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The Location of Both Upper and Lower Critical Phase Boundaries in a Polystyrene-Poly(Vinyl Methyl Ether) Blend

J.M.G. Cowie and S. Saeki*

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

SUMMARY

A method has been developed for the location of both upper and lower critical cloudpoint curves in miscible polymer blends. Ternary, solvent (1)/polymer (2)/ polymer (3) systems have been used and the phase separation temperatures have been measured in solutions containing a fixed ratio of the two polymers. Extrapolation to zero solvent then gives the critical temperatures for the blend. By measuring these for several blend compositions a miscibility range can be established for a quasi-binary blend of components with specific molecular weights. Using this method, both upper and lower critical temperatures have been established for a polystyrene-poly(vinyl methyl ether) mixture.

INTRODUCTION

There is now ample evidence, both experimental and theoretical (McMASTER, 1973; PAUL and NEWMAN, 1978; OLABISI et al., 1979) to show that quasi-binary blends of miscible polymers can exhibit lower critical solution temperatures (L C S T). The presence of an upper critical solution temperature (U C S T) is often observed in mixtures of oligomers, especially when the heat of mixing is endothermic, but is less likely to be seen in high molecular weight blends where the thermodynamic parameters tend to be unfavourable. It has also been suggested, that if a U C S T does exist, but lies below the glass transition temperature (Tg) of the blend, then it would be difficult to detect its presence experimentally.

For most quasi-binary polymer blends in which the L.C.S T has been found, the cloud point curves have been established by measuring the temperatures at which clear (miscible) blends of varying composition

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* Present Address: Faculty of Engineering, Fukui University, Fukui Shi 910, Japan

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have become opaque. This method can be used when the refractive indices of the two components are significantly different but it also assumes that phase separation in the blend is sufficiently rapid to allow an accurate determination of the demixing temperature. These criteria appear to be satisfied for blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME), for which lower critical cloud point curves have been measured (NISHI and KWEI, 1975). There does appear to be some time lag during thermally stimulated phase separation in these films, however, as NISHI et al.(1975) have reported both an 'initiation' and a 'completion' temperature which differ by about 15°-20°C even at a slow heating rate of 0.2°C/min.

In order to try to circumvent some of these difficulties, a new approach was attempted making use of ternary solvent (1)/polymer (2)/polymer (3) systems. In simple terms it involves measuring the UCST and LCST for several solutions of two polymers in a common solvent, at fixed ratios of polymer (2) to polymer (3), and extrapolating these data to zero solvent content. It has been found possible to make measurements up to weight fractions (W) (total polymer) of 0.8 thereby making the extrapolation to W=1 quite short. These extrapolated temperatures are then taken to be the LCST and UCST for the particular blend composition under study.

EXPERIMENTAL

Polymer samples. Polystyrene samples with narrow molecular weight distributions were obtained from the Pressure Chemical Co., and one with M_w = 110,000 was selected for this study. Poly(vinyl methyl ether) was purchased from Polysciences and had $M_v \sim 31,000$. It was used without further fractionation and may be quite polydisperse.

Measurement of UCST and LCST. Solutions of the two polymers were prepared in toluene at fixed compositions of the two polymers but at varying total polymer concentration. Incipient phase separation temperatures, Tc, in both the upper and lower critical region were detected by measuring the decrease of intensity of a He-Ne laser beam, observed in the incident direction after it had passed through a capillary cell (i.d. 3mm) containing the solution. The temperature of the cell was controlled by placing it in a silicon oil bath accurate to 0.1°C. Two measuring techniques were used:

a) A "static" observation in which the solution was held at a fixed temperature for 1-6 days. If no phase separation occurred during that time, the temperature was altered by a small increment, either up or down, and the solution examined again for evidence of phase separation over a period of days. This was repeated until phase separation took place, consequently, the first point Tc, in both the upper and lower critical regions, could take some considerable time to establish. Having once located a cloud point temperature, for one concentration, the others followed more rapidly using the first as a guide.

b) A 'dynamic' method was also used in which the temperature was raised, or lowered, at 0.2°C/min and the temperature recorded at which phase separation occurred. While this gave slightly different values of Tc, these differences decreased as the total polymer concentration increased.

Values of Tc were extrapolated to zero solvent concentration and both methods, on extrapolation, gave the same limiting values Tc^o for the blends in the absence of solvent. Phase diagrams were constructed by plotting both upper and lower Tc^o values as a function of blend composition thereby establishing the cloud point curves.

