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Miscible Polymer Mixture Driven by Segmental Microconformations

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There is presently an intense interest in polymer blends because of the potential opportunities in obtaining a synergy in properties that would essentially be unattainable with the unblended polymer components.[1–7] In a majority of polymer blends, the components are immiscible due, in essence, to a vanishingly small entropy of mixing of the macromolecules. As a result, the components easily phase separate with correspondingly weak interfacial characteristics. Poor mechanical properties result. A general approach in overcoming this limitation is to "add" polymeric compatibilizers, typically block or graft copolymers, which are able to "bridge" the interfacial region.[7–9] These materials behave as an emulsifier, i.e., polymeric surfactant, because of the mutual solubility of sections of the compatibilizer into the respective components of the blend. Therefore, it is of fundamental importance to study the miscibility phenomenon as well as the coexistence curve in polymers because of the latter considerations and also because polymer blends are of scientific and technical importance in their own right. As an example, polymer blends are ideal systems for investigation of phase separation kinetics because of their low mobility and mean-field behavior.[10–13] The study of the demixing process is also important in the design and control of the structure and properties of multicomponent materials.[1–7] In any case, the determination of the coexistence curve is the starting point for these studies. In polymer blends, the configurational entropy is vanishingly small and the free energy of mixing can be expressed as:

$$\Delta G_{\mathrm{m}} \approx \Delta H_{\mathrm{m}} - T\Delta S^{(\mathrm{exc})} \tag{1}$$

where ΔH_{m} and $\Delta S^{(\mathrm{exc})}$ are the enthalpy and the excess entropy of mixing, respectively. Within the Flory–Huggins mean field, this leads to the well-known empirical formulation of the interaction parameter[14]

$$\chi = A + B/T \tag{2}$$

In *weakly interacting* blends, the excess entropy $\Delta S^{(\mathrm{exc})}$ can overcome a slight positive enthalpy ΔH_{m} if there is a favorable packing arrangement of the segments. A salient example of this phenomenon is the blend of polystyrene and poly(methyl acrylate)[15] which is a known immiscible blend over the entire composition range, and no morphological mixing was observed under normal pressure up to their decomposition temperature. However, replacing the methyl group by a bulkier group such as cyclohexyl (i.e., poly(cyclohexyl acrylate) (PCHA) results in miscibility with polystyrene over the entire composition range[16] and up to ~470 K. In both cases, the attractive intersegmental interaction is dominated by a weak short-range intermolecular potential (dipole-induced dipole) of the form $\Delta U_{ji} \propto -\alpha\mu^2/kTr_{ij}^6$, where $\alpha = 100$ Å^3 is the polarizability of the benzene ring,[17] $\mu = 1.7$ D is the dipole moment of the ester group,[18] and r_{ij} is the intermolecular distance between segment i and j. Our preliminary results,[19] based on rotational isomeric states (RIS)[20] and static simulation of the amorphous solid ("amorphous cell" method[21]), show that the size of the cyclohexyl side-chain group severely restricts the segment to a fixed rotational state. This restriction of the segment allows for a favorable packing arrangement with the PS segment. The detailed calculations will be reported elsewhere. In this paper, we report on the phase behavior of polystyrene with poly(cyclohexyl acrylate) and show that the mixture behaves ideally (i.e., obeys volume additivity). Differential scanning calorimetry was used to determine the glass transition temperature, phase behavior at 523 K, and phase remixing at a lower temperature, 423 K. The coexistence curves of the blends were monitored by small-angle light scattering (SALS) equipped with a programmable hot stage. The results were analyzed within the framework of the Flory–Huggins lattice model and the Gordon–Taylor prediction.

The poly(cyclohexyl acrylate) used in this study was a middle cut fraction (toluene/methanol, solvent/nonsolvent) of a polymer obtained by radical polymerization of cyclohexyl acrylate. The polymerization was conducted, under high-vacuum conditions, in benzene solution at 60 °C using 2,2′-azobis(isobutyronitrile) as the initiator. The molecular weight was determined by size-exclusion chromatography (Waters Model 510 pump and 401 differential refractometer) in THF (flow rate: 1 mL/min) at 30 °C. The unit was calibrated with narrow molecular weight polystyrene standards. The weight-average molecular weight was $M_{\mathrm{w}} = 108\,000$ g/mol with a polydispersity index $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.3$. The polystyrene (Polysciences, Inc.) had a number-average molecular weight of 300 000 g/mol and a polydispersity index of 1.1. All blends were prepared by dissolution in chloroform followed by precipitation into a nonsolvent (methanol). The blends were dried in a vacuum oven at 373 K to remove any residual solvent. These blends were directly used for DSC studies. For small-angle light scattering measurements the blends were dissolved in tetrahydrofuran, cast onto a glass plate, dried at low temperature, and annealed at 373 K to ensure that all residual solvent was removed.

The thermal treatments (annealing) were conducted on a Perkin-Elmer DSC-2, and the results of the calorimetric measurements were obtained from a Seiko DSC Model 220C at a heating rate of 10 °C/min under a nitrogen blanket. Indium and tin were used as calibration standards. The glass transition temperature, T_{g}, was determined as the temperature of the midpoint of the heat capacity change.

