# Phase behaviour of blend systems containing nitrile copolymers examined by solid-state nuclear magnetic resonance and differential scanning calorimetry

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Solid-state cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (n.m.r.) and differential scanning calorimetry (d.s.c.) methods have been applied to examine the phase behaviour of binary blends of acrylonitrile/methyl acrylate/butadiene terpolymer (B210) with poly(ethylene-*co*-maleic anhydride) (PEMA) and poly(oxycarbonyloxy-1,4-phenyleneisopropylylidene-1,4-phenylene) (PC). Spin-lattice relaxation times of the protons in the rotating frame for blends and pure components have been measured by monitoring the CP-MAS generated carbon signal intensities as a function of variable proton spin-lock time. Since single component n.m.r. relaxation behaviour was observed over the entire range of compositions, phase homogeneity was demonstrated for the B210/PEMA system. These monophase blends exhibit single-component rotating frame spin-lattice relaxation times, intermediate in value as compared to the pure components. The d.s.c. examinations also showed that B210/PEMA blends have a single composition-dependent glass transition temperature ($T_g$). By contrast, the solid state CP-MAS n.m.r. study of B210/PC blends revealed that they display multicomponent relaxation behaviour indicating the presence of a mixed phase along with pure phases of each individual polymer. Additionally, based on the d.s.c. measurements, the $T_g$ behaviour of B210/PC blends appears to have a three-component character consistent with a multiphase system.

**(Keywords: single-phase polymer blend; multicomponent phase behaviour; proton spin-lattice relaxation time; glass transition temperature)**

## INTRODUCTION

Polymer–polymer blending is one of the most exciting and promising avenues to generate novel materials with improved performance, from largely available polymers. Among different types of blends one can distinguish two important categories. The first category includes so-called homogeneous polymer alloys. They exhibit properties intermediate between those of the individual components following a simple monotonic function which depend more or less on the ratio of the two polymers in the blend. The other category involves heterogeneous polymer blends. This type of blend has an important potential advantage, that of providing additivity of the phase properties along with new features deriving from a particular morphology.

The examination of glass transition behaviour has largely prevailed as a diagnostic test of miscibility in polymer blends. It relies on the assumption that the manifestation of a single glass transition may be intrinsically equated with segmental level homogeneity. More recently, solid-state nuclear magnetic resonance (n.m.r.) techniques also have been successfully employed to study polymer miscibility via measurement of spin-lattice relaxation times in both the laboratory frame and rotating frame, measurement of spin-diffusion, or cross-polarization for deuterated components.

In this study, both monophase and heterophase polymer blend systems have been examined by using solid-state cross-polarization magic angle spinning (CP-MAS), n.m.r. and differential scanning calorimetry (d.s.c.).

All the blends under investigation contain a high nitrile polymer (B210) as one of the components. Homogeneity over the entire range of compositions was found for binary blends of acrylonitrile/methyl acrylate/butadiene terpolymer (B210) with poly(ethylene-*co*-maleic anhydride) (PEMA). Blends of the nitrile polymer with poly(oxycarbonyloxy-1,4-phenyleneisopropylylidene-1,4-phenylene) (PC) have been proven to exhibit multiphase behaviour.

## EXPERIMENTAL

### *Sample preparation*

The high nitrile polymer used throughout this study is a copolymer of acrylonitrile and methyl acrylate (75/25) grafted onto a rubbery copolymer of butadiene and acrylonitrile (70/30), and having a number average molecular weight of about 50 000. This material is a commercial product sold under the trade name of Barex 210 by BP America Inc. PEMA and PC were purchased

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from Aldrich Chemical Co. and used without further purification. Blends were prepared in molten state in a torque rheometer (C.W. Inc., model EPL-V5501) Brabender. Films were obtained by compression moulding the melt in a Carver press set at 190°C followed by slow cooling.

