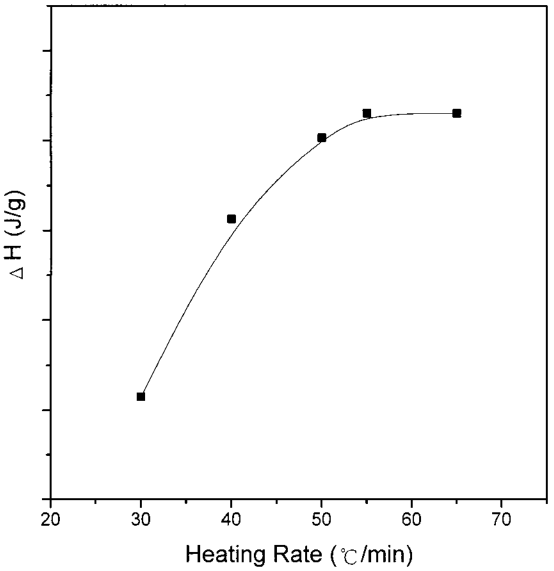

Figure 4. Dependence of the mixing enthalpy on the heating rate for PEO46/PVAc126 blend (80/20). The solid line is the extrapolation of the mixing enthalpy to zero heating rate.

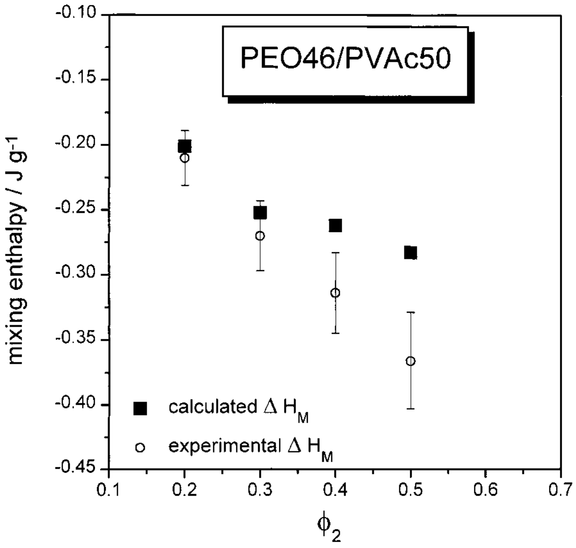

Figure 5. Comparison of mixing enthalpy between experimental points and calculated points for PEO46/PVAc50 with different compositions. The theoretical points are calculated at corresponding temperatures.

As shown in Figures 5 and 6, the enthalpies of mixing obtained from DSC experiments and those calculated

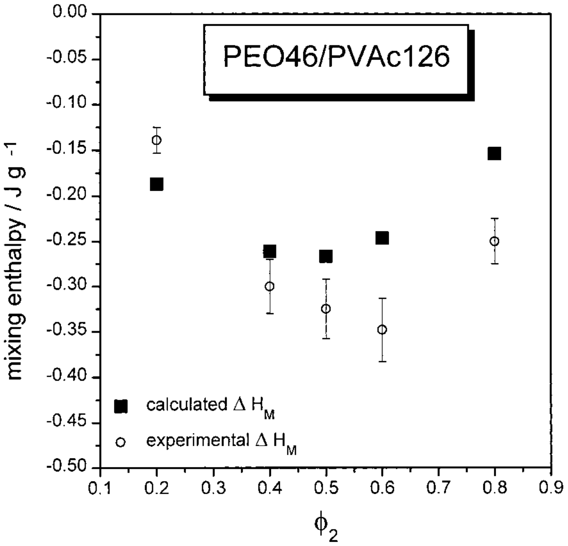

Figure 6. Comparison of mixing enthalpy between experimental points and calculated points for PEO46/PVAc126 with different compositions. The theoretical points are calculated at corresponding temperatures.

by LF theory are totally negative in the investigated ranges of molecular weights of components, of compositions, and of temperatures. It gives the fact that the mixing of PEO and PVAc in the amorphous phase is exothermic. From Figures 5 and 6, it can be observed that the enthalpies of mixing determined by DSC is close to the calculated values by LF theory. It seems that the enthalpy of mixing measured by DSC could be accepted as the real enthalpy of mixing for the blends in a sense.

Conclusion

(1) According to the relationship between the Flory−Huggins parameter and the molecular weight of components given by de Gennes,[28a] eq 24 is obtained and proven to be true. It is shown in phase diagrams and Figures 5 and 6 how well the calculated curves and points agree with experimental results. We can assume that the thermal behavior of PEO46 mixed with PVAc of any molecular weight can be predicted by using eq 24 and LF theory.

(2) Phase diagrams of PEO/PVAc blends with different molecular weights of PVAc are obtained for the first time. LCST behavior is investigated in accordance with the prediction.[1,17] With increasing molecular weight of PVAc, the spinodal line and binodal line have been pushed down to lower temperature and the critical composition has been shifted to higher PEO concentration.

(3) Negative values of mixing enthalpy demonstrate that this polymer pair is completely miscible. The miscibility and the content of miscibility increases with decreasing the molecular weight of PVAc. The influence of composition on heat of mixing is also investigated, although the value of mixing enthalpy is relatively small which is attributed to the weak interactions between polymer units.

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