

Phase separation temperatures in the polystyrene–poly(α -methyl styrene)–methylcyclohexane system

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The phase separation temperatures (*PST*) in the ternary system polystyrene (PS) ($M_w = 1.75 \times 10^4 \text{ g mol}^{-1}$) – poly(α -methyl styrene) (P α MS) ($M_w = 6.0 \times 10^4$) – methylcyclohexane (MCH) and the binary systems PS–MCH and P α MS–MCH have been determined by using a He–Ne laser light-scattering apparatus over the total polymer weight fraction ($W_{\text{PS} + \text{P}\alpha\text{MS}}$) range of 0.018 to 0.80 and various polymer blend ratios. The *PST* determined at a scattering angle of 0° agreed with those at 90° for the binary systems over polymer concentrations of 0.1 to 0.7 and for the ternary over $W_{\text{PS} + \text{P}\alpha\text{MS}}$ of higher than 0.3. Deviations of the *PST* determined at an angle of 90° from those at 0° were observed in the ternary system when $W_{\text{PS} + \text{P}\alpha\text{MS}}$ was lower than 0.3. Two phase separation temperatures, at which the intensity scattered from zero angle changed discontinuously, are observed at concentrations lower than $W_{\text{PS} + \text{P}\alpha\text{MS}} = 0.042$ in the ternary system. The *PST* in the ternary system decreases monotonically with increasing $W_{\text{PS} + \text{P}\alpha\text{MS}}$ over 0.3 to 0.7. The phase diagram for the PS–P α MS–MCH system at $W_{\text{PS} + \text{P}\alpha\text{MS}} = 0.8$ is characterized by a maximum *PST* around -14°C .

Keywords Polymer blends; phase separation temperature; phase diagram; polystyrene; poly(α -methyl styrene); ternary system; binary system

INTRODUCTION

The phase diagrams (PD) of polymer mixtures are very important in discussing the compatibility phenomena between polymeric materials. Investigations of the PD of binary polymer mixtures^{1–11} and ternary systems of polymer(1)–polymer(2)–solvent^{12–18} and polymer(1)–polymer(2)–polymer(3)¹⁹ have been undertaken theoretically and experimentally. Koningsveld *et al.*⁵ have determined the cloud points, critical points and spinodals in short-chain liquid polymer mixtures of polyisobutylene/polystyrene. The spinodal decomposition or nucleation and growth in phase separation of polystyrene–poly(vinyl methyl ether) have been investigated by Nishi *et al.*² Patterson *et al.*^{16,17} have discussed the phase separation behaviour of ternary systems by considering the effect of the difference in strengths of interactions between polymer(1)–solvent and polymer(2)–solvent. The role of casting solvent in the blending process of polymeric materials is one of the important factors in determining the compatibility between polymer(1) and polymer(2). Schultz *et al.*²⁰ have tried to make homogeneous blends of non-compatible polymer pairs by a rapid freeze-drying of co-solutions of polymer(1)–polymer(2)–solvent. The evaporation temperature of the solvent in the production of a polymer blend from the ternary solution is also an important factor in determining the properties of the blend.

When the components of a system are polymers of high molecular weights and high glass transition temperatures, it is very difficult to make a homogeneous polymer blend and to determine the phase separation temperature

(*PST*). However, the ternary phase diagram of a polymer(1)–polymer(2)–solvent system affords a method of determining the PD of binary polymer mixtures with high viscosity and nearly equal refractive index by extrapolation of the solvent concentration to zero²¹. The ternary phase diagrams also provide useful information on the effect of the casting solvent on the binary phase diagram. In this work we have determined the ternary phase diagram of PS–P α MS–MCH at various blend ratios and over a wide concentration range of $W_{\text{PS} + \text{P}\alpha\text{MS}}$. The PS–P α MS blend system was selected because it is one of a number of non-polar polymer blends showing partial compatibility and is suitable for discussing the effect of casting solvent on polymer–polymer compatibility.

