Quasi-Equilibrium in the Mixture of Polystyrene and Poly(methylphenylsiloxane)

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ABSTRACT: For liquid mixture of polystyrene (PS) and poly(methylphenylsiloxane), we determined cloud points, glass transition temperatures of the homogeneous blends, and the compositions of phases separated at various temperatures in the two-phase region. In this system, phase separation and glass transition occur in ranges of comparable temperature. For this characteristic, one of the separated phases, which was rich in PS, did not reach equilibrium compositions but approached quasi-equilibrium compositions. A theory has been developed to examine the effect of the settling-down of one phase to a quasi-equilibrium composition on the composition of the conjugate phase.
    KEY WORDS   Polymer Blend / Quasi-Equilibrium /Phase Separation / Cloud Point / Glass Transition /

   Usually, a binary polymer mixture in the partially compatible region exhibits two glass transition temperatures T_g corresponding to the compositions of the separated phases. Thus, T_g measurement can be utilized to judge the compatibility of polymer blends and to estimate the composition of partially compatible polymer blends.[1-4] In applying this method to the determination of the equilibrium composition of separated phases, however, it is necessary that we are concerned with the phase separation at the temperature far above the T_g vs. composition curve for the system studied. Otherwise, observation cannot be made of equilibrium phase separation within experimentally accessible time due to the low mobility of polymer molecules in the glassy state.

   This paper deals with a mixture of two liquid polymers in which the cloud point curve and the T_g vs. composition curve appear in ranges of comparable temperature. If this polymer blend is quenched from a temperature above the cloud point curve to a temperature T_0 in the two-phase region at a very fast rate, phase separation actually starts taking place when T_0 has been reached, but one of the separated phases, which is rich in the component with higher T_g, cannot approach an equilibrium composition within an accessible period of time.

Instead, it eventually takes on and stays at a certain composition different from the equilibrium composition. By thermodynamic analysis it is found that this settling-down of one phase to a quasi-equilibrium composition effects the composition of the conjugate phase rich in the component with lower T_g. On the other hand, if the blend is cooled very slowly toward T_0, there appears at each temperature down to T_0 a new phase again rich in the component with higher T_g and a settling-down to a quasi-equilibrium composition. Thus, on reaching T_0, the blend is a mixture consisting of a series of phases; one phase rich in lower-T_g component and the others (rich in higher-T_g component) with continuously varying compositions which may approximately follow the T_g vs. composition curve.

   In the present paper, the former case is studied, *i.e.*, the rapid quenching of a blend to the two-phase region. Liquid mixtures of low-molecular-weight polystyrene (PS) and poly(methylphenylsiloxane) (PMPS) were chosen for the experiment. Some mixtures have been reported in which the phase separation and glass transition occur in ranges of comparable temperature.[4-8] In these mixtures, however, crystallization occurs during the liquid-liquid phase separation, giving rise to various

complications which the present system avoids, since both polymers are non-crystalline. The compositions of the separated phases were determined as functions of initial composition, separation temperature, and separation time, together with the cloud point curve and T_g vs. composition relationship. Furthermore, a thermodynamic theory has been developed on the effect exerted on the composition of one phase when that of the conjugate phase is frozen at a value different from the equilibrium composition.

EXPERIMENTAL

Materials

The polystyrene (PS) sample used was a product of Pressure Chemical Co., and the weight-average molecular weight M_w and the ratio of M_w to the number-average molecular weight M_n were 9,000 and about 1.06, respectively. The poly(methylphenylsiloxane) (PMPS) used was a commercial product of Toray Silicone, and dried for 50 h under vacuum to eliminate impurities before use. Its M_w and M_w/M_n determined by gel permeation chromatography were 2,800 and 1.57, respectively.

Preparation of Blends

Two methods were used to prepare mixtures of these two polymers, depending on the composition, which is here expressed in terms of the weight percent of PS. For higher compositions, both polymers were dissolved in a common solvent benzene at a total concentration less than 25 wt%. The solution was then cast on a glass plate, and the solvent was evaporated by heating for 50 h at 110°C.[9] For lower compositions, the two polymers were directly mixed above 120°C. The blends prepared by these two methods gave a consistent cloud point curve.

