

## Phase diagram for polystyrene/poly(vinylmethyl ether) blends by $^{13}\text{C}$ -NMR

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### SUMMARY

The composition of each phase separated domain, thus the phase diagram, has been determined by  $^{13}\text{C}$  NMR methods for thermally phase separated polystyrene (PS)/poly(vinylmethyl ether) (PVME) blends. Even in compatible PS/PVME blend  $T_{1\rho}^{\text{H}}$  at  $-5^\circ\text{C}$ , determined indirectly via  $^{13}\text{C}$  intensities show microheterogeneity at an estimated  $20 \text{ \AA}$  level if the PVME content is greater than 50%.

### INTRODUCTION

Many techniques have been used to characterize miscibility and phase separation in polystyrene/poly(vinylmethyl ether) (PS/PVME) blends including equilibrium solvent absorption(1), excimer fluorescence(2), FTIR(3), SANS(4) and NMR(1). By the NMR technique all the protons in a homogeneous domain relax uniformly due to spin diffusion processes. Consequently, heterogeneity can be detected from multi-exponential decay of spin magnetization. The observing scale, i.e. the dimension of phase separation, depends upon the type and rate of relaxation, i.e.  $T_1^{\text{H}}$ ,  $T_1^{\text{C}}$ , and their counterpart in the rotating frame  $T_{1\rho}^{\text{H}}$ ,  $T_{1\rho}^{\text{C}}$ . Several studies had established the value of NMR in quantitative studies of polyblends(5,6). Kwei(1) observed a single  $T_1^{\text{H}}$  for PS/PVME blends of all compositions cast from toluene solution. However two  $T_1^{\text{H}}$ 's were found when the temperature was raised above the lower critical solution temperature(LCST) or in blends cast from chloroform solution. Recently, Ernst(7) used saturation transfer to determine the composition in each phase. Kaplan(8) analyzed the  $^{13}\text{C}$  magic angle spinning Goldman-Shen data to show that mixing occurs at segmental level(0.6-2 nm) in compatible blends. In the above investigation, the composition of domains after phase separation were unknown

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The central purpose of this study is to determine the LCST phase diagram of PS/PVME.

#### EXPERIMENTAL

PS was from Pressure Chemical Co. having  $M_w=100,000$   $M_w/M_n=1.06$ . PVME, from Aldrich as 50% solution in toluene, was dried at 60°C in a vacuum oven to constant weight. Films of PS/PVME mixtures were cast on glass slides from 5% toluene or chloroform solution and the solvent evaporated for one day at ambient temperature followed by 60°C in-vacuo for three days. A transparent film was obtained when the mixture was cast from toluene solution in contrast to a cloudy film from chloroform solution. Phase separation was accomplished by heating samples to specified temperature in an oil bath ( $\pm 2^\circ\text{C}$ ) for 30 minutes then quenched with ice/water. These blends were subsequently ground to a powder at 77°K in a freezer miller (Spex Industries, Edison NJ). The NMR spectrometer and pulse sequence have been described elsewhere(9).

#### RESULTS

Films cast from chloroform are cloudy and are obviously immiscible blends. The resonances of the PS have the same  $T_{1\rho}^H$  as the homopolymer. The disappearance of the  $\text{OCH}_3$  and  $\text{OCH}$  peaks of PVME is due to ineffective cross-polarization and unrestricted mobility(8).

Films cast from toluene solution at all PS/PVME compositions are transparent indicating homogeneity in the visible region. However, films of various blend compositions differ in their miscibility at the molecular level. Specimens containing less than 50% of PVME are characterized by a common  $T_{1\rho}^H$  for all protons of both PS and PVME. The blends are thus homogeneous at roughly a 25 Å scale due to averaging of proton relaxation results via spin diffusion. The results are consonant with Goldman-Shen measurement(8). However, samples containing more than 50% of PVME are characterized by a biphasic decay of spin magnetization. The results showed these blends to be microscopically heterogeneous at about a 20 Å scale. This microheterogeneity was also deduced by Kwei(1) from his observation of two  $T_2$ 's for the 50/50 PS/PVME blend.

The composition of phase separated domains can be determined from the  $T_{1\rho}^H$  values. There is a relationship where the  $T_{1\rho}^H$  of a miscible blend is the proton mole fraction average of the  $T_{1\rho}^H$ 's of the constituent

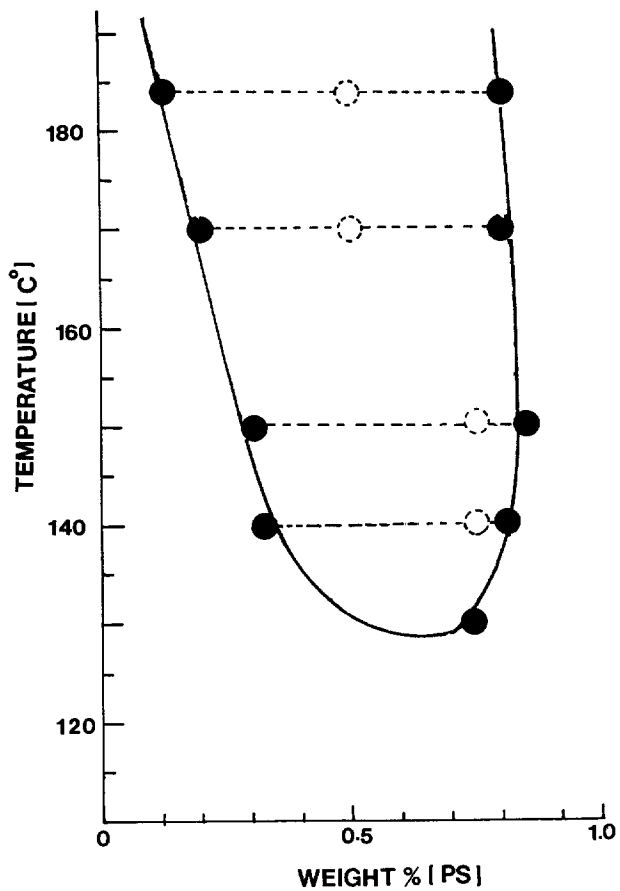


Figure 1: Weight composition of PS versus temperature. The full circles represent the composition after phase separation. The dotted circles represent starting compositions.

homopolymers. This proportionality was seen in certain system(6), but does not hold for the PS/PVME blends. The proton relaxation of PVME in the blend is slower than in homo-PVME due to reduction of its chain mobility in the blend. The contribution to  $T_{1\rho}^H$  from the glassy PS is also reduced. In order to obtain the phase separated domain compositions, the variation of  $T_{1\rho}^H$  versus PS content, i.e. blend composition, was determined experimentally to give the needed calibration curve.

Toluene solutions of PS and PVME with 75 and 50 weight% of PS were cast into films. Specimens were heated to a desired temperature, held there for 30 mins, and quenched. From the relaxation data and using the calibration curve a phase diagram was established (Figure 1). This determination demonstrates that  $^{13}\text{C}$  NMR spectroscopy is capable of greatly extending the quantitative description of the phase diagram phenomena. The NMR phase diagram is narrower than the corresponding cloud point curve(4). Explanation of the difference is underway which may contribute toward the detailed understanding of spinodal decomposition.

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