EXPERIMENTAL

Samples of polystyrene ($M_w = 1.75 \times 10^4 \text{ g mol}^{-1}$) and poly(α -methyl styrene) ($M_w = 6.0 \times 10^4$) used in this work were obtained from the Pressure Chemical Co. and Aldrich Chemical Co., respectively. Methylcyclohexane was reagent grade and obtained from Wako Pure Chemical. The solvent was distilled after removing a trace of water by K_2CO_2 . The blend samples were obtained as follows. Solutions of PS and P α MS mixtures of fixed blend ratio in methylcyclohexane of about $W_{\text{PS} + \text{P}\alpha\text{MS}} = 0.08$ are spread thinly over a glass plate heated at about 55°C . Most of the solvent was allowed to evaporate in the oven and the sample was then dried under vacuum for several hours at 55°C . This produced a thin sheet of polymer film. Samples were then scraped into a cylindrical cell with i.d. 3.5 mm. Solutions of the ternary system PS–P α MS–MCH were flame sealed under vacuum in the cell

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and then mixed homogeneously using the centrifuge apparatus. The samples were kept at a constant temperature above the *PST* for 2–4 days before measurements.

The intensity of light scattered from the solution was detected at angles of 0° and 90° by phototransistors (TPS 604, PL3). The light source used in this work was a He–Ne gas laser (Nihon Kagaku Engineering Co.). The *PST* is determined as the temperature at which the output voltage of the transistor indicates a discontinuous change (see Figure 1). The *PST* was determined by cooling the samples at the rate 0.3–1.1°C min⁻¹. Measurement of the *PST* was repeated two to five times and reproducible data were obtained within ±0.2°C. The *PST* were also determined by heating the samples from a temperature below the *PST* and good agreement was obtained with the data determined by cooling, for concentrated solutions, within ±1°C.

RESULTS

The output voltage V_{CE} of the phototransistor, produced by the light scattered from the solutions, is plotted against temperature in Figures 1 to 4. The *PST* determined at angles of 0° and 90° for the binary systems PS–MCH and P α MS–MCH and the ternary system PS–P α MS–MCH are shown in Figures 5 to 7. The determination of the *PST* in the binary systems at extremely high concentration is interrupted by the pseudo-glass transition temperatures (T_g), at which the solution in the cell solidifies and can be peeled off the surface of the cell. The pseudo T_g is observed for weight fractions of polymer higher than 0.7 for the PS–MCH and P α MS–MCH systems (see Figure 5).

Deviations of the *PST*, determined at an angle of 90° from that at 0°, were observed in the samples of blend

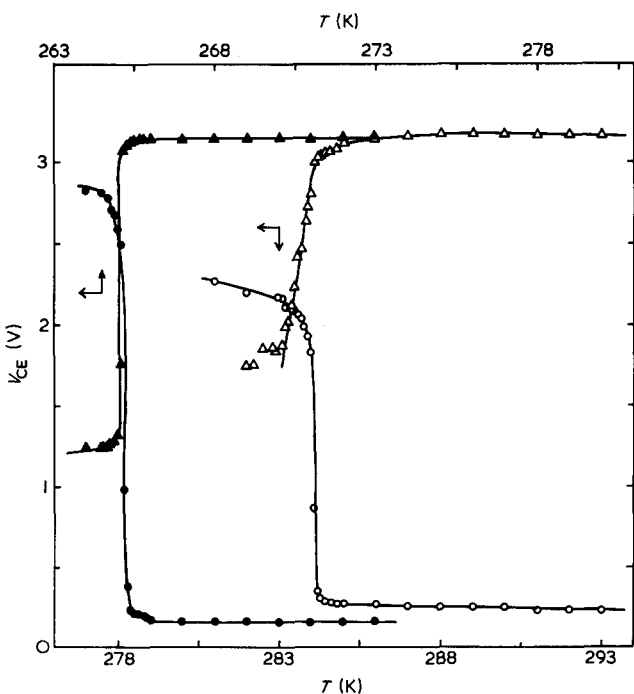


Figure 1 Voltage of phototransistor between collector and emitter (V_{CE}) caused by the scattered light at angles of 90° (Δ , \blacktriangle) and 0° (\circ , \bullet) plotted against temperature in the PS–P α MS–MCH system. The blend ratio of PS/P α MS is 75/25 and total weight fraction of polymer $W_{PS+P\alpha MS}$ is 0.500 (\circ , Δ) and 0.7281 (\bullet , \blacktriangle)