### *Measurements*

The CP-MAS $^{13}C$ n.m.r. spectra of all samples were obtained on a Nicolet S-100 solid-state spectrometer. This spectrometer operates at 25.2 MHz $^{13}C$ resonance frequency and 100.1 MHz proton frequency. The 90° proton pulse was 5.0 $\mu$s. For all polymer and polymer blend samples, a 2 s recycle delay was used, and a 1 ms contact time. For $T_{1\rho}$ experiments, the pulse sequence of Stejskal *et al.*[1] was employed, and the spin-lock condition was varied from 0–25 ms. Magic-angle spinning was accomplished in a zirconia rotor at approximately 4 kHz spinning speed in a Chemagnetics stator adapted for the S-100. The samples were typically films which were cut into small squares and packed into the zirconia rotor. In some cases, a Teflon sleeve was first inserted into the rotor, and sample then packed into the opening of the sleeve, in order to provide a uniform weighting at the outer edge of the rotor for improved spinning.

Differential scanning calorimetry measurements were performed on a Perkin–Elmer instrument, model DSC-4 equipped with a computerized data station. The d.s.c. scans were performed at a heating rate of 10°C min$^{-1}$. The glass transition temperature ($T_g$) was defined as the midpoint of the change in heat capacity.

## SOLID STATE N.M.R. BACKGROUND

The use of high resolution, solid $^{13}C$ n.m.r. methods for polymer analysis is now fairly routine[2–9]. The most commonly used experiment is the CP-MAS $^{13}C$ n.m.r.[1]. Many variations of this experiment are conceivable, due to the many pulse sequences that have been developed for exploiting different features from the solid-state n.m.r. data[10,11]. It has been recently shown that direct cross-polarization from protonated polymer to a perdeuterated polymer is a very powerful method to prove blend miscibility, since the cross-polarization process is effective only over short distances[12,13]. This technique is not always practical, since a perdeuterated polymer is required as one of the components of the blend. One of the CP-MAS experiments that is accessible is a $^{13}C$ resolved experiment for measuring proton $T_{1\rho}$ values, and this has been shown to be valuable in studying polymer blend compatibility by Stejskal *et al.*[1]. Under the experimental conditions, the intensity of the carbon signals decays based on the proton $T_{1\rho}$ relaxation rates. The resulting high resolution $^{13}C$ n.m.r. spectra can usually be used to resolve the different components of the blend, and therefore, assign the proton $T_{1\rho}$ values to each component. This is not always possible when the $T_{1\rho}$ is measured directly from proton 'wide line' n.m.r. experiments since the differences in $T_{1\rho}$ values are not always large enough to resolve. When the resonances of a mixture are resolved in the $^{13}C$ n.m.r. spectrum, it is possible to study a multicomponent system very easily. This experimental approach was taken to analyse the binary polymeric blends of B210 with PEMA and PC.

## RESULTS AND DISCUSSION

### *Blends of B210 and PEMA*

*Solid-state n.m.r. study.* An example of the data set from a CP-MAS $^{13}C$ n.m.r. generated proton $T_{1\rho}$ relaxation experiment for B210 is shown in *Figure 1*. The following signals are observed: a methyl acrylate carbonyl at 175 ppm; a broad nitrile peak at 150–80 ppm; a methyl acrylate methoxy at 53 ppm; and a peak centred at approximately 30 ppm, which is due to CH and $CH_2$ carbons of acrylonitrile and methyl acrylate. The nitrile peak is broad and asymmetric due to a large $^{14}N$ quadrupolar interaction. As was indicated before, all protons in a homogeneous material have a single $T_{1\rho}$ value. It can be seen in *Figure 1* that all of the signals of the B210 decay at the same rate. A linear fit of the intensities from this data set is shown in *Figure 2*. For this particular fit, the peak at approximately 30 ppm was used because it is the largest one in the spectrum. However, the same result is obtained for any of the peaks, since they all decay with the same rate constant. The proton $T_{1\rho}$ values of a series of B210 samples were obtained, and it was determined that $T_{1\rho}$ was in the range of 14–16 ms. The observed variance is not unexpected, since the composition of the B210 does have some degree of variability from sample to sample, especially with respect to the amount of elastomer and stabilizer additives. It was found that under the conditions of 1 ms contact time, there were no signals observed from the additives or elastomer phase in any of the B210 samples. Due to their increased degree of mobility, and therefore reduced dipolar interactions, the additives and elastomer do not cross-polarize efficiently at 1 ms contact time. However, their presence and the degree of grafting to the elastomer can affect the entire polymer's mobility and

