

Miscibility of syndiotactic polystyrene/poly(vinyl methyl ether) blends

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The dependence of miscibility on blend composition and temperature for syndiotactic polystyrene/poly(vinyl methyl ether) (SPS/PVME) blends, was investigated by solid state n.m.r. spectroscopy and d.s.c. and compared with that of the blend containing atactic polystyrene (APS). The temperature dependence of ^{13}C cross polarization/magic angle spinning intensities for the resonance of SPS/PVME blends indicates that these blends are phase separated, whereas for the APS/PVME blends, there is evidence of extensive mixing. These results are supported by the presence of one and two glass transition temperatures for the SPS/PVME and APS/PVME blends, respectively, on the d.s.c. thermograms.

(Keywords: syndiotactic polystyrene; poly(vinyl methyl ether); blends; miscibility; n.m.r.; d.s.c.)

Introduction

It has recently been reported that the morphology and the spherulite growth rate of syndiotactic polystyrene (SPS) in melt crystallized samples is strongly altered by blending with poly(vinyl methyl ether) (PVME)¹⁻³. In particular, whereas for the pure SPS only spherulites having positive birefringence are observed, in the case of the blend negative birefringence spherulites are also present. For the same crystallization temperature, (T_c), and composition the positive spherulites grow faster than the negative ones. The spherulite growth rate, G , of positive SPS spherulites grown from SPS/PVME blends at a given T_c is higher for blends than for pure SPS. This result was related to the increase of the mobility of the crystallizable molecules in the melt due to the addition of PVME, suggesting a certain degree of miscibility between the two components. The objective of this work is to use n.m.r. spectroscopy to analyse the miscibility behaviour of SPS/PVME blends in comparison with blends containing atactic polystyrene (APS).

Solid state n.m.r. spectroscopy was previously used to provide evidence of miscibility in APS/PVME blends. In particular Kaplan⁴ used magic angle spinning ^{13}C n.m.r. to investigate the compatibility of such blends. He found that the motion of the blend components was perturbed by blending and that the mixing occurred at a molecular level. Kwei *et al.*⁵ used pulsed n.m.r. to study the phase separation induced by thermal treatments. They observed that below 100°C, extensive mixing takes place even though complete interpenetration of APS and PVME chains does not occur because of physical restriction. Caravatti *et al.*⁶ used solid state two-dimensional ^1H - ^1H homonuclear correlation n.m.r., through spin diffusion on the same system. Spin diffusion between the two

species occurs for blends precipitated from toluene, confirming that mixed domains are present in these blends.

Experimental

Material and blend preparation. The molecular characteristics of the polymers used in the present work are reported in Table 1.

The APS/PVME and SPS/PVME blends were prepared by casting. The APS/PVME polymers were dissolved in toluene at about 60°C, whereas the SPS/PVME polymers were dissolved in *o*-dichlorobenzene at about 130°C.

N.m.r. experiments. Solid state ^{13}C cross polarization/magic angle spinning (CP/MAS) n.m.r. spectra were obtained at 75 MHz with a Bruker MSL-300 n.m.r. instrument, with H and ^{13}C 90° pulse widths of 4 ms. The spinning rate was chosen to be between 3 and 4 kHz in order to avoid side-band overlap for resonances of interest.

X-ray analysis. Wide angle X-ray scattering (WAXS) measurements were carried out on a Philips (PW 1050 model) powder diffractometer. The WAXS pattern of the SPS/PVME 70/30 blend is shown in Figure 1. Comparison of the spectrum with those reported in the literature for amorphous SPS⁷ indicates that the SPS is not able to crystallize during the preparation and that the sample is completely amorphous.

Calorimetric measurements. The glass transition temperatures, T_g , of the SPS/PVME blends were analysed by d.s.c. (Mettler TA 3000). The T_g s were obtained by heating the samples (about 10 mg) from -100 to 350°C at a rate of 10°C min⁻¹ and by recording the heat evolved during the scanning process as a function

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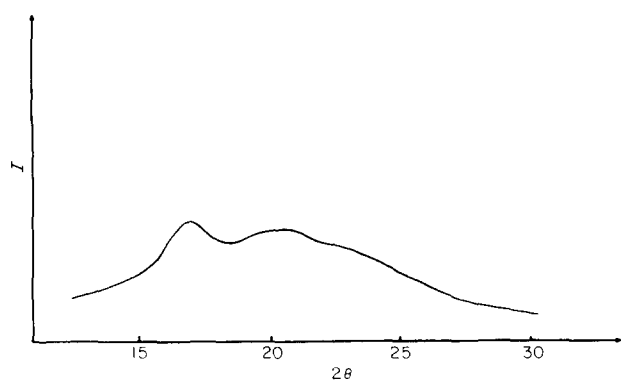