Determination of Cloud Points and T_g vs. Composition Relation

Cloud points were determined by measuring the change in intensity of light transmitted through a sample cell with an optical path of about 1 mm. The temperature $T_c(R)$ at which the sample started becoming turbid when cooled at a rate R was measured for various R from 0.02 to 0.3°C min^{-1}, and the data were extrapolated to $R=0$ to obtain the cloud point $T_c(0)$. Figure 1 illustrates the $T_c(R)$
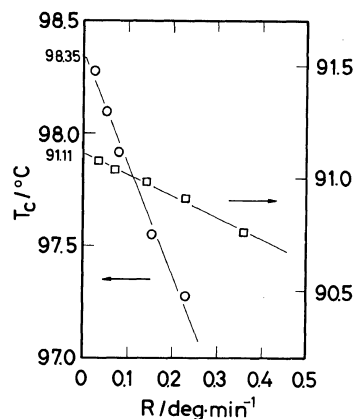

Figure 1. Cloud point temperature T_c as a function of cooling rate R: ○, 47.4 wt% PS; □, 32.5 wt% PS.

data for the two blends. The slope of $T_c(R)$ against R, which was linear for all cases examined, varied with the composition of the blend. In the PMPS-rich region, it first decreased, reached a minimum at 30 wt%, and then increased as the PS content was increased. Turbid blends became immediately transparent when warmed above $T_c(0)$.

To determine the T_g of a homogeneous blend of known composition the sample maintained above 110°C was quenched to the temperature of liquid nitrogen, -196°C, and subjected to a differential scanning calorimetry (DSC) measurement using a Parkin-Elmer DSC Model II and a heating rate of 20°C min^{-1}. Transparent glassy blends were obtained only in the PS-rich region. As illustrated in Figure 3, the DSC thermograms obtained exhibited two breaks which may be defined as the points of intersection of the upper and lower base lines with the tangent at the inflection point. The glass transition temperatures corresponding to these breaks are denoted by $T_g{}^+$ and $T_g{}^-$, as indicated in Figure 3.

Composition Determination of Separated Phases

A blend of known composition was cooled from 120°C to a desired temperature T_0 below the cloud point curve at a rate as fast as 320°C min^{-1}, maintained at T_0 for a prescribed period of time and then quenched to -73°C in the DSC apparatus for a DSC measurement. This experiment was carried out for two blends of 50.4 and 55.0 wt% at various T_0 down to values near T_g for these compositions, with 20 h for 55.0 wt% and 30 min and 20 h for 50.4

270

wt% as the period of time for the phase separation. Actually, the phase separation for 30 min was made in the DSC apparatus, and that for 20 h in an external thermostat. In all cases, the DSC measurements on the phase-separated blends were carried out at a heating rate of 20°C min^{-1}. The compositions in the separated phases were determined by T_g^+ and T_g^- on the DSC thermogram so obtained.

RESULTS AND DISCUSSION

Cloud Point Curve and T_g vs. Composition Relation

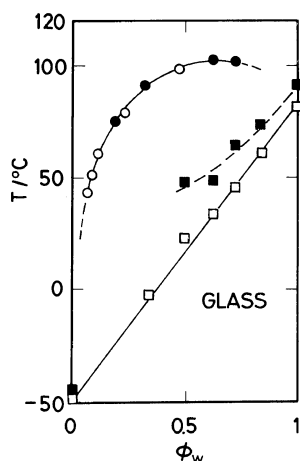Figure 2 shows the cloud point curve obtained.

Figure 2. Cloud points and glass transition temperatures: ●, blend cast from benzene solution; ○, blend mixed directly; □, glass transition temperature obtained from T_g^-; ■, glass transition temperature obtained from T_g^+.
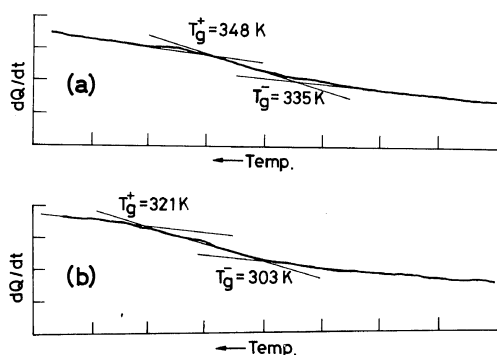

Figure 3. DSC thermograms of the homogeneous blends: a), 84.0 wt% PS; b), 62.4 wt% PS.

When the PS composition ϕ_w was above 75 wt%, no inception of turbidity was observed even at the slowest cooling rate of 0.02°C min^{-1}.

Figure 2 also displays T_g^+ and T_g^- of homogeneous blends as functions of ϕ_w. It is evident that T_g^- varies linearly with ϕ_w throughout the entire composition range, yielding -49 (± 1)°C for pure PMPS and 82 (± 2)°C for pure PS; the latter is a little lower than the literature values.[10,11] As ϕ_w is lowered, the spread of T_g, i.e., $T_g^+ - T_g^-$ increases, as can be seen from Figure 3 which also shows the DSC thermograms for different ϕ_w, 84.0 wt% (a) and 62.4 wt% (b). At $\phi_w = 35$ wt%, the DSC thermogram exhibited, in addition to T_g^+ and T_g^-, another glass transition which could be assigned to pure PMPS.