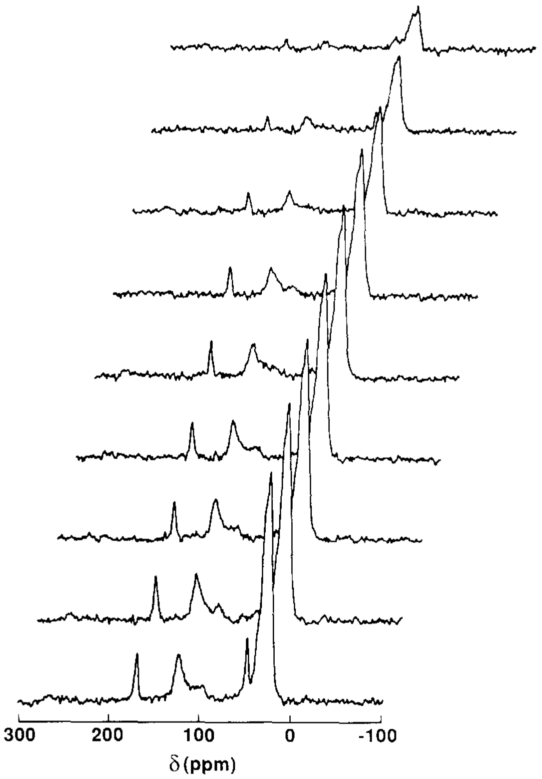

**Figure 1** B210 proton $T_{1\rho}$ data set from $^{13}C$ CP-MAS n.m.r. spectra at varying proton spin-lock times

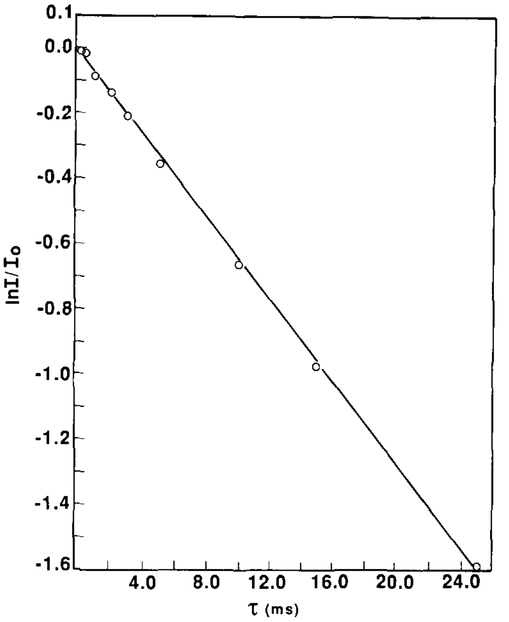

**Figure 2** Fit of intensity data *versus* spin-lock time from $^{13}$C CP-MAS spectra of B210 from $T_{1\rho} = 15.7$ ms