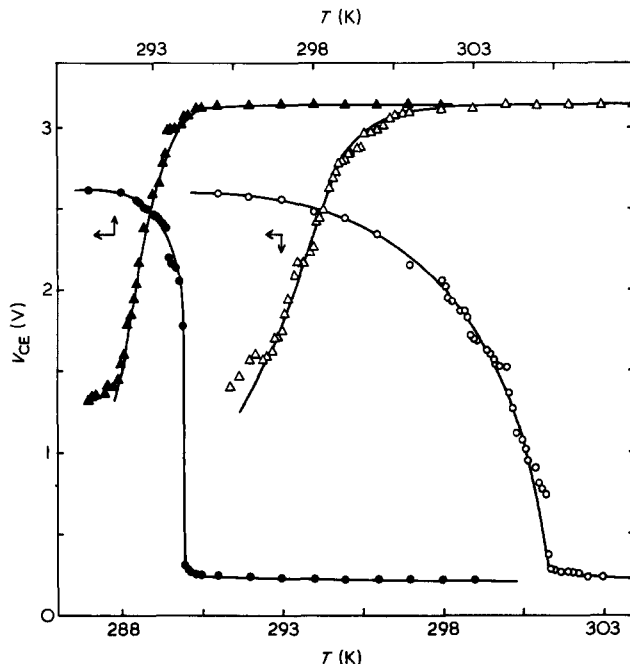


Figure 2 V_{CE} –temperature plot in the PS–P α MS–MCH system. The blend ratio of PS/P α MS is 75/25 and $W_{PS+P\alpha MS}$ is 0.2097 (\circ , Δ) and 0.3009 (\bullet , \blacktriangle). The scattering angles are 90° (Δ , \blacktriangle) and 0° (\circ , \bullet)

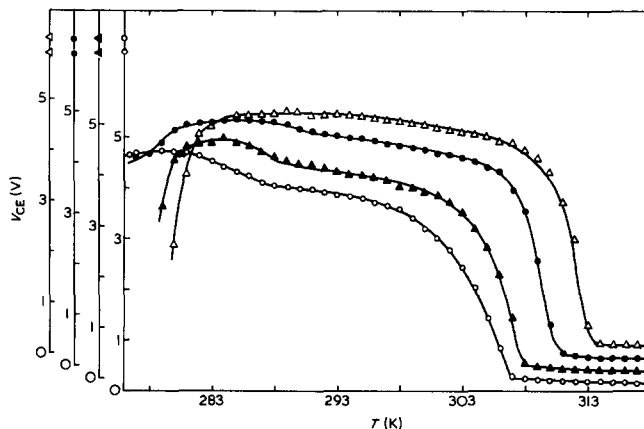


Figure 3 V_{CE} –temperature plot at a scattering angle of 0° in the PS–P α MS–MCH system. The blend ratio of PS/P α MS is 75/25 and $W_{PS+P\alpha MS}$ is 0.063 (Δ), 0.042 (\bullet), 0.029 (\blacktriangle) and 0.018 (\circ)

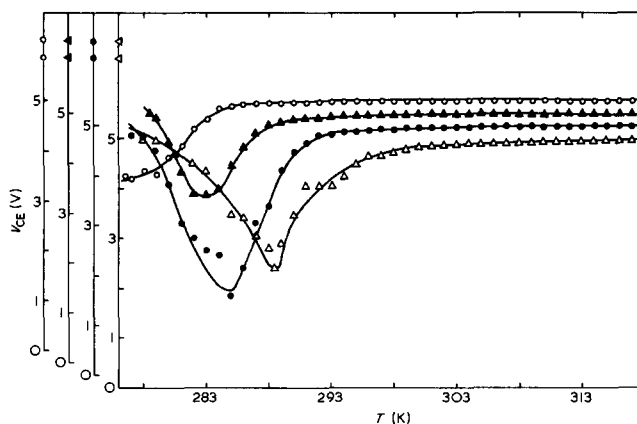


Figure 4 V_{CE} –temperature plot at a scattering angle of 90° in the PS–P α MS–MCH system. The blend ratio and other symbols are the same as those in Figure 3