In Figure 2, attention should be directed to the fact that the phase separation and glass transition of the present system of liquid polymers occur in ranges of comparable temperature.

The appearence of two glass transition temperatures T_g^+ and T_g^- may be explained as follows. While being quenched to liquid nitrogen temperature for DSC measurement, a blend should undergo partial phase separation. As the temperature is lowered, the PMPS-rich phase evolved becomes richer in PMPS, smaller in size, and eventually no longer detectable by DSC.[12,13] However, a series of PS-rich phases that appear at successive temperatures in this process are frozen by vitrification. This indicates that the quenched blend contains a range of PS-rich phases that varying in compositions and T_g^+ and T_g^- correspond to the upper and lower bounds of this range, respectively.[14,15] It is noted that the lower bound corresponding to T_g^- is the composition of the initial homogeneous blend, since the PS composition of PS-rich phases separated during the quenching is always higher than that of the initial blend.

Two reasons may be given for the composition change in $T_g^+ - T_g^-$ as shown in Figure 2. First, as the PS composition is lowered, the blend passes through a longer two-phase liquid region until quenched to the liquid nitrogen temperature. This facilitates the separation of phases richer in PS in the blend, thus leading to a greater $T_g^+ - T_g^-$. Second, the average rate of the phase separation should be larger for lower PS compositions, since the phases undergo separation more easily at such compositions in a less glassy state with high mo-
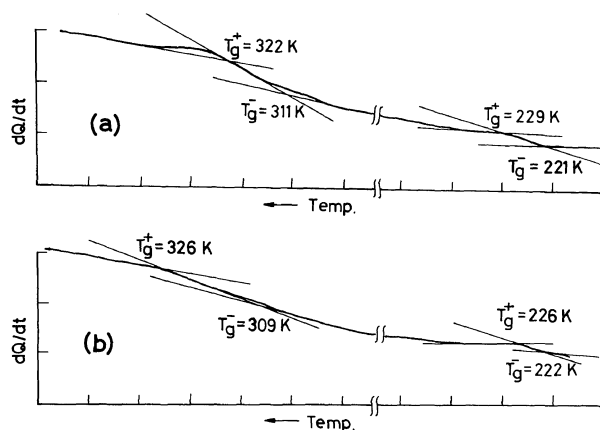
Figure 4. DSC thermograms of the phase-separated blends. Initial composition is 50.4 wt% PS: a), annealed at 37°C for 30 min; b), annealed at 77°C for 30 min.

bility of the polymer molecules.

Compositions of Separated Phases

Figure 4 illustrates the DSC thermograms for 50.4 wt% blend subjected to phase separation at 37°C (a) and 77°C (b) for a period of 30 min. For each of these thermograms, the T_g^+ and T_g^- on the left side were assignable to PS-rich phases of varying compositions; those on the right side were assigned to pure PMPS. No T_g^+ or T_g^- assignable to the PMPS-rich phases could be seen. This suggests that the PMPS-rich phase was separated further into pure components when the blend was quenched for DSC measurement.

In Figure 5 are shown the compositions calculated from T_g^+ and T_g^- for the PS-rich phases of the blend of 50.4 wt% subjected to phase separation at various T_0 for 30 min. The horizontal bar in the figure indicates the composition spread obtained when the same blend was quenched directly at the temperature of liquid nitrogen. In deriving these results, it was assumed that T_g^- varies with composition, following the solid straight line in Figure 2, and that T_g^+ also varies linearly with composition, following the straight line connecting the filled square points for pure PS and PMPS in Figure 2 and indicated by a broken line in Figure 5.

It can be seen that the compositions from T_g^+ at different T_0 are almost constant and equal to the upper limit of the bar. This implies that the phases corresponding to T_g^+ evolved not during the standing at T_0, but during the subsequent quenching for
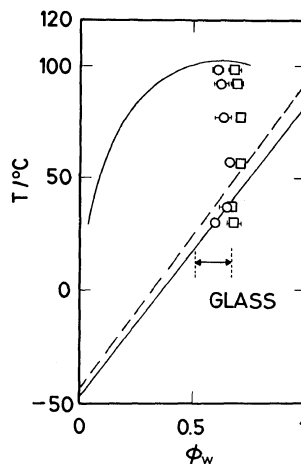

Figure 5. The compositions of phases separated for 30 min. Initial composition is 50.4 wt% PS: ○, obtained from T_g^-; □, obtained from T_g^+. The bar (↔) indicates composition distribution when the homogeneous blend is quenched into the glassy state.