RESULTS AND DISCUSSION

The validity of the method was tested by making measurements on a system for which lower critical cloud point curves had been reported but where these had been established using an alternative technique. The system selected was toluene (1)/ polystyrene (2)/poly(vinyl methyl ether) (3) with molecular weights PS = 110,000 and PVME = 31000. The final phase diagram, as shown in Figure 1, was constructed by taking the upper and lower critical values of Tc^o (ie Tc extrapolated to zero toluene concentration) for each of four blend compositions and drawing smooth cloud point curves through the data. The diagram demonstrates that there are regions of immiscibility above 75°C and below 35°C, with a miscible one phase region in between which tends to expand as the weight fraction of PS increases beyond 0.2. Comparison of our data in the lower critical region, with that of NISHI et al. (1975) for a PS(200,000)/PVME(51,500) blend shows that our phase separation temperatures correspond most closely with their "onset" temperatures rather than their "completion" temperatures. If demixing in

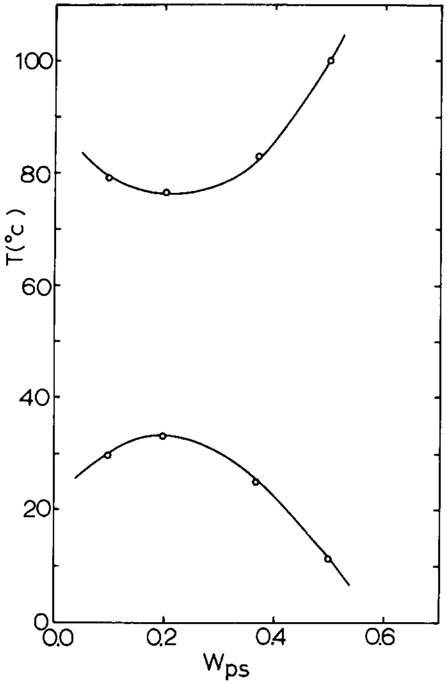

FIGURE 1. Upper and lower critical cloud point curves for a polystyrene(110,000)/poly vinyl methyl ether) (31,000) blend, obtained by extrapolation from toluene solutions.

NISHI's solvent free blends was slow, in spite of the low heating rate, as seems likely, then their "onset" temperatures may be a more realistic indication of the cloud points. The agreement between our results would then be quite reasonable, and as our measurements were made over a longer time interval and in less viscous media they should be more representative of the true cloud point curves.

No comparison can be made with other data for the UCST, but this clearly exists in PS/PVME blends, if our measurements are meaningful. The fact that one can establish a UCST curve may be due to the fact that the solvent present depresses Tg and so Tc^{o} is not measured directly for a blend in the glassy state.

Although one must rely on the validity of the extrapolation, the apparent success in establishing a realistic LCST curve gives some credence to the corresponding UCST curve.

While the extrapolations were short, and should be relatively accurate, we are aware of the possibility that a system under investigation could have a phase diagram of the type shown schematically in Figure 2.

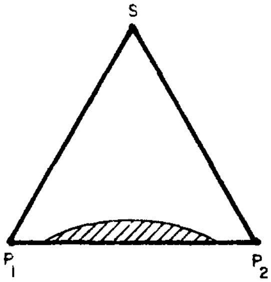

FIGURE 2. Schematic representation of a phase diagram for a solvent (S)/polymer (P_1)/polymer (P_2) system in which the polymers are incompatible in the bulk but are miscible in a common solvent.

In such a case, if the two phase region lay below the limiting solvent concentration of our experimental technique then misleading results would be obtained. This situation should not exist in the present system.

BANK et al.(1971) have demonstrated the importance of solvent in the PS/PVME system. Whereas benzene, toluene and tetrachloroethene gave miscible blends, the use of $CHCl_3$, dichloromethane and trichloroethene led to immiscibility. This aspect was investigated further by PATTERSON et al.(1977a,b) who demonstrated the importance of the "$|\Delta\chi|$ effect". They showed that when the difference in polymer/solvent interaction parameters $|\chi_{12}-\chi_{13}|$ was small, then miscible blends resulted, but that immiscible blends were formed when $|\Delta\chi|$ was large. Toluene has a low $|\Delta\chi|$ and our data show a good miscibility range, but we are now investigating the effect of solvents with high $|\Delta\chi|$ on the shape of the cloud point curves.

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