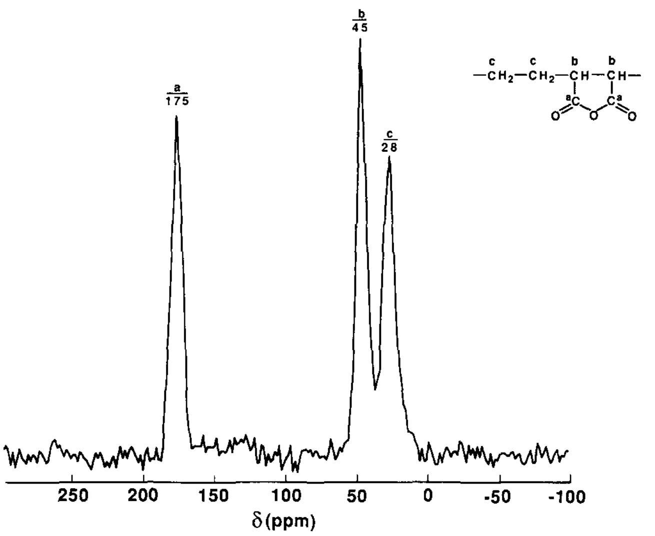

**Figure 3** $^{13}$C CP-MAS n.m.r. spectrum of PEMA

therefore the $T_{1\rho}$ value observed. This could explain the range of $T_{1\rho}$ values observed.

The CP-MAS spectrum of PEMA is shown in *Figure 3*. The assignments for peaks in this spectrum are: maleic anhydride carbonyl at 175 ppm; the maleic anhydride CH at 45 ppm; and the ethylene $CH_2$ at 28 ppm. The $T_{1\rho}$ experiment for this material also was performed, and the $T_{1\rho}$ value was found to be 4.2 ms. The $T_{1\rho}$ data set for a 50/50 (wt%) blend of B210 and PEMA is shown in *Figure 4*. As can be seen, there is a significant degree of overlap for the B210 and PEMA spectra. The methoxy and nitrile peaks of the B210 are somewhat resolved, but neither are the optimum peaks for generating the intensity data fit. The PEMA peak at 45 ppm is almost resolved, but has the B210 peaks at 30 and 53 ppm at its shoulders. However, it is obvious from the data that both the B210 and PEMA components are relaxing at the same rate constant. This is especially obvious from the last spectrum of the series, which had a 20 ms spin-lock condition. The peak at approximately 45 ppm for the PEMA and the peak at 30 ppm for both PEMA and B210 are still present at essentially the same ratio that they were in the first spectrum, even though the total intensity is approximately 90% diminished compared to the first spectrum. The $T_{1\rho}$ calculated from this data is 8.6 ms. This value is nearly half way between the 4.2 and 15.0 ms values for the individual polymers, and therefore is exactly what would be expected for a completely miscible blend. Since both components are relaxing with the same rate constant, the need for resolved peaks is not as important. Using the calculation as discussed by Parmer *et al.*[5], the B210 and PEMA in this blend are compatible at approximately a scale of 3 nm.

In testing the miscibility at other compositions of this blend, it was found that 25/75 and 75/25 blend compositions also had single $T_{1\rho}$ values that fit the n.m.r. relaxation data. The entire fitted data sets for the pure polymers and all compositions of this blend are shown in *Figure 5* with common axes. Each composition is best fitted by a single exponential. The $T_{1\rho}$ values for the 25/75 and 75/25 B210 to PEMA compositions at 7.9 and 10.3 ms, respectively, are not exactly the values that are expected, which would be approximately half-way between the 50/50 and pure polymer representative lines. This may be explained on a molecular mixing scale, indicating the components of the blend have a special interaction that forces the molecular motions to result in a $T_{1\rho}$ in the 8–10 ms range regardless of the composition. However, some of this behaviour might be explained with respect to the PEMA composition. It was found that several of the PEMA samples varied in the amount of intact anhydride species present. They also contained significant amounts of acid and ester functionalities, which are probably the result of the reaction of the anhydride with moisture and alcohols, either during synthesis or storage of the polymer. During thermal

