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Notes

Prediction and Experimental Verification on Blend Phase Diagrams of Two Structurally Isomeric Polymers: Poly(4-methylstyrene) and Poly(α-methylstyrene)

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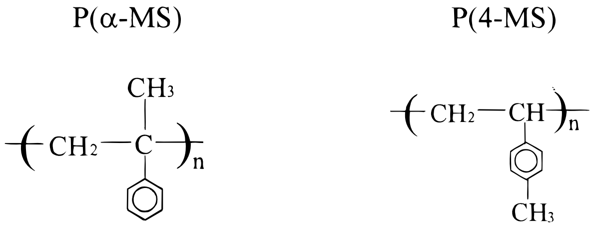
Introduction

Polymer miscibility in blends involving polystyrene (PS) has not been common. This may be an expected result from the fact that PS does not possess any functional groups that are capable of interacting specifically with other polymer molecules. The miscibility behavior of blends of polystyrene (PS) and poly(α-methylstyrene) (PαMS) has been widely studied.[1−7] Polymer mixtures with miscibility at ambient temperature can usually exhibit phase separation at elevation temperatures, which is a phenomenon showing a phase transition known as lower critical solution temperature (LCST). Interestingly, PS and PαMS are generally not miscible at ambient temperature but can exhibit miscibility at elevated temperatures, showing an upper critical solution temperature (UCST) behavior, which is dependent on MW of the polymers. Graessley et al.[8−10] have reported extensively on the subjects of thermodynamics of LCST/UCST phase separation, interactions, and mixing behavior of polyolefins by utilizing a powerful technique of small-angle neutron scattering (SANS). However, the topics of styrenic isomers, which differ from the polyolefins by possessing a slightly more polar phenyl group, have not been documented.

In general, miscible blends involving two styrenic polymers are rare and less reported. By introducing a CH_3 group to the 4-position of phenyl ring, PS becomes poly(4-methylstyrene) (P4MS). It is interesting to investigate structure−phase relationships in blends involving such polymers. Interestingly P4MS and PαMS are two structural isomers. The objectives of this study were to examine the phase behavior of two structurally isomeric P4MS/PαMS polymers, experimentally and through a model prediction approach.

Experimental Section

Two isomeric methyl-substituted polystyrenes were available from a specialty polymer supplier. Poly(4-methylstyrene) (P4MS) was obtained from Scientific Polymers Product (SP2), Inc. (USA), with an approximate M_w = 70 000 g/mol (gel permeation chromatograph, GPC) and T_g = 106 °C. Another methyl-substituted polystyrene, poly(α-methylstyrene) (PαMS), is an isomer to P4MS. Systematic variation of molecular weights was done on one of the two constituents. Several grades of PαMS were used for blending with P4MS. First, PαMS of a very low M_w was used and hereby designated as LMW. The LMW PαMS is of a wide polydispersity index (PI), and our laboratory characterization on its intrinsic viscosity revealed M_v = 5000−7500 g/mol and T_g = ∼40 °C. In addition, PαMS of three much higher molecular weights (with a narrow distribution of PI nearly 1.0) were also supplied by Scientific Polymers Product, Inc. (USA). They are designated as MMW-I = 11 800 (medium M_w), MMW-II = 31 400 (medium M_w), and HMW (high M_w) = 398 000 g/mol (GPC), and their T_g's are 160−170 °C. The chemical structures of P4MS and PαMS are as follows:



Blend samples in this study were prepared by solution-casting (THF) at two different temperatures (20 or 45 °C, respectively).

The glass transition temperatures were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with an intracooler and a computer for data acquisition/analysis. A polarized-light microscope (Nikon Optiphot-2, POL) was used. The as-cast blends were spread as thin films on glass slides and dried properly in a temperature-controlled oven before they were examined using the optical microscope. For comparison, samples for optical examination were prepared using the same solvents and casting temperature as those in thermal analysis samples. Preliminary blend morphology and cloud point measurement were examined using optical microscopy by placing the samples on a microscope heating stage, at approximately 2 °C/min from room temperature up to 300 °C. In addition, phase homogeneity in the blends was examined using a scanning electron microscope (SEM, JEOL JXA-840).