DSC measurements. The compositions from T_g^- also are almost independent of T_0, but are higher than the lower limit of the bar corresponding to the composition of the given homogeneous blend, 50.4 wt% in the present case. Thus, the compositions from T_g^- should represent those of the PS-rich phases separated during the standing at T_0 for 30 min. The fact that they are independent of T_0 may be explained as follows.

Roughly speaking, the rate of phase separation is

272

determined by the product of the mobility of component polymers in the blend and the instability of the system.[16] The latter is expressed in terms of the second derivative of the free energy with respect to the composition in the early stage of spinodal decomposition and is enhanced by lowering the temperature at which phase separation is allowed to take place. Thus, thermodynamic instability accelerates phase separation when carried out at lower temperature. However, in the present system, the mobility of polymer molecules is more suppressed at lower temperature, since the system approaches the glassy state more closely. This effect retards the evolution of phase separation. These two oppositely acting effects determine the ratio of phase separation, and hence the composition from $T_g{}^-$, approximately independent of T_0.

Figure 6 shows the compositions of the PS-rich phases calculated from $T_g{}^+$ and $T_g{}^-$ for the blends of 50.4 wt% and 55.0 wt% subjected to phase separation at various T_0 for 20 h. The data points appear to the right of the corresponding dotted curves which fit the data points shown in Figure 5. This fact indicates that further phase separation occurred when the blend was left at T_0 for a longer period of time, as can be expected. The compositions from $T_g{}^-$ at higher T_0 shift to the right more from the corresponding dotted curve. This phenomenon is consistent with fact that the mobility of polymer molecules is greater for higher T_0.
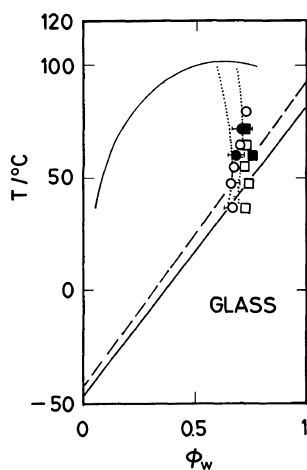
In Figure 6, we see that the compositions, calculated from either $T_g{}^+$ or $T_g{}^-$, for blends of 50.4 and 55.0 wt% fall approximately on a single curve. We carried out similar phase separation experiments at various T_0 with a standing time of 20 h for two blends of 25 and 35 wt%, and found that the compositions fell on the same curve. These results indicate that the compositions of the PS-rich phase separated at a given temperature for a period of 20 h are essentially independent of the composition of the initial homogeneous blend. These differ considerably from the equilibrium compositions predictable from the cloud point curve, and simply represent quasi-equilibrium compositions. The attainment of true equilibrium compositions for the values of T_0 chosen in this work would far exceed the time allowable for our experiments.

Theory

Suppose that a binary polymer blend is rapidly cooled to a temperature in the two-phase region and that one of the separated phases is frozen at a certain composition different from the equilibrium composition corresponding to the fixed temperature. It may be asked what deviation from the equilibrium composition of the conjugate phase occurs when the mobility of the polymer chains in this phase is sufficiently high.

The frozen-in phase and its conjugate phase are denoted by double and single primes, respectively. The equilibrium between these two phases at constant temperature and pressure is established when the chemical potentials μ_1 and μ_2 satisfy the relation,

$$dG = (\mu_1'dn_1 + \mu_2'dn_2) - (\mu_1''dn_1 + \mu_2''dn_2)$$

$$= (\mu_1' - \mu_1'')dn_1 + (\mu_2' - \mu_2'')dn_2 = 0 \qquad (1)$$

where the subscripts 1 and 2 denote the components of the blend, and dn_i is an infinitesimal amount of component i actually transferred from the double prime to the single prime phase. Since, in the present case, the composition of the double prime phase is fixed at a certain value, say ϕ_g, dn_1 and dn_2 are not allowed to undergo independent change and must obey the restriction,

$$x_1 dn_1/(x_1 dn_1 + x_2 dn_2) = \phi_g \qquad (2)$$

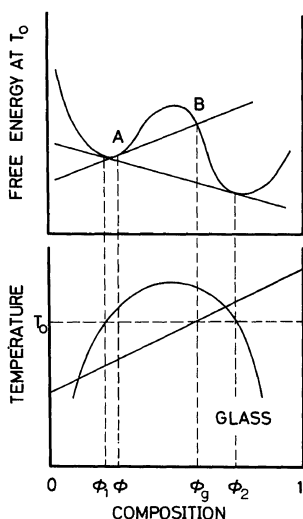where x_i is the number of segments in component i.