Figure 1 WAXS pattern for the SPS/PVME 70/30 blend film as obtained by solution casting

Table 1 Molecular characteristics of polymers

Sample	M_n	M_w	T_g (°C)
APS	9.4×10^4	1.0×10^5	100
SPS	2.3×10^5	7.1×10^5	93
PVME	3.4×10^4	6.5×10^3	-28

Table 2 Glass transition temperature for the SPS/PVME and APS/PVME blends as a function of composition

% PS	T_g (°C)	
	SPS/PVME	APS/PVME ^a
100	93	102
90	80	80
80	-18, 78	66
70	-17, 80	42
50	-16, 79	
0	-28	-28

^aData from ref. 13

of temperature. The T_g was taken as the temperature corresponding to 50% of the transition.

Results and discussion

Glass transition temperature. The T_g values of pure homopolymers and the SPS/PVME blends, as obtained by casting, are reported as a function of composition in Table 2. The T_g values of the APS/PVME blends from reference 13 are also reported. For the APS/PVME blends one T_g is always detected, with values depending on composition. The SPS/PVME blends with PVME contents higher than 10 wt%, on the other hand, show two T_g s whose values are different from those of the homopolymers but are almost independent of composition. These results indicate that the APS/PVME system is homogeneous, whereas the SPS/PVME blend is phase separated. The highest T_g could be due to an SPS-rich phase and the other to a PVME-rich phase. The approximate composition (wt%) of these two phases could be found by applying the Fox equation⁸:

$$\frac{100}{T_g(\text{blend})} = \frac{\text{wt}(\text{SPS})}{T_g(\text{SPS})} + \frac{\text{wt}(\text{PVME})}{T_g(\text{PVME})}$$

The resulting composition of the two phases is found to be about 92/08 SPS/PVME for the SPS-rich phase and 17/83 SPS/PVME for the PVME-rich phase.

N.m.r. results. Figure 2 shows CP/MAS spectra of APS/PVME 50/50, and SPS/PVME 70/30 and 50/50 blends, obtained at two different temperatures (25 and -50°C). The assignments of the observed resonances were obtained by comparison with previous assignments for pure SPS and pure PVME reported in the literature⁴.

In the case of APS/PVME blends it was found, by using FTi.r.^{9,10}, that the miscibility of the two components is due only to interactions between the electrons of the PVME methoxy group and those of the aromatic ring of PS. We are therefore particularly interested in the peak corresponding to the relaxation of PVME pendant methoxy group and comparing qualitatively the intensity of this peak (60 ppm, peak 1) with that relative to the relaxation behaviour of the carbons of the polystyrene pendant ring (129 ppm, peak 2). The results show clearly that the miscibility of these blends is dependent on the tacticity of PS.

For the APS/PVME 50/50 (wt/wt) blends (Figure 2a) the methoxy resonance has a large intensity at both temperatures, indicating that extensive mixing must occur to restrict PVME mobility so that significant cross polarization is achieved. This behaviour is in agreement with that observed by Kaplan *et al.* on the same system⁴. The ratio of the signal intensity of peak 1 and peak 2 for this blend is well below the value calculated for a mechanical mixture of the two components (3:1, ratio of areas), suggesting interpenetration of the APS ring carbons in the PVME domains. When temperature is decreased, the ratio of the area of the two peaks does not change significantly, whereas a large increase is observed for the other PVME peaks, indicating that the interpenetration of the PS and PVME domains is limited to the PS pendant ring with the PVME methoxy carbons, in agreement with the results reported in the literature^{9,10}.

For both SPS/PVME blends weak signals are detected at 25°C from the PVME carbons, indicating an incomplete cross polarization of the PVME blend component (Figures 2b and c). This result indicates that the blends are immiscible or phase separated, in agreement with d.s.c. results and the morphological evidence reported in references 1 and 2. In fact at this temperature the PVME phase is well above its glass transition and is motionally labile. When the temperature is decreased to -50°C the PVME mobility is restricted and an increase in signal intensity from all the PVME carbons is observed.

Experiments are in progress using solid state two-dimensional heteronuclear n.m.r., which allows examination of H spin diffusion between the two phases of these two blends. Preliminary results seem to indicate that the domain size associated with PVME in the blend is greater than 2.0 nm. We aim to obtain a more precise picture of the composition of the phases over a variety of domain sizes, and to gather data on the effect of chain microstructure on the morphology associated with the interaction of these two blend components.

Conclusions

We have used n.m.r. techniques (CP/MAS, ¹³C spectroscopy) together with d.s.c. to investigate the compatibility of PS/PVME blends as dependent on PS tacticity.