Results and Discussion

When observed using the optical microscope (OM), the cast-film samples (ca. 100 μm) of P4MS/PαMS (LMW) were clear and free of any discernible phase domains. The SEM characterization on the miscible blends revealed a smooth fracture surface and no discernible phase domains in all P4MS/PαMS (LMW) blend compositions. DSC was performed to characterize P4MS PαMS blends, where the PαMS is of low MW = ∼7500 g/mol. The T_g-vs-composition relationship was also investigated. Figure 1 (diagram A) shows the DSC thermograms, which reveal only a single T_g for each of the blend compositions, as indicated in the curves. By applying the conventional T_g criterion for determining phase miscibility, the P4MS/PαMS blend is apparently miscible. The transition breadth for each measured single T_g varied slightly depending on composition. Although slightly broadened (15−20 °C in breadth), the

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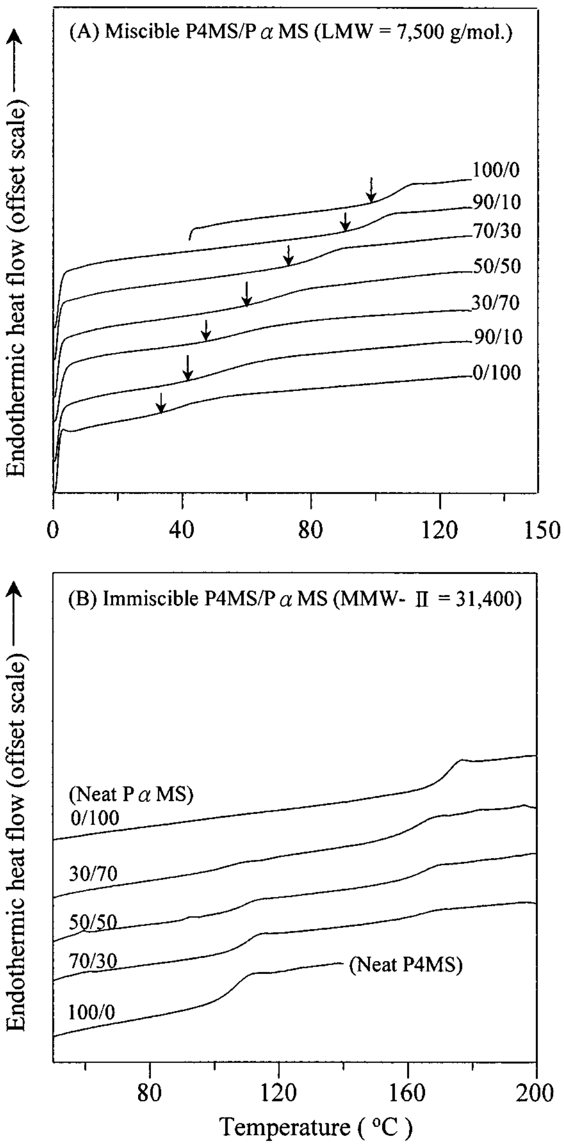

Figure 1. (A) DSC traces showing T_g–composition relationship for miscible P4MS/PαMS (LMW = 7500 g/mol), where arrow indicates the onset of T_g, and (B) DSC results for the phase-separated mixture (P4MS/PαMS, MMW-II = 31 400).

single T_g is apparently composition-dependent. The T_g–composition dependence in the miscible P4MS/PαMS blend was examined by fitting with the classical T_g model of the Gordon–Taylor equation,[11] i.e., $T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2})/(\omega_1 + k\omega_2)$, where ω_i is the mass (weight) fraction of polymer component *i*, and *k* is a fitting parameter. A value of $k = 0.52$ was obtained for this blend, suggesting reasonably good phase homogeneity. However, at increased molecular weights of one of the two constituent polymers (e.g., PαMS), phase behavior of the isomeric P4MS/PαMS system underwent a change. For contrasting with the miscible one, one set of DSC traces for the phase-separated mixture (P4MS/PαMS, MMW-II = 31 400) was placed as diagram B of Figure 1 for direct comparison. Two T_g's were easily identified in the DSC traces. More detailed discussions on experimental verification of phase behavior will be made later.