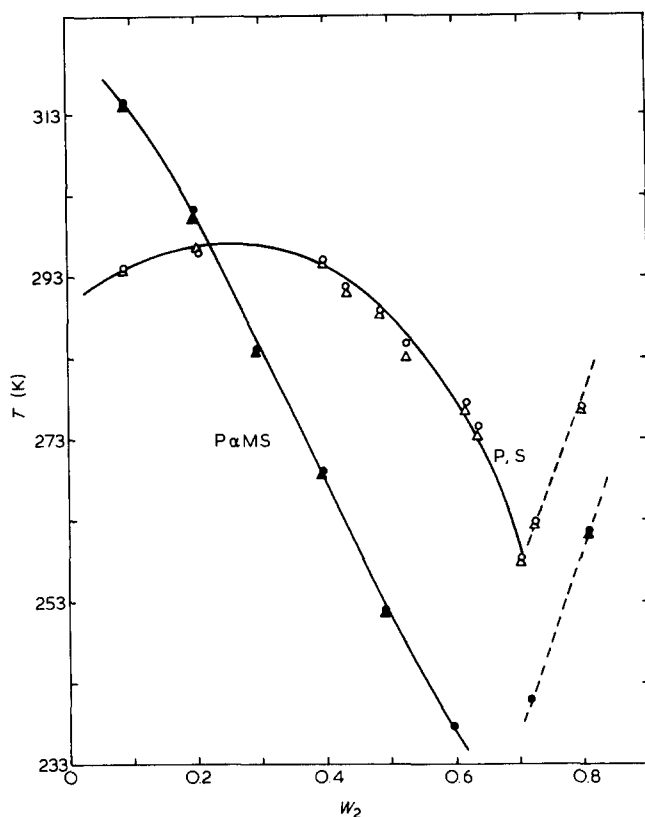


Figure 5 Phase separation temperature plotted against weight fraction of polymer (W_2) in the PS ($M_w \sim 1.75 \times 10^4$) - MCH (\circ, Δ) and P α MS (6.0×10^4) - MCH (\bullet, \blacktriangle) systems. The dotted lines indicate the pseudo T_g

