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High resolution solid state ^{13}C nuclear magnetic resonance study of poly(ether sulphone)/polyimide blends

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N.m.r. evidence has been obtained for miscibility on a molecular scale in blends of the poly(ether sulphone) (PES) and the polyimide (PI) XU 218 (the condensation product of 3,3'-4,4'-benzophenonetetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindan). Changes in the imide carbonyl line shape of the ^{13}C CP/MAS spectrum of XU 218 indicate an increase in polarity of the environment of this carbonyl which is the result of solvation of polyimide by the PES chain. The presence of XU 218 in a blend with PES results in a decrease in the value of $T_{1\rho}^{\text{H}}$ for the polyimide from 14.3 ms for the pure component to 7.1 ms for a 25/75 wt% PES/PI blend. The $T_{1\rho}^{\text{H}}$ of pure PES is 4.5 ms. Log plots of the decay in the ^{13}C CP/MAS resonance intensity with contact time are linear. This relaxation behaviour is consistent with miscibility in these blends with a domain size less than 20 Å.

(Keywords: ^{13}C n.m.r.; poly(ether sulphone); polyimide; blends; miscibility)

Introduction

The apparent miscibility of polymer blends containing poly(ether sulphone) (PES) and several polyimides (PI) (including that shown in *Figure 1*) (refs. 1, 2) has been reported. The goal has been to understand the molecular nature of the interaction between the components of these blends and to obtain information about the internal molecular structure and dynamics which would aid in the understanding of the thermodynamic and mechanical properties. In particular, solid state n.m.r. spectroscopy can provide information about specific molecular interactions and dynamics in blends. In this communication we present the characterization of the ^{13}C CP/MAS n.m.r. spectra of the PES/XU 218 blend system and report evidence of miscibility obtained in a study of the proton rotating frame spin lattice relaxation time $T_{1\rho}^{\text{H}}$.

Experimental

The condensation product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindan (XU 218) was provided by Ciba-Geigy Corporation, USA. Poly(ether sulphone), trademark Victrex, was supplied by ICI Americas Inc., USA.

Both XU 218 and PES are amorphous polymers with reported glass transition temperatures of 320°C and 230°C respectively. Blends were prepared by mixing 3% (wt/vol) solutions of the two components in the desired proportions followed by precipitation with 80/20 (wt/vol) methanol/water. The blend samples were filtered, washed with water and vacuum dried at 150°C for several days. The resulting blends were shown to be miscible by use of differential scanning calorimetry (d.s.c.) although it is also known that phase separation begins to occur immediately above the blend T_g (ref. 1).

^{13}C CP/MAS experiments were carried out at 50.3 MHz on an IBM Instruments AF-200 spectrometer at ambient temperature with ^{13}C and ^1H radiofrequency field strength of 50 kHz, and the proton field was maintained at full power for decoupling³. Samples were

contained in sapphire rotors (Doty Scientific) with Kel F endcaps and were spun at approximately 4 KHz. Spectra were obtained with a contact time of 1.5 ms, a repetition time of 3 s and with 600–1200 transients. The value of $T_{1\rho}^{\text{H}}$ was obtained from the decay of the ^{13}C CP/MAS intensity with increasing contact time at long contact times^{4–8}. Chemical shifts are reported relative to tetramethylsilane (TMS).

Results

Figure 1 shows the structures of the two blend components, PES and XU 218 and their respective ^{13}C CP/MAS spectra. The chemical shift assignment of the ^{13}C CP/MAS spectrum of XU 218 has been presented elsewhere⁹. This assignment, and that of the PES component, is shown in *Figure 1* and in *Table 1*. These assignments were based on a comparison of literature chemical shift data and have been supported in part through the use of interrupted decoupling methods¹⁰.

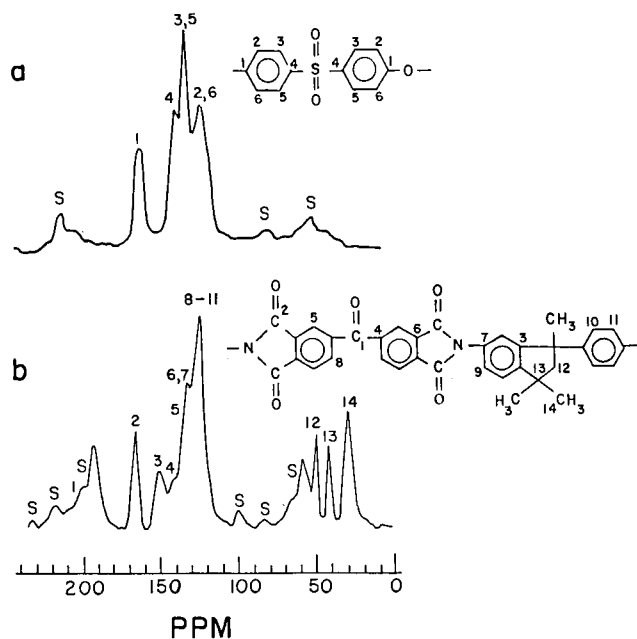


Figure 1 ^{13}C CP/MAS n.m.r. spectra of (a) PES, (b) XU 218. Structures and assignment are shown, side bands are denoted as S