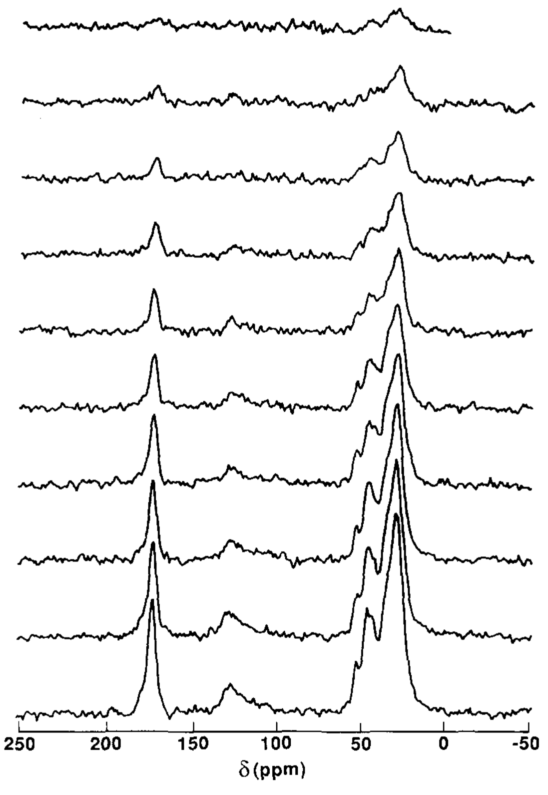

**Figure 4** $T_{1\rho}$ set for a 50/50 blend of B210 and PEMA

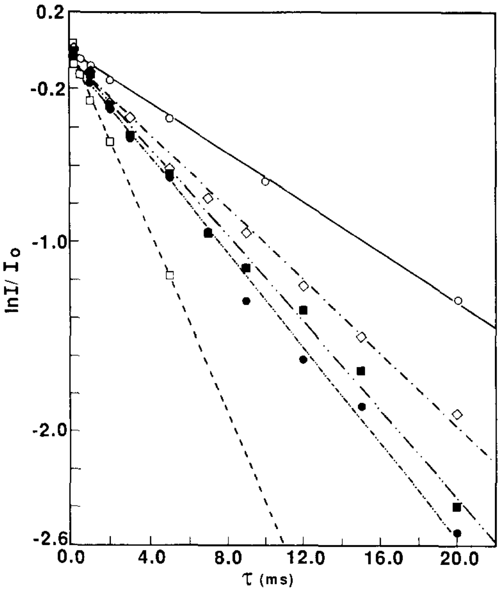

**Figure 5** Fitted $T_{1\rho}$ values for B210 (○), PEMA (□), and their blends: 75/25 B210/PEMA (◇); 50/50 B210/PEMA (■); 25/75 B210/PEMA (●)

**Table 1** Thermal behaviour of blends of B210 and PEMA

| Weight fraction of PEMA | $T_g$ (°C) | $\Delta C_p$ (cal g$^{-1}$ °C$^{-1}$) ( × 10$^2$) |
|---|---|---|
| 0.00 | 86.0 | 11.10 |
| 0.25 | 92.8 | 9.30 |
| 0.50 | 94.9 | 5.9 |
| 0.75 | 111.0 | 7.01 |
| 0.90 | 135.0 | 7.55 |
| 1.00 | 143.7 | 5.63 |

processing of the blends, some of the anhydride may be regenerated by elimination of the water or alcohol, thus resulting in a variable level of the anhydride species in the blend. This difference in composition apparently does not change the miscibility, but could affect the $T_{1\rho}$ value of the blended polymers.

*D.s.c. study*. The thermal behaviour of blends of B210 and PEMA is shown in *Table 1*. All the films are completely transparent and exhibit a single $T_g$ at temperatures intermediate to those of the pure components. These results clearly indicate that miscibility in these blends occurs over the entire range of compositions. This behaviour is better illustrated in *Figure 6* which represents a plot of experimental $T_g$ values *versus* weight fractions of PEMA with a broken line showing the behaviour predicted by a simple weight-average expression. Several equations commonly used in the literature to express the $T_g$ composition relationship have also been applied to describe this miscible system. The representation of $T_g$ values calculated with Fox, Gordon–Taylor and Kwei equations[14–16] can be seen in *Figure 6*. The deviation from linearity of both experimental and predicted values can be attributed to the existence of specific non-bonding interactions between the individual polymer chains[17,18].

