

# Miscibility of poly(vinyl chloride) and poly(phenyl methacrylate)

M. Sankarapandian and K. Kishore\*

*Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore  
 560 012, India*

*(Received 8 June 1995)*

The phase behaviour of poly(vinyl chloride)/poly(phenyl methacrylate) blends has been investigated by glass transition temperature ( $T_g$ ) and proton spin lattice relaxation time ( $T_{1\rho}({}^1\text{H})$ ) measurements. The results indicate that the domain sizes are between 3 and 15 nm. The miscibility in this system stems from the presence of weak hydrogen bonding between the components, as is evident from the Fourier transform infra-red spectroscopic studies of the model compounds. The trend in the miscibility of poly(vinyl chloride) blends with related polymethacrylates containing similar, bulky substituents like cyclohexyl and benzyl groups has been investigated. The miscibility could not be explained in terms of a steric effect as the sizes of the molar volumes of the repeat units did not show any perceptible trend. The modified neglect of diatomic overlap calculations on the model compounds, however, suggest that the interaction between the components is the predominant factor, thus explaining the miscibility trend in these systems. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: miscibility; glass transition temperature; spin lattice relaxation time)**

## INTRODUCTION

Poly(vinyl chloride) (PVC) is known to be miscible with a wide range of polymethacrylates<sup>1–9</sup>. It is generally observed that the miscibility in these systems is reduced when the polymethacrylate contains larger alkyl groups. The miscibility in these systems is attributed to the exothermic mixing arising from the formation of weak hydrogen bonds between the carbonyl groups of the esters and the methine protons of PVC<sup>7,10–12</sup>. Calorimetric studies on the heats of mixing of various oligomeric polymethacrylates with PVC reveal the existence of a maximum interaction for the lower alkyl methacrylates<sup>8</sup>. The higher concentration of carbonyl groups in the lower methacrylates is responsible for the better miscibility with PVC, leading to lower critical solution temperatures ( $LCSTs$ ) that are higher in these blends<sup>7</sup>. The presence of additional functional moieties like carbonyls, ether oxygens and pendent hydroxyl groups in the polymethacrylate can have a significant effect on its miscibility behaviour with PVC<sup>13</sup>.

In contrast to their aliphatic counterparts, the blends of poly(aryl methacrylate)s with PVC have not received much attention<sup>12</sup>. Studies on these blends would be interesting since the phenyl rings in these esters offer the convenience of the insertion of interacting sites for controlling the phase morphology. In the present investigation, the miscibility behaviour of the PVC/poly(phenyl methacrylate) (PPMA) system has been studied. The level of miscibility in this system has been examined by glass transition temperature ( $T_g$ ) and proton spin lattice relaxation time ( $T_{1\rho}({}^1\text{H})$ ) measurements.

## EXPERIMENTAL

A commercial sample of PVC (Calico, Bombay;  $[\eta] = 1.13 \text{ dl g}^{-1}$  in tetrahydrofuran at 25°C) was reprecipitated twice from tetrahydrofuran (THF) solution into methanol and dried under vacuum. PPMA ( $[\eta] = 0.72 \text{ dl g}^{-1}$  in  $\text{CHCl}_3$  at 25°C) was synthesized according to the literature procedure<sup>14</sup>. The blends were prepared by dissolving the polymers in THF and precipitating the solution into a large excess of methanol. The resulting powders were dried at 50°C under vacuum to a constant weight. The  $T_g$  measurements were made on a DuPont TA1090 instrument; the  $T_g$  values were obtained on the second heating at a scan rate of 10 K min<sup>-1</sup>. The  $T_g$  was taken as the onset of the change in the heat capacity curve. Fourier transform infra-red (FTi.r.) spectra were recorded on a Bio-Rad FTS7 spectrometer with a resolution of 2 cm<sup>-1</sup>.

The cross-polarization/magic angle spinning (CP/MAS) <sup>13</sup>C nuclear magnetic resonance (n.m.r.) spectra were obtained with a Bruker MSL-300 solid state n.m.r. spectrometer operating at a <sup>13</sup>C resonance frequency of 75.5 MHz. The sample spinning rates were more than 3 kHz. The chemical shifts were referenced to tetramethylsilane. A 90° pulse of 3.8 μs was employed and the proton spin lattice relaxation times in the rotating frame ( $T_{1\rho}({}^1\text{H})$ ) were measured via carbon signal intensities using a 90<sub>x</sub>-τ-spinlock pulse sequence prior to cross-polarization<sup>12,15</sup>. Acquisition was performed with <sup>1</sup>H decoupling and delay times varied from 1 μs to 10 ms. For all the samples, scans were accumulated with a 5 s delay between pulse sequence repetitions. The carbon signal intensities of the decay curves were fitted to a standard first-order kinetic expression to obtain the  $T_{1\rho}({}^1\text{H})$  values<sup>16</sup>. MNDO calculations were performed

\* To whom correspondence should be addressed

on model compounds, namely cyclohexyl, phenyl and benzyl esters of 3-carboxypentane.