Experimental vs Predicted Phase Diagrams. Figure 2A summarizes the result of experimental phase diagram (cloud point initiation temperature) and observed phase decomposition mechanism. The critical point (LCST) is about 140 °C. As the phase structure of the blend at below the cloud point was determined to be completely homogeneous and free of any microheterogeneity, the occurrence of a cloud point phenomenon suggested phase separation from its original miscibility state.

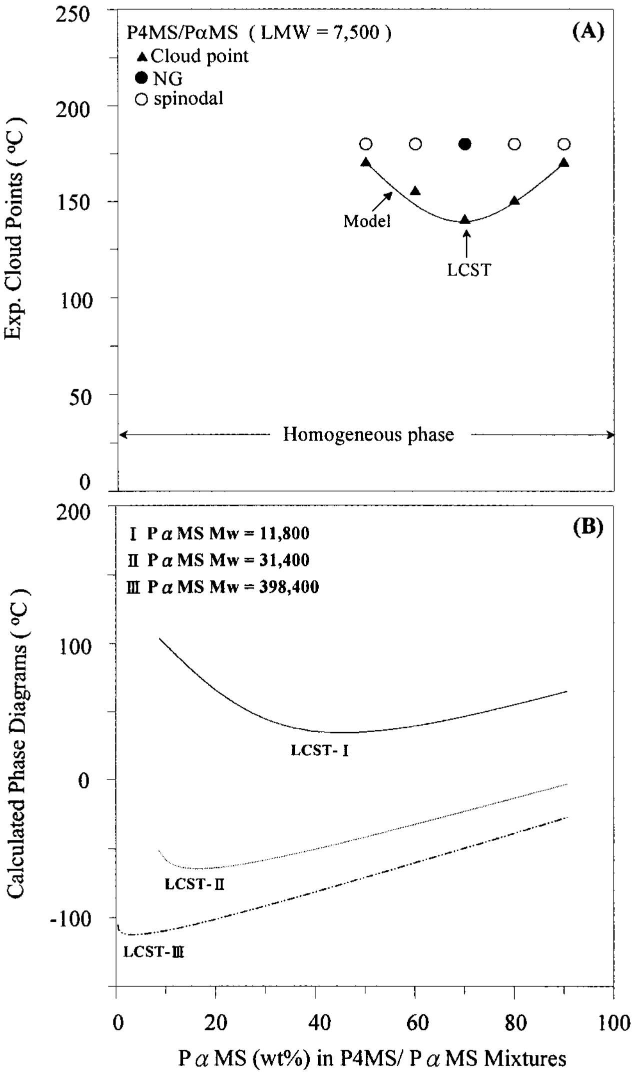

Figure 2. (A) Experimental phase diagram for P4MS/PαMS (LMW = 7500 g/mol) vs (B) predicted phase diagram for P4MS/PαMS blends: (I) PαMS MMW-I = 11 800, (II) MMW-II = 31 400, (III) HMW = 398 000 g/mol.

This was then used as the data for constructing a model. The Flory–Huggins expression for the free energy of mixing is expressed:[12]

$$\Delta G_M = RT\left[\frac{1}{V_1}\phi_1 \ln \phi_1 + \frac{1}{V_2}\phi_2 \ln \phi_2\right] + B\phi_1\phi_2 \quad (1)$$

where V_1 and V_2 are the molar volumes of P4MS and PαMS, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the polymers. *B*, as a parametric form, is the interaction energy density between these two components:[2,4,7,13]