### *Blends of B210 and PC*

*Solid-state n.m.r. study*. The CP-MAS spectrum of PC is shown in *Figure 7*. The peaks can be assigned as follows: carbonate carbonyl, aromatic oxygenated carbon, and alkyl-substituted aromatic carbon, all centred at 148 ppm; protonated aromatic carbons at 128 and 120 ppm; aliphatic quaternary carbon at 42 ppm; and *gem*-dimethyl carbons at 31 ppm. The homopolymer PC was found to have a proton $T_{1\rho}$ value of approximately 3.3 ms. The $T_{1\rho}$ data for a 50/50 blend of B210/PC is shown in *Figure 8*. The data points represented by circles are from a peak of the B210 fraction of the blend, while the squares are from a PC peak. It can be seen that neither set of points represents a single exponential fit, but most appropriately a biexponential fit as shown by the two lines which were fitted to parts of each of the data sets. The long $T_{1\rho}$ component for the B210 data

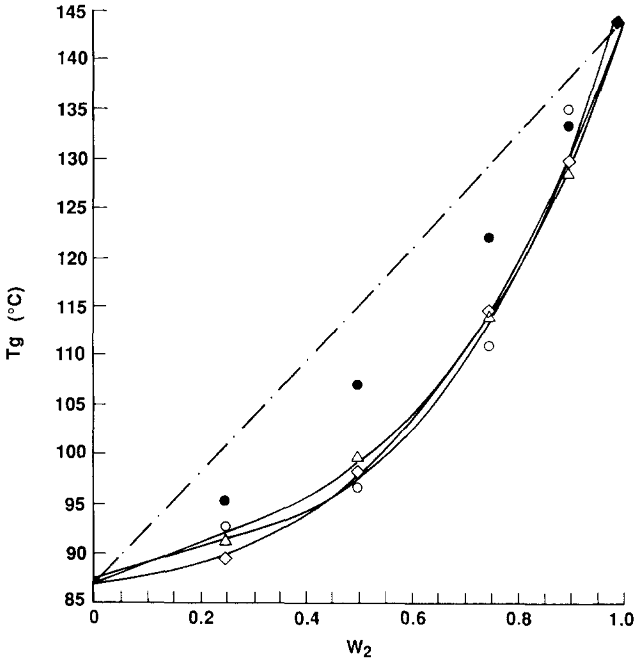

**Figure 6** Experimental (○) $T_g$ values of B210/PEMA blend system and calculated curves as described by Fox (●), Gordon–Taylor (Δ, $K = 0.32$) and Kwei equations (—·, $K = 0.42$, $q = -18.15$). Weight average $T_g$ (◇) and weight fraction ($w_2$)