## RESULTS AND DISCUSSION

$T_g$  measurements were made as a function of composition for the blends (Figure 1). All the blends exhibit single, composition dependent  $T_g$  values, indicating that they are miscible in all proportions. The dashed line in Figure 1 represents the behaviour expected for a single weight proportionality function. From Figure 1, it is clear that the  $T_g$  values of the PVC/PPMA blends lie close to the dashed line. The width of the  $T_g$  was also determined, and its dependence on blend composition is indicated in Figure 2. The increase in  $T_g$  width starts at about 50 wt% of PPMA in the blend with a peak value at 85 wt% of PPMA. The  $T_g$  width remains almost constant for PPMA contents up to 50 wt% in the blend. This behaviour is similar to that of PVC/PMMA blends<sup>6,12</sup>. The width of the transition reflects the magnitude of local composition fluctuations in the

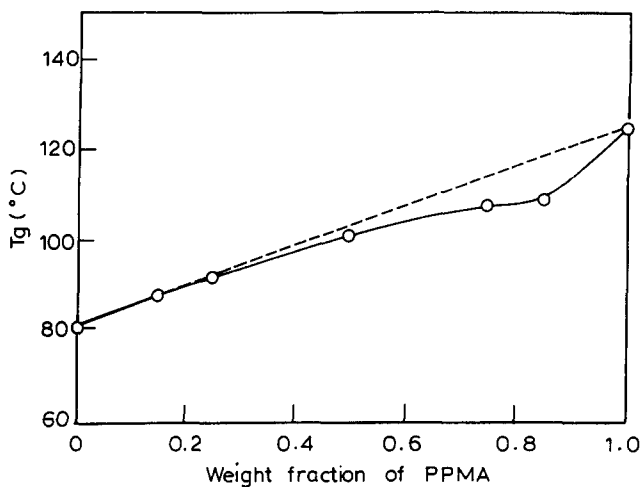


Figure 1 Plot of glass transition temperature as a function of PPMA content in PVC/PPMA blends. The dashed line represents the weight average values

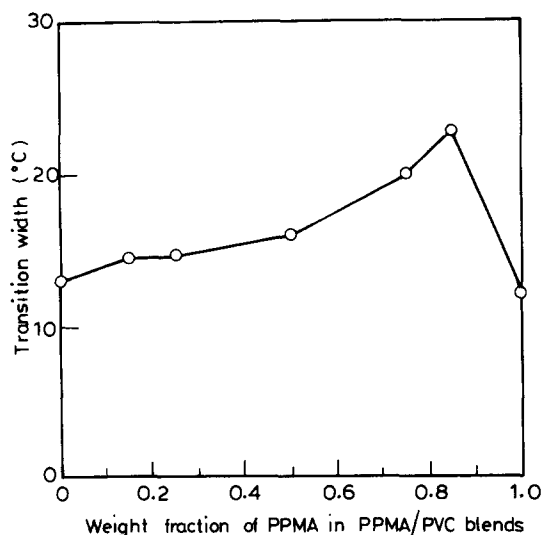


Figure 2 Dependence of glass transition width on the weight fraction of PPMA in PVC/PPMA blends

polymer blend<sup>17</sup>. Thus, the PVC/PPMA blends containing less than 50 wt% of PVC appear to be homogeneous, beyond which local composition fluctuations exist.

The miscibility of the polymethacrylates with PVC can be explained in terms of the presence of weak hydrogen bonds between the carbonyl groups of the ester units and the methine protons of PVC, resulting in the heterochain association<sup>7,10-12</sup>. In order to verify the presence of such hydrogen bonding in the present case, we performed FTi.r. studies on solutions of the model compound phenyl acetate (PA), in place of PPMA, in PVC analogue solvents like 1,2-dichloroethane and dichloromethane. A reference solution was made in  $CCl_4$ , where the acidic hydrogen is absent. The line shape and/or frequency shifts were monitored for the carbonyl band of PA on these solutions. The carbonyl regions of the FTi.r. spectra of these solutions are shown in Figure 3, which indicates that there is a broadening and a frequency shift for the carbonyl peak of PA in 1,2-dichloroethane and dichloromethane solutions relative to the  $CCl_4$  reference solution. The magnitudes of these effects are 5 and 6  $cm^{-1}$ , respectively. These results support the presence of weak hydrogen bonding between the aromatic ester groups of PPMA and the acidic methine protons of PVC.

The information obtained by differential scanning calorimetry (d.s.c.) on the miscibility of polymer blends is only sensitive to phase sizes<sup>18</sup> greater than about 15 nm. The measurements of  $T_{1\rho}(^1H)$  are superior to  $T_g$  measurements since they are sensitive to phase sizes of a few angstroms<sup>19,20</sup>. The effective spin diffusion through dipolar coupling causes the neighbouring protons in a molecule to relax at identical rates and hence leads to a single  $T_{1\rho}(^1H)$ . In contrast, protons which are far away or in a different environment relax independently<sup>19,20</sup>. Thus, the protons in an intimately mixed blend show identical relaxation rates, resulting in a single  $T_{1\rho}(^1H)$  value for both components of the blend. A partially miscible blend or an immiscible blend will show either partial averaging of the relaxation rates or no averaging at all, depending on the scale of phase separation.

The CP/MAS  $^{13}C$  n.m.r. spectra of the homopolymers and their 1:1 blend are displayed in Figures 4-6. It may be seen that the  $CH_2$  and the  $CCl$  carbon peaks