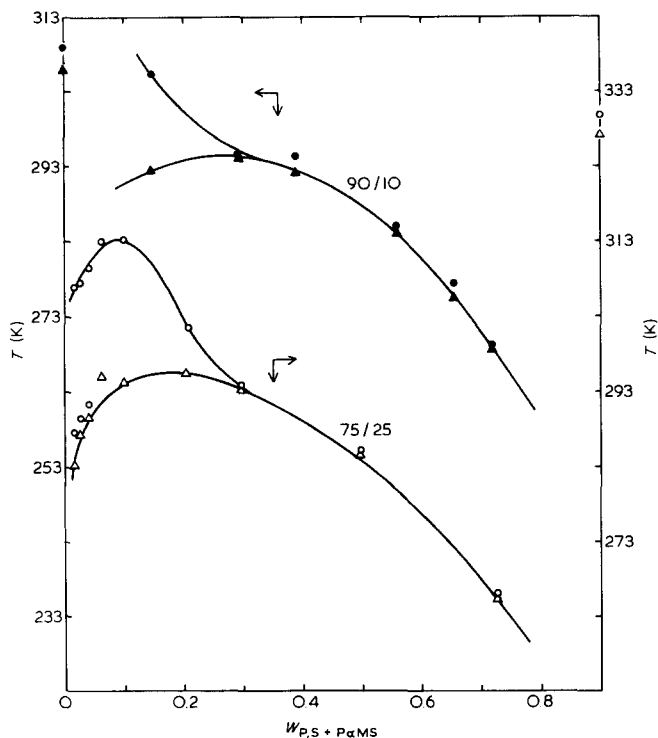


Figure 6 Phase separation temperature plotted against total weight fraction of polymer $W_{PS+P\alpha MS}$ in the ternary system of PS-P α MS-MCH. The blend ratio of PS/P α MS is 90/10 (\bullet, \blacktriangle) and 75/25 (\circ, Δ). Data are obtained at scattering angles of 0° (\bullet, \circ) and 90° (\blacktriangle, Δ)

ratio (PS/P α MS) of 90/10, 75/25, 60/40, 50/50 and 25/75 at concentrations $W_{PS+P\alpha MS}$ lower than 0.3 (see Figures 6 and 7). On the other hand the PST determined at an angle of 0° agreed with those at 90° for the binary systems PS-MCH and P α MS-MCH and also for the ternary system at $W_{PS+P\alpha MS}$ higher than 0.3.

DISCUSSION

The main purpose of this work is to establish the phase diagram of the PS-P α MS system from the ternary phase diagram of the PS-P α MS-MCH system by extrapolating to zero solvent concentration. In previous work²² it has been found, from the T_g measurement of PS-P α MS mixtures, that PS ($M_w = 2.04 \times 10^4$) and P α MS (9.09×10^4) blends show one T_g in all proportions if they are cast from toluene, while they show two T_g s over a wide concentration range if cast from propylene oxide. It is very interesting to determine the PD of the binary PS-P α MS system using the PD of the ternary system to elucidate the process of formation of polymer blends. As is shown in Figures 6 and 7 the PST in the ternary system decreases monotonically up to $W_{PS+P\alpha MS} = 0.8$. It may be very difficult to determine the PST for the PS-P α MS-MCH system over $0.8 < W_{PS+P\alpha MS} \leq 1.0$, which appear under the T_g of the system.

The blend samples in this work were obtained by casting from dilute solutions ($W_{PS+P\alpha MS} = 0.08$) of PS/P α MS in MCH and allowing MCH to evaporate at a temperature of $\sim 55^\circ\text{C}$, which is higher than the PST for $W_{PS+P\alpha MS} = 0.08$. This means that the dried blend samples do not pass through the phase separation region during the evaporation of the solvent, while the process passing

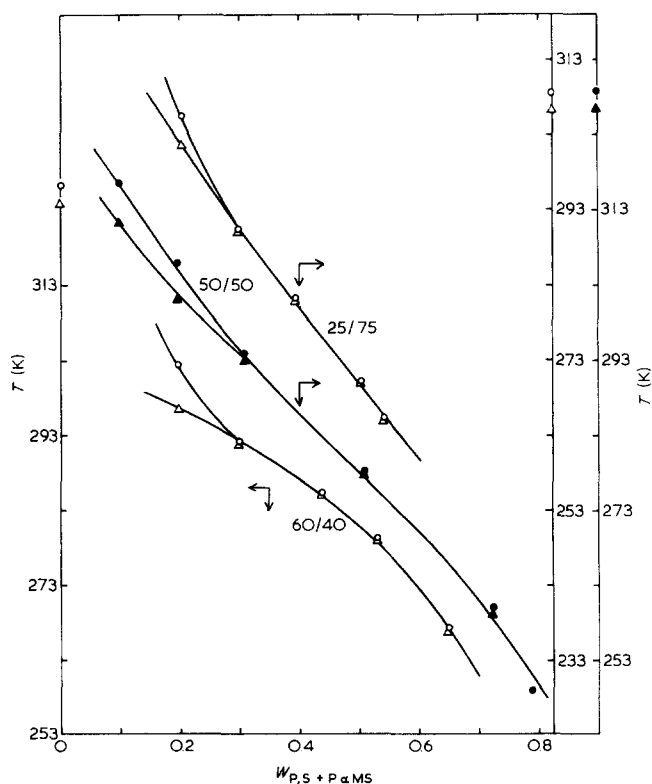


Figure 7 Phase separation temperature plotted against total weight fraction of polymer $W_{PS+P\alpha MS}$ in ternary system of PS-P α MS-MCH. The blend ratio of PS/P α MS is 25/75 (\circ, Δ), 50/50 (\bullet, \blacktriangle) and 60/40 (\circ, Δ)