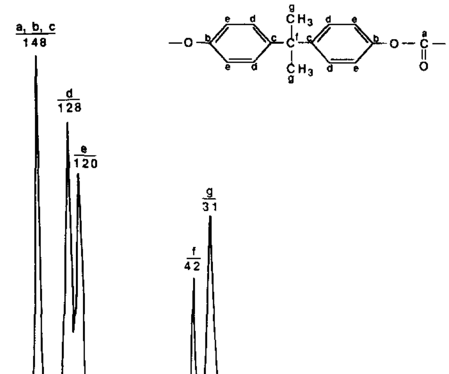

**Figure 7** $^{13}$C CP-MAS n.m.r. spectrum of PC

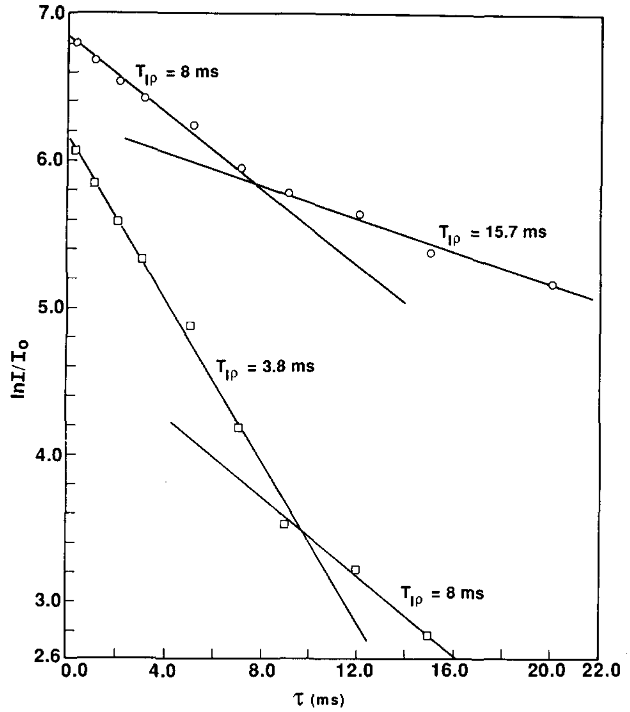

**Figure 8** Proton $T_{1\rho}$ intensity data for a 50/50 B210 (○)/PC (□) blend

and the short $T_{1\rho}$ component for the PC data represent pure phases of B210 (15.7 ms) and PC (3.8 ms), respectively. The short $T_{1\rho}$ component for the B210 data and the long $T_{1\rho}$ component for the PC data both have the same value at approximately 8 ms. These data imply a miscible phase is present, along with pure phase of both polymers.

Nuclear magnetic resonance relaxation data from a 75/25 B210/PC blend are shown in *Figure 9*. The results again implicate bi-exponential behaviour for the $T_{1\rho}$ relaxation of both components, which suggests the presence of pure B210 and PC phase, and a mixed phase. The calculated $T_{1\rho}$ values for the Barex and PC components of the mixed phase are not identical (6.7 *versus* 4.9 ms). This may indicate that there is some heterogeneity within this phase or that the data points generated are not sufficient to adequately characterize the relaxation curve. Measurement of the PC component's relaxation is more difficult than that of Barex due to its short $T_{1\rho}$ values and this could be the cause. However, the bi-exponential n.m.r. relaxation behaviour at both compositions of the blend strongly indicates that intermediate mixed phase is formed from these components.

Partially miscible polymer blends have been reported in the literature. A recent example was by Dickinson *et al.*[13] on poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) and poly($\alpha$-methyl styrene) blends. Also, Stejskal *et al.*[11] reported that a small amount of pure polystyrene was present in a polystyrene/PPO blend. In one case of 50/50 poly(2-methyl styrene) and PPO reported by Dickinson, a single broad $T_g$ from d.s.c. measurements was observed even though the solid-state n.m.r. data showed obvious heterogeneity.

*D.s.c. study.* The thermal behaviour of blends of B210 and PC is summarized in *Table 2*. For two compositions studied, the $T_g$ of B210/PC blends appears to have a three-component character consistent with partially mixed polymer blend systems. The presence of these three $T_g$ values indicates that the level of segregation in both cases must be larger than the 10–20 nm measurable by the d.s.c. The 50/50 B210/PC blend exhibits two distinct $T_g$s and an additional weak one. The first $T_g$ occurring at 86.1°C is characteristic of a pure B210 phase. The second $T_g$ is 18.5°C lower than that of pure PC. This intermediate $T_g$ between B210 and PC strongly supports the presence of a mixed PC/B210 phase. The third $T_g$ is less pronounced, yet can be taken as sufficient evidence to show the presence of the pure PC phase in the blend. The same trend is observed for the 75/25 B210/PC blend. The $T_g$ of the mixed phase, as expected, occurs at lower temperatures than in the 50/50 B210/PC blend. In contrast to the 50/50 B210/PC blend, the intermediate $T_g$ is not as clearly defined, while the presence of the PC pure phase is better evidenced. No assumptions can be made on this behaviour which might be due to a poorer mixing of the two components in the blend. In very good