Figure 6. The composition of phases separated for 20 h: initial composition of PS, 50.4 wt% (O, □) and 55.0 wt% (●, ■); O, ●; obtained from $T_g{}^-$, □, ■; obtained from $T_g{}^+$.

Figure 7. Deviation of a quasi-equilibrium composition from the equilibrium composition with the free energy vs. composition curve.
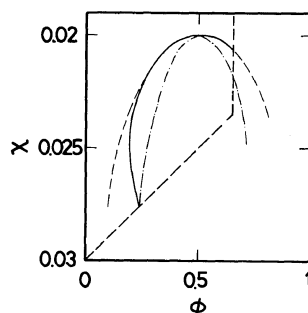

Figure 8. Quasi-equilibrium binodal calculated from eq 5 for variables indicated in the text: ——, quasi-equilibrium binodal curve; ---, equilibrium binodal curve; —·—·—, spinodal curve.
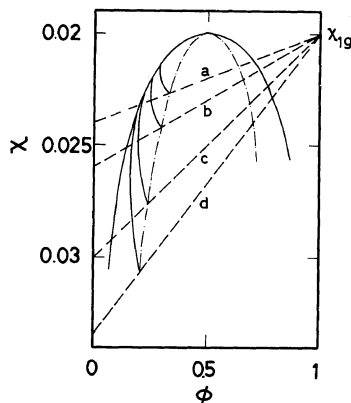

Figure 9. χ_{2g} dependence of the binodal: $x_1 = x_2 = 100$, $\chi_{1g} = 0.02$, and $\chi_{2g} =$ (a) 0.024, (b) 0.026, (c) 0.030, (d) 0.034.

From eq 1 and 2 we obtain as the equilibrium condition

$$(\mu_1' - \mu_1'')\phi_g/x_1 + (\mu_2' - \mu_2'')(1 - \phi_g)/x_2 = 0 \tag{3}$$

This permits computation of the composition ϕ of the single prime phase as a function of temperature for a given temperature dependence of ϕ_g.

In the free energy vs. composition curve delineated in Figure 7, point B corresponds to ϕ_g and the line passing through this point touches the free energy curve at point A. According to eq 3, the composition at point A is equal to the quasi-equilibrium composition ϕ of the single prime phase which deviates from the equilibrium one ϕ_1.

We substitute Scott's expression for the free energy of mixing ΔG,[17] i.e.,

$$\Delta G = RT[(\phi/x_1)\ln\phi + \{(1 - \phi)/x_2\}\ln(1 - \phi)$$
$$+ \chi\phi(1 - \phi)] \tag{4}$$

into eq 3. Here χ denotes the Flory–Huggins interaction parameter. The result reads

$$[(1 - \phi_g)/x_2]\ln[(1 - \phi)/(1 - \phi_g)]$$
$$+ (\phi_g/x_1)\ln(\phi/\phi_g) + (\phi_g - \phi)(1/x_1 - 1/x_2) \tag{5}$$
$$+ \chi(\phi_g - \phi)^2 = 0$$

To calculate ϕ as a function of χ from eq 5, we

take $x_1 = 100$, $x_2 = 100$, $\chi_{1g} = 0.02$, and $\chi_{2g} = 0.03$, where χ_{1g} and χ_{2g} are the values of χ at the glass transition temperatures for components 1 and 2, respectively, and assume by referring to the experimental results shown in Figure 6 that ϕ_g varies with χ as indicated by the thick broken line in Figure 8. The calculated quasi-equilibrium binodal is shown by the solid curve in Figure 8. This curve lies inside the equilibrium binodal represented by a thin broken curve and intersects the spinodal represented by a dot-dash curve at a point on the χ vs. ϕ_g line.

Figure 9 illustrates the change in the quasi-equilibrium binodal as the T_g's of the pure components approach each other. In calculating these curves, it was assumed that T_g varies with ϕ according to the Fox relation[18] for glass transition tem-

perature of binary mixture. It can be seen that at a given temperature the miscibility region on the left side of the quasi-equilibrium binodal spreads as χ_{2g} approaches χ_{1g}.

It should be noted that the present model may be too much of a simplification to warrant application to real systems in estimating quasi-equilibrium composition, since the assumption of the high mobility of polymer chains for the single prime phase may, for example, break down near the glass transition region in real systems.

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