below T_g line during the evaporation results in the freezing of molecular motion of polymer segments in the blend. From these facts one can say that the blend samples of PS/P α MS in this work are in the miscible state originally. It is very important in the preparation of extremely highly concentrated samples to know whether the original blend samples are or are not in the miscible state. The PD of PS/P α MS for the concentrations $W_{PS+P\alpha MS} = 0.6, 0.7$ and 0.8 obtained in this work are given in Figure 8.

Three types of phase separation behaviour are observed in the PS-P α MS-MCH system. The first one is observed at concentrations $W_{PS+P\alpha MS}$ lower than 0.042 where two PST are observed at an angle of 0° and one PST at 90° . The two PST are located in the vicinity of the PST for the binary systems PS-MCH and P α MS-MCH and the lower one of the two PST disappears with increasing $W_{PS+P\alpha MS}$. The second is characterized by the fact that the PST detected at an angle of 0° are higher than those at 90° and approach those at 90° with increasing polymer concentration ($W_{PS+P\alpha MS}$) over the range 0.2 to 0.3. The third one is characterized by the feature that the PST at the angle of 0° are equal to those at 90° . It is noteworthy that the value of $W_{PS+P\alpha MS} = 0.3$ is a characteristic concentration, at which the two PST detected at angles of 0° and 90° converge to one PST irrespective of the blend ratio.

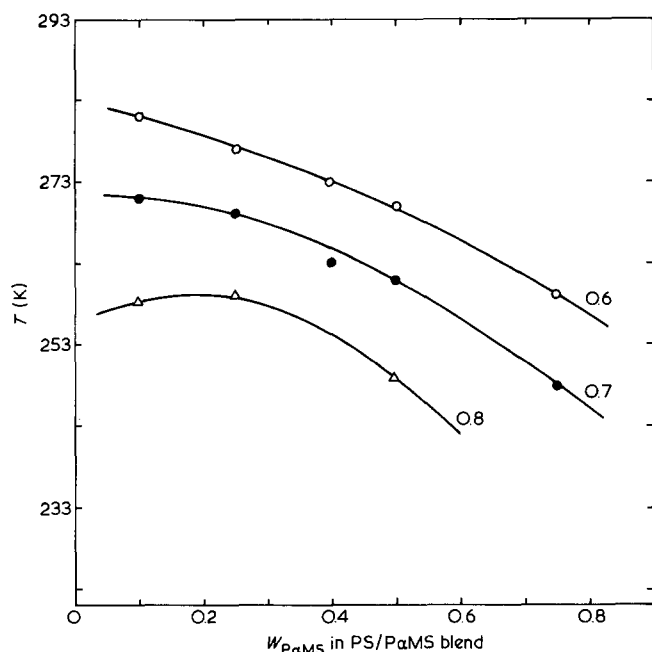


Figure 8 Phase separation temperature plotted against weight fraction of P α MS ($W_{P\alpha MS}$) in the PS/P α MS blend. The values of $W_{PS+P\alpha MS}$ are 0.6 (○), 0.7 (●) and 0.8 (△)

CONCLUSIONS

It has been established from the phase diagram of the PS-P α MS-MCH system that the polymer blend of PS ($M_w = 1.75 \times 10^4$) and P α MS (6.0×10^4) cast from MCH at about 55°C is compatible at room temperature and the maximum PST for the PS-P α MS-MCH at the concentration $W_{PS+P\alpha MS} = 0.8$ is around -14°C . However, the PST for the binary PS-P α MS system was not determined in this work. It is suggested that the evaporation temperature in the production of the polymer blend from ternary solution is one of the important factors controlling the compatibility of a blend.

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