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Table 1 ¹³C CP/MAS chemical shifts of XU 218 and PES (ppm from TMS)

XU 218		PES	
Chemical shift	Carbon	Chemical shift	Carbon
~200	1	—	—
165	2	159	1
150	3	—	—
140	4	—	—
133	5	136	2,6
130	6, 7	130	3,5
124	8–11	121	4
50	12	—	—
42	13	—	—
30	14	—	—

The spectrum of PES consists of four lines arising from the four types of carbon present. The resonances at 159 ppm and 136 ppm have been attributed to the carbons bound directly to ether oxygens and to sulphur atoms respectively. The absorption at 130 ppm has been assigned to carbons 3 and 5 and the absorption at 121 ppm has been assigned to carbons 2 and 6. These assignments are consistent with the generally observed inductive effects of oxygen and sulphur upon the *ortho*, *meta* and *para* positions of the phenylene ring^{11,12}. The resonances at 159 ppm and 136 ppm have been shown to originate from non-protonated carbons through the use of interrupted decoupling and short contact time methods¹⁰. Thus these resonances remain in a ¹³C CP/MAS spectrum with a short (60 μs) interruption of decoupling before acquisition, while they disappear from a spectrum obtained with a short (20 μs) contact time. The opposite is true for the protonated resonances at 130 ppm and 121 ppm. The resonance at 121 ppm (due to protonated carbons 2 and 6, *Figure 1*) has a greater line width than the resonance at 130 ppm (due to protonated carbons 3 and 5) and this resonance appears to be a doublet. The broadening which results from non-equivalence can be attributed to a ring conformation which is not symmetric with respect to the C—O—C bond. The spectrum of XU 218 is shown in *Figure 1b* with the chemical shift assignments which have been reported elsewhere⁹.

Figure 2 shows the ¹³C CP/MAS spectra of three blend compositions of PES and XU 218, i.e. 25/75, 50/50 and 75/25 wt% PES/XU 218, for the aromatic region between 80 and 180 ppm. The spectra of the blends are shown with a solid line, and for comparison the spectra of a mechanical mixture of the two components are shown with a dotted line. The spectra of the mechanical mixtures are strictly the sum of the spectra of the two pure components. The greatest difference between the spectra of the blends and those of the mechanical mixtures occurs in the spectral region between 160 and 170 ppm. This region contains two absorption lines, the first at 159 ppm (due to carbon 1 of PES) and the second at 165 ppm (due to the imide carbonyl of XU 218). The resonance at 165 ppm is predominant in the PI-rich blend (*Figure 2a*) and the resonance at 159 ppm is predominant in the PES-rich blend (*Figure 2c*). In each curve of *Figure 2* it can be seen that the PI carbonyl resonance of the blend spectrum is of lower intensity than the corresponding resonance in the spectrum of the mechanical mixture and in *Figure 2c* the PI carbonyl

resonance is also broadened by 2 ppm towards higher ppm values. This intensity change can be attributed to an increase in line width of the PI carbonyl resonance line which is proportional to PES composition of the blends.

A chemical shift towards higher ppm values is consistent with the solvation of the imide carbonyl in a more polar environment¹³. Such a polar environment could be provided through interaction with the ether oxygen or sulphone groups of PES and should depend upon the geometry of interaction between the two chains. For these blends of two amorphous polymers, in which there is no single geometry of interaction between chains, there should be a distribution of carbonyl environments and this distribution should result in a distribution of imide carbonyl carbon chemical shifts. The result should be a broadening of the resonance line towards higher ppm values. A similar change in the PI carbonyl line width has been observed for blends of PI with polybenzimidazole (PBI)⁹. For PBI/PI blends the change in line shape of the imide carbonyl shows that up to 40% of the imide carbonyl carbons are shifted upfield by up to 5 ppm. This change has been attributed to hydrogen bonding between the imide carbonyl and the imidazolic proton of PBI. One should expect a polar interaction between PES and PI to result in a smaller chemical shift than a hydrogen bond. This change in line shape is the only observable difference between the spectra of blends and mechanical mixtures. Though small, the presence of this difference provides direct evidence for an interaction between the two polymer chains in the blend.