Our n.m.r. experiments reveal that for an SPS/PVME blend the molecular motions of the two components are not perturbed by blending. From the d.s.c. results, phase

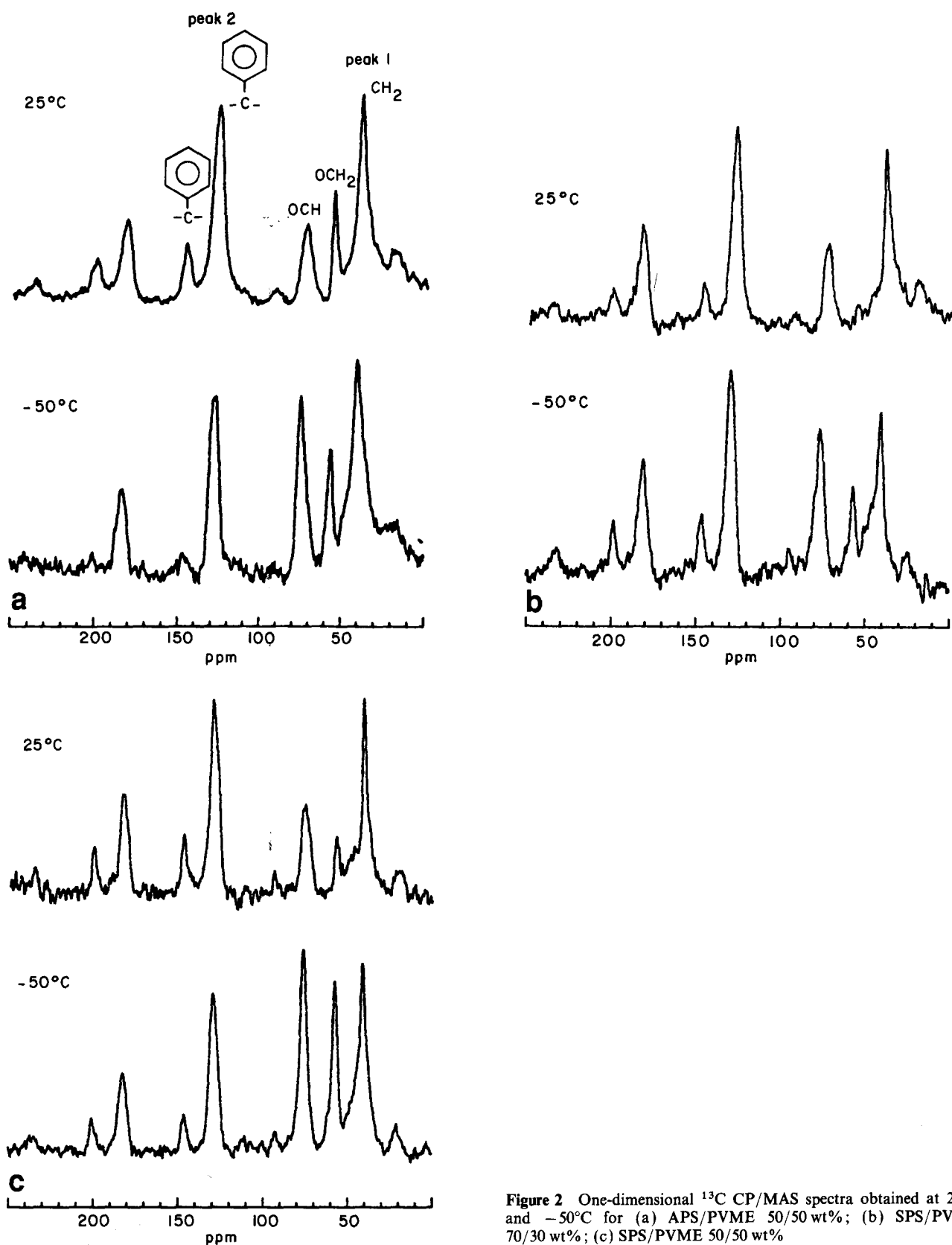


Figure 2 One-dimensional ^{13}C CP/MAS spectra obtained at 25°C and -50°C for (a) APS/PVME 50/50 wt%; (b) SPS/PVME 70/30 wt%; (c) SPS/PVME 50/50 wt%

separation can be assumed. In the case of blends containing APS, mixing is found to occur, which is in agreement with several papers reported in the literature for APS/PVME blends. This result indicates that APS is more miscible with PVME than is SPS.

The influence of component tacticity on blend miscibility was studied previously for the poly(ethylene oxide)/poly(methyl methacrylate) system^{11,12}. From

that study it was also found that the blend containing the atactic polymer was more miscible than the blend containing the polymer with regular configuration.

The difference in miscibility observed in this paper for the APS/PVME and the SPS/PVME blends may also be due to the different solvents and/or casting temperatures used in the blend preparation^{13,14}. In fact for the APS/PVME blend it is found that the miscibility

is strongly dependent on the solvent used as well as on the temperature. Further work is in progress on this subject.

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