$$B = b_0 + b_1\phi_2 + b_2 T \quad (2)$$

This expression was fitted against the miscible blend of P4MS/PαMS (LMW = 7500 g/mol). The experimental data for this blend were then used for obtaining the model parameters (b_i) by using a nonlinear leastsquares fitting. The following expression for the interactions between two polymers was obtained: $B = -0.01134 - 0.06322\phi_2 + 0.000765T$. The fitted model was then used to predict the phase behavior of P4MS/PαMS blends of higher PαMS molecular weights ($M_w = 11\,800$, 31 400, and 398 000 g/mol). Figure 2B shows calculated phase diagrams (curves I, II, III) for P4MS/PαMS blends of three different M_w's. Apparently, the calculated results predict that these blends would assume a two-phase morphology at the ambient temperature, which is well above the LCST. Apparently, the model predicts partial miscibility or outright phase separation for the as-cast (ambient temperature) P4MS/PαMS blends, in which PαMS $M_w = 11\,800$, 31 400, and 398 000 g/mol, respectively. The model predicts that, at increasingly higher molecular weights of PαMS, the blends exhibited a trend of lower LCST's (all at below the ambient temperature), and the phase behavior of the blends shifted from partial miscibility to complete phase separation. For PαMS molecular weights equal to or higher than 12 000 g/mol or so, the P4MS/PαMS blends would assume a two-phase morphology within the whole composition range.

The modeling predicts that the P4MS/PαMS (MMW-I = 11 800) blend system would exhibit a partial miscibility that borders on transition to more apparent immiscibility. The as-cast P4MS/PαMS (MMW-I) blend was visually transparent and optically clear when examined using OM. However, SEM revealed tiny domains (0.1−0.5 μm) for the blend of certain intermediate compositions (30/70 and 50/50 for examples). Thermal analysis was performed on these visually clear blend samples to reveal its T_g behavior. Figure 3A shows the experimental DSC result of phase behavior. The blend samples whose compositions were outside the intermediate range exhibited a single T_g, suggesting immiscibility in the intermediate composition range and miscibility outside the range. This is typical of partial immiscibility in polymer blends. Second, experimental evidence was searched for blends of higher M_w's. The as-cast P4MS/PαMS blends of higher molecular weights were apparently hazy and phase-separated. Diagrams B and C of Figure 3 show two T_g's and immiscibility in the PαMS/P4MS blends, in which the PαMS constituent possesses a higher MW = 31 400 and 398 000 g/mol, respectively. With increase in the molecular weights of PαMS, the phase behavior of PαMS/P4MS blends turned from miscibility into phase separation. The experimental result indicated that the blends of high M_w's are phase-separated at ambient temperature and any temperatures above. This is in agreement with the experimental results of phase separation for these two blend systems. It must be noted, however, this study demonstrated that LCST phenomenon was observed in the P4MS/PαMS blend, an opposite phenomenon to the fact that UCST exists in the PS/PαMS blend system.[3−7]