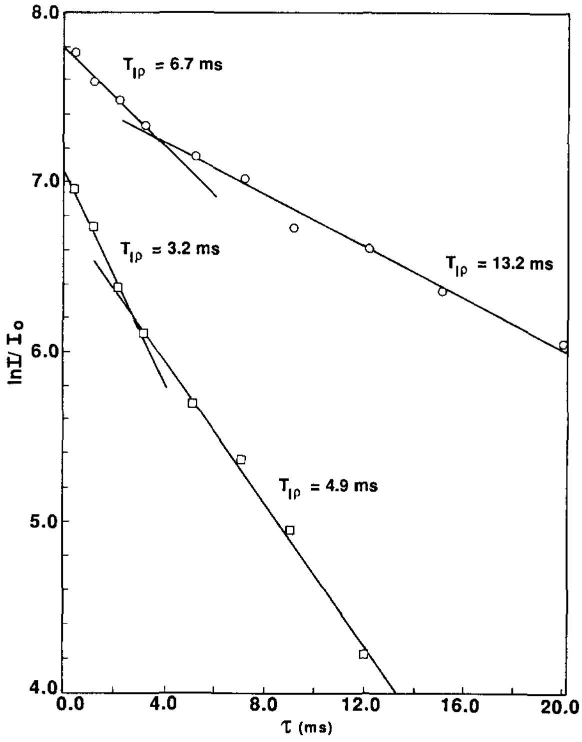

**Figure 9** Proton $T_{1\rho}$ intensity data for a 75/25 B210 (○)/PC (□) blend

**Table 2** Thermal behaviour of blends of B210 and PC

| Weight fraction of PC | $T_g$ (°C) | $\Delta C_p$ (cal g$^{-1}$ °C$^{-1}$) ( × 10$^2$) |
|---|---|---|
| 0.00 | 86.0 | 11.1 |
| 0.25 | $T_{g_1}$ = 86.0<br>$T_{g_2}$ = 121.5<br>$T_{g_3}$ = 147.2 | $\Delta C_{p_1}$ = 8.3<br>$\Delta C_{p_2}$ = 1.5<br>$\Delta C_{p_3}$ = 1.6 |
| 0.50 | $T_{g_1}$ = 86.0<br>$T_{g_2}$ = 132.3<br>$T_{g_3}$ = 150.0 | $\Delta C_{p_1}$ = 3.3<br>$\Delta C_{p_2}$ = 1.9<br>$\Delta C_{p_3}$ = 1.2 |
| 1.00 | 150.8 | 6.0 |

agreement with these d.s.c. data are the n.m.r. results which clearly suggest that the mixed phase of the 50/50 B210/PC composition is homogeneous while the mixed phase of the 75/25 B210/PC composition is heterogeneous. It is actually surprising that B210 and PC can be mixed at all since their pure phase $T_g$ values are about 64°C apart. Due to this difference, it is very difficult to achieve processing conditions such that B210 and PC can be melt blended without decomposition of B210.

## CONCLUSIONS

Solid-state CP-MAS n.m.r. and d.s.c. methods have been applied to study the phase behaviour in polymer blends of B210 with PEMA, and B210 with PC. By monitoring the change in carbon signal intensities as a function of variable proton spin-lock times, the rotating frame proton spin-lattice relaxation times for these blends and component polymers have been determined. The n.m.r. results have been compared with d.s.c. data revealing the occurrence of thermal transitions in blends and individual polymeric components. It was found that B210/PEMA blends exhibit single component rotating frame spin-lattice relaxation times, intermediate in value as compared to the pure components. Based on these data, miscibility in blends of B210 and PEMA was evaluated to occur on a scale of 3 nm. The d.s.c. data also indicated single component $T_g$s, and as the PEMA content of the blend was increased, the $T_g$ constantly increased over the entire range of compositions studied. Both 50/50 and 75/25 B210/PC compositions exhibited multicomponent decay processes indicating the presence of a mixed phase along with pure phases of each component. The d.s.c. results for B210/PC blends also were consistent with a phase-separated system consisting of pure phases as well as a mixed B210/PC phase with $T_g$ intermediate to the individual polymer components.

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