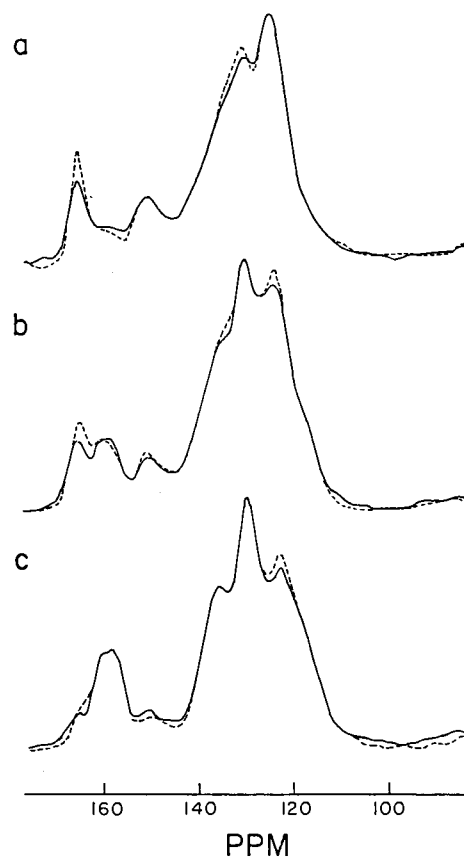


Figure 2 ¹³C CP/MAS n.m.r. spectra of (—) PES/XU 218 blends and (---) mechanical mixtures. 1.5 ms contact time, 4 KHz spinning rate. (a) 25/75 wt%; (b) 50/50 wt%; (c) 75/25 wt%

Table 2 Proton rotating frame spin-lattice relaxation times, $T_{1\rho}^H$ (ms) for PES, XU 218 and 75/25, 50/50 and 25/75 wt% PES/XU 218 blends

PES		PES/XU 218 75/25 wt%		PES/XU 218 50/50 wt%		PES/XU 218 25/75 wt%		XU 218	
Observed peak ^a	$T_{1\rho}^H$	Observed peak ^a	$T_{1\rho}^H$	Observed peak ^a	$T_{1\rho}^H$	Observed peak ^a	$T_{1\rho}^H$	Observed peak ^a	$T_{1\rho}^H$
				165	10	165	11.6	165	17
159	4.5	159	7.1	159	8.1	—	—	—	—
136	4.3	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	130	14.5
—	—	—	—	—	—	—	—	124	14.0
—	—	—	—	50	8.1	50	10.4	50	14.2
—	—	42	7.1	42	8.2	42	10.4	42	14.4
—	—	30	7.1	30	8.1	—	—	30	14.2
—	4.4 ^b	—	7.4 ^b	—	9.1 ^b	—	12.2 ^b	—	14.3 ^b

^a In ppm downfield from TMS^b Theoretical average values of $T_{1\rho}^H$ (refs. 15, 16)

The proton rotating frame spin lattice relaxation times, $T_{1\rho}^H$, of these PES/PI blends have been examined and the results also provide evidence for miscibility. It is known that when the domain size of each component is less than about 30 Å*, the protons of the two polymer chains couple through spin diffusion. The protons of the component with the longer $T_{1\rho}^H$ have a relaxation time determined by the domain size and the relaxation time of the component with the smaller value of $T_{1\rho}^H$. To show that spin diffusion determines $T_{1\rho}^H$ it is necessary to show that all protons of the blend have the same value and to show that each decay is a single exponential. This measurement has become an accepted n.m.r. criterion for miscibility⁴⁻⁷.

Table 2 lists the values of $T_{1\rho}^H$ at the major carbon resonances of PES, XU 218 and their blends. These values have been determined from the dependence of the ¹³C CP/MAS resonance intensity upon cross polarization contact time for contact times greater than 2 ms. It can be seen in Table 2 that for each blend the cross polarization of every carbon resonance is determined by the same value of $T_{1\rho}^H$. Also it can be seen that the value of $T_{1\rho}^H$ for each is an average value between the values for the pure components. The theoretical average values of $T_{1\rho}^H$ of each blend are shown at the bottom of the table for comparison. These averages are based upon the mole fraction of protons of each chain type. It can be seen that $T_{1\rho}^H$ relaxation of PI, caused by PES, is greater than that predicted by a simple average of the $T_{1\rho}^H$ values for the pure components. A second mechanism, perhaps a change in internal molecular dynamics, may account for this stronger interaction between the two chains¹⁴. This possibility is under study.

Figure 3 shows several log plots of ¹³C CP/MAS resonance intensity versus contact time for several selected carbons of the two chains. Plots are shown for resonances which can unambiguously be assigned to a given chain. The resonances chosen were the three methyls (at 50, 42 and 30 ppm; 30 ppm is shown in Figure 3) of PI and the resonance of PES at 159 ppm. For the 25/75 wt% PES/PI blend the PI carbonyl resonance (165 ppm) overlapped the PES resonance at 159 ppm and thus this resonance is not presented. It can

be seen in Figure 3 that each of the log plots is linear and consistent with a single $T_{1\rho}^H$.