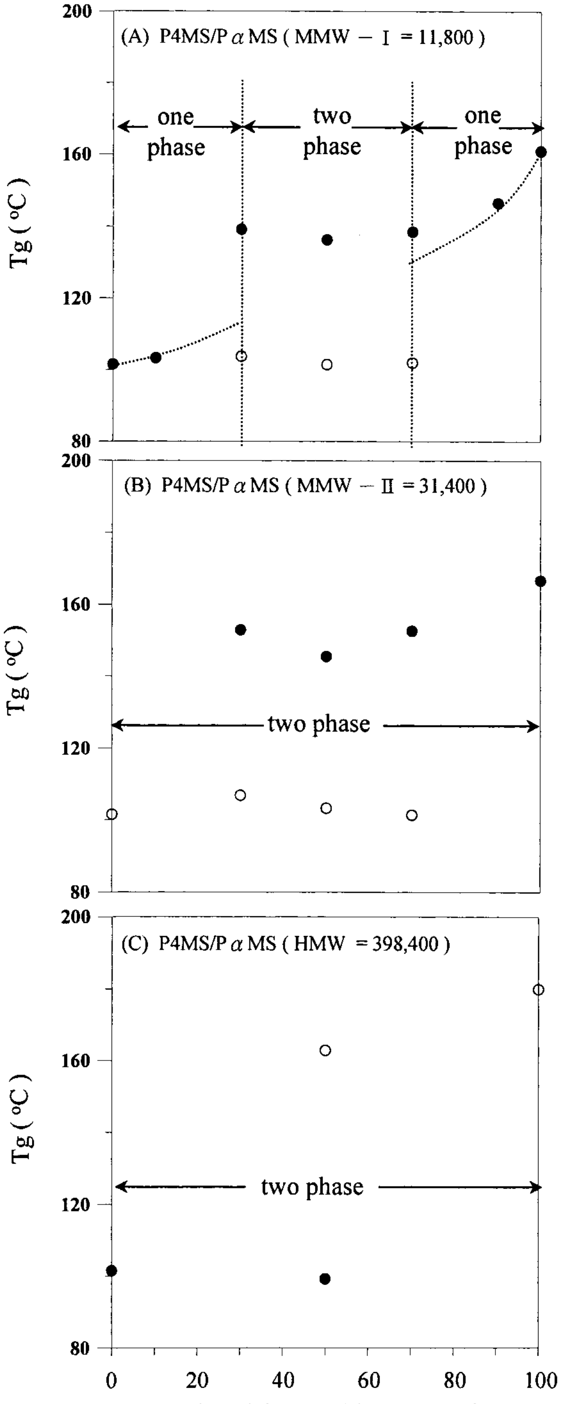

Figure 3. Experimental T_g's verifying the model prediction of partial miscibility and/or immiscibility phases in the P4MS/PαMS blend, in which PαMS MW's = (A) 11 800, (B) 31 400, and (C) 398 000 g/mol.

Conclusion

For the first time, the phase behavior of blends comprising two isomeric polymers, P4MS and PαMS, was analyzed. Both model prediction and experimental confirmation were conducted. The conclusions are summarized: (1) At low PαMS molecular weights (7500 g/mol or lower), the blend of isomeric polymers is miscible with LCST at about 140 °C. This behavior is just opposite from that observed in the widely studied PS/PαMS blend system, which is immiscible at ambient temperature with an UCST. (2) A model based on a modified Flory−Huggins interaction expression was then developed by utilizing the experimental phase diagram of miscible blends comprising LMW constituents. The model predicts that at higher molecular weights (11 800 g/mol or higher) the P4MS/PαMS mixtures become immiscible. Excellent agreement with the experimental result has been found. More in-depth analysis and investigation of structural effects on LCST vs UCST behavior in blends are ongoing.

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References and Notes

(1) Saeki, S.; Cowie, J. M. G.; McEwen, I. J. *Polymer* **1983**, *24*, 60.
(2) Cowie, J. M. G.; McEwen, I. J. *Polymer* **1985**, *26*, 1667.
(3) Widmaier, J.-M.; Mignard, G. *Eur. Polym. J.* **1987**, *23*, 989.
(4) Lin, J.-L.; Roe, R.-J. *Macromolecules* **1987**, *20*, 218.
(5) Schneider, H. A.; Dilger, P. *Polym. Bull.* **1989**, *21*, 265.
(6) Rameau, A.; Gallot, Y.; Marie, P.; Farnoux, B. *Polymer* **1989**, *30*, 386.
(7) Callaghan, T. A.; Paul, D. R. *Macromolecules* **1993**, *26*, 2439.
(8) Krishnamoorti, R.; Graessley, W. W.; Fetters, L. J.; Garner, R. T.; Lohse, D. J. *Macromolecules* **1995**, *28*, 1251.
(9) Krishnamoorti, R.; Graessley, W. W.; Dee, G. T.; Walsh, D. J.; Fetters, L. J.; Lohse, D. J. *Macromolecules* **1996**, *29*, 367.
(10) Reichart, G. C.; Graessley, W. W.; Register, R. A.; Krishnamoorti, R.; Lohse, D. J. *Macromolecules* **1997**, *30*, 3036.
(11) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(12) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1978; Chapter XII.
(13) Kim, J. K.; Lee, H. H.; Son, H. W. *Macromolecules* **1998**, *31*, 8566.

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