SALS experiments were performed using a two-dimensional 14-bit charge-couple device detector (OMAIII from EG&G Princeton Applied Research). The incident light was a He–Ne laser ($\lambda = 6328$ Å). The scattered light was made parallel with two large aperture lenses and subsequently collected on CCD arrays. The geometry of the CCD was selected so that the entire scattering pattern could be observed. This mode of detection permits the measurement of the scattered light at different angles simultaneously. Data processing was performed with an on-line computer. The sample stage consisted of two independently controlled heating blocks. The temperature of the main block is controlled by a proportional–integral–differential controller to ensure a set point within 0.1 °C stability. The cloud-point curve in Figure 1 was con-

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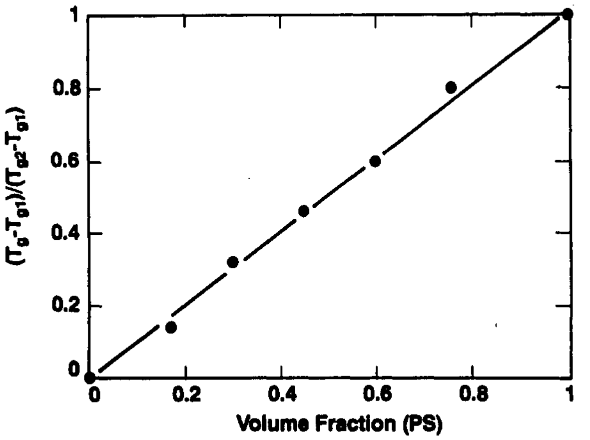

Figure 1. Reduced glass transition temperature of PS–PCHA blends as a function of PS content.

Table I. Glass Transition Temperature of PS–PCHA Blends

composition (wt fraction PS)	glass transition temp (K)	composition (wt fraction PS)	glass transition temp (K)
0.0	303	0.65	346
0.20	313	0.80	361
0.35	326	1.0	368
0.50	336		

structed by using data from isothermal experiments. If no apparent increase in light scattering intensity was observed within a 1-h period at a specified temperature, the sample was considered to be below the polymer blend cloud-point temperature. If an increase in scattering intensity was observed, the blend was in the two-phase region. The observed lower-critical solution temperature cloud point is reliable to 1 °C.

Extensive DSC studies found that a PS–PCHA blend possessed a single, narrow, compositionally-dependent glass transition $T_g(\varphi)$ (see Table I). The experimental data are adequately fitted by a simple volume additivity function of the form

$$T_g = \sum_{i=1}^{2} \varphi_i T_{gi} \tag{3}$$

where φ_i and T_{gi} are the volume fraction and glass transition of the component i, respectively. The normalized form of eq 3, $(T_g - T_{g1})/(T_{g2} - T_{g1})$, expressed in terms of volume fraction φ_2, of the second component, yields

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = \varphi_2 \tag{4}$$

The volume fraction φ_2 can be expressed as a function of the weight fraction w_2 as[22]

$$\varphi_2 = \frac{k w_2}{w_1 + k w_2} \tag{5}$$

The constant k is given by $\rho_1 \Delta\alpha_2/\rho_2 \Delta\alpha_1$ where ρ_i are the densities and $\Delta\alpha_i$ the increments at T_{gi} of the expansion coefficients of the blend components. As a first approximation k can be replaced by $\rho_1 T_{g1}/\rho_2 T_{g2}$ (Simha–Boyer rule[23]). T_{g1} (=303 K) and T_{g2} (=368 K) are the glass transition of PCHA and PS, respectively. In the following analysis the ratio ρ_1/ρ_2 is taken to be unity. Figure 1 displays the reduced glass transition temperature $(T_g - T_{g1})/(T_{g2} - T_{g1})$ as a function of the volume fraction φ_2 of the PS component. The linear dependence of T_g on the volume fraction is remarkable. That is, PS–PCHA behaves as an *ideal system*.[24] An interesting feature of the PS–PCHA blend is also its thermodynamically reversible behavior. Small-angle light scattering confirmed that PCHA–PS undergoes phase separation upon annealing above 473 K. Two glass transition temperatures (≈303 and ≈363 K) were also observed. To explore the reversibility of this transition, a blend with a 50/50 weight ratio was investigated on thermal aging experiments.

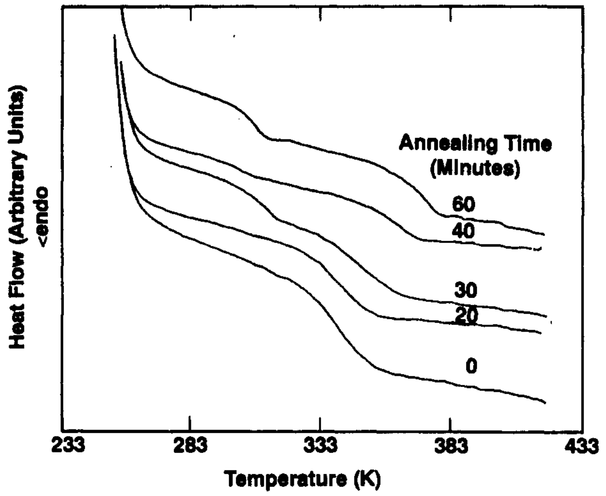

Figure 2. Time dependence of the differential scanning calorimetry thermograms for a 50/50 weight % PS–PCHA blend annealed at 523 K.

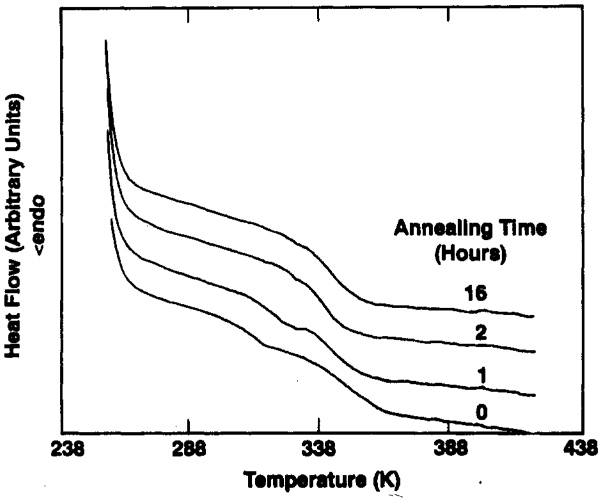

Figure 3. Time dependence of the differential scanning calorimetry thermogram of a 50/50 weight % PS–PCHA blend thermally pretreated at 523 K for 30 min and subsequently annealed at 423 K.

As shown in Figure 2, increasing the annealing time (at 523 K) causes the single T_g of the blend to split into two transitions after approximately 20 min. The two T_g's become more distinct and are further separated at longer annealing times. This procedure produces turbid blends with no visible discoloration, indicative of marked phase separation in which no chemical degradation took place during the annealing period. A further investigation was conducted on blends with a 50/50 weight ratio thermally treated for 30 min at 523 K. These blends were subsequently annealed at 423 K for various times. As shown in Figure 3, these blends prior to the 423 K annealing possessed two distinct T_g's. With increased annealing time, the two transitions became closer and eventually merged into a single, slightly broadened T_g. The blend possessed a single, narrow T_g similar to that of the original sample after approximately 16 h. These observations further confirm that no chemical decomposition has occurred during the above annealing experiments and

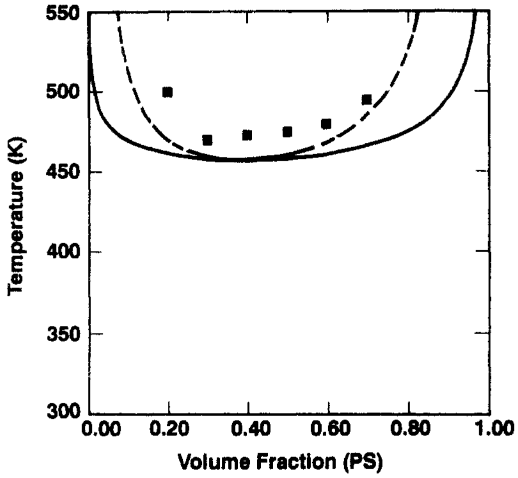

Figure 4. Calculated spinodal (- - -) and cloud-point (—) curves together with the experimental data of a PS–PCHA blend.

thermodynamic reversibility can be achieved. The measured coexistence curve of the PS–PCHA blend is shown in Figure 4. The blend exhibits a lower critical solution temperature (LCST) with $T_c = 463$ K at $\varphi_c = 0.35$. The dashed and dotted curves represent the spinodal and coexistence curves, respectively, for a best fit of the Flory–Huggins free-energy density:

$$\Delta G_m = \frac{RT}{V_r}\left\{\frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} + \chi\phi_1\phi_2\right\} \qquad (6)$$

N_i are the polymerization indices of the two species, and V_r is the reference volume (not specified). In fitting the data to eq 5, the binary interaction parameter χ was assumed to be independent of composition and can be expressed in the following form:

$$\chi = d_0 + d_1/T \qquad (7)$$

where d_0 and d_1 are fitting parameters. The best fit of the data to eq 5 yields $d_0 = 0.02$ and $d_1 = -6.75$. The χ parameter of the present system has a rather small temperature dependence when compared, for example, to the d-PS–PVME blends[25] which have a marked temperature dependence $\chi = 0.078\text{-}30/T$ (per lattice volume). This suggests that miscibility in the PCHA–PS mixture is dominated by an excess entropy/packing contribution.

In summary, it has been shown that polystyrene and poly(cyclohexyl acrylate) form a partially miscible blend with a reversible lower critical solution temperature. Our preliminary results show that the bulky cyclohexyl group severely limits the segment to finite rotational states and, as a result, enhances the weak dipole-induced dipole interaction. This "*microconformation*" of the segment is believed to be the primary driving force for miscibility in this system.

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