It should be noted that the apparent value of $T_{1\rho}^H$ for the imide carbonyl of pure PI is 3 ms greater than that obtained for the other carbons. This apparent difference is probably the result of poor carbon-proton coupling and an anomalously long cross polarization build-up time, and not a result of a different value of $T_{1\rho}^H$. Nevertheless, for the spectra of these blends, the $T_{1\rho}^H$ of the imide carbonyl carbon is similar to that of other carbons. The above observation implies that the distance between the imide carbonyl and its nearest neighbour protons is greater in the pure PI than in the blends. It should be noted that the effect of a longer cross polarization build-up time on the pure PI resonance intensity is small. This effect would tend to suppress the carbonyl resonance intensity in the mechanical mixture

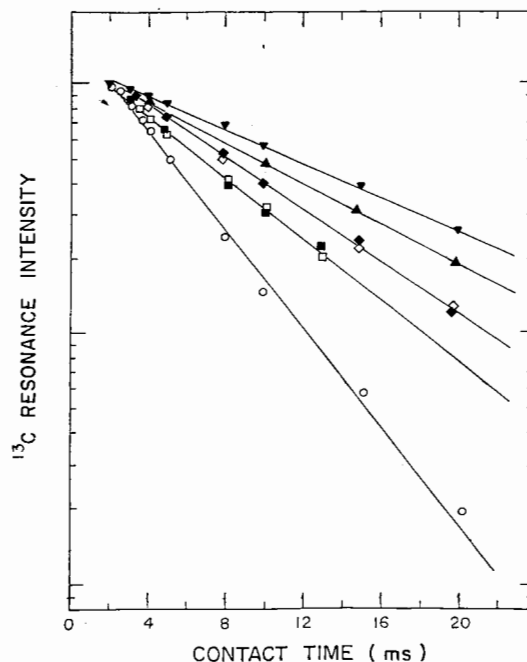


Figure 3 ¹³C CP/MAS resonance intensity versus contact time for PES (○), XU 218 (▼) and PES/XU 218 blends; 75/25 wt% (□, ■), 50/50 wt% (◇, ◆) and 25/75 wt% (▲). The open symbols refer to PES relaxation at 159 ppm; the filled symbols refer to XU 218 relaxation at 30 ppm

and so could not be responsible for the decrease in intensity of the imide carbonyl carbon in the blend (Figure 2).

The $T_{1\rho}^H$ measurements imply that the respective chains of PES and XU 218 are in intimate contact. The average contact distance can be estimated from the average diffusive path length $\langle r \rangle$, for spin diffusion, given by equation (1)^{15,16}:

$$\langle r \rangle = (6DT_{1\rho}^H)^{1/2} \quad (1)$$

The value D is the spin diffusion coefficient, a fixed value determined by the average proton-to-proton distance and the strength of the dipolar interaction; it has a typical value of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (refs. 15, 16). For a $T_{1\rho}^H$ of 10 ms, one obtains $\langle r \rangle = 20 \text{ \AA}$. Thus one can conclude that homogeneous mixing of these two blend components occurs on a scale of approximately 20 Å or less.

It should be noted that the values for the decay of $T_{1\rho}^H$ could also be affected by a change in the phenylene ring molecular dynamics of PES, for example an alteration in the distribution of 180° rotational jump rates¹⁴. A study of the dynamics of PES by deuterium quadrupole echo n.m.r. is in progress to determine the effects of dynamics on $T_{1\rho}^H$ and in general to determine the effect of blending on chain molecular dynamics. Nevertheless, either a spin-diffusion or a molecular dynamics mechanism for the change in $T_{1\rho}^H$ would require blends which possess short range spatial proximity between chains.

For these PES/PI blends, ¹³C line shape data and proton relaxation data have both provided evidence for molecular scale miscibility. The relaxation data have established that the domain size in these blends is less than 20 Å. A change in the ¹³C line shape of the PI carbonyl has indicated that a substantial number of contacts exists between the two chains.

The data in this report have shown that a simple polar interaction between two blend components can result in a detectable change in the ¹³C CP/MAS line shape of a blend component. The ¹³C CP/MAS spectra of blends are readily obtained and such changes can at least be used analytically to monitor the results of blend processing or potentially to provide data about specific

interactions between blend components. For most polymers the structural causes of the ¹³C CP/MAS line width broadening are still poorly understood, and usually simple line shape changes in the ¹³C spectra of blends are overlooked. The data presented here have indicated that, despite this uncertainty, a sufficiently strong interaction between blend components can lead to useful n.m.r. information about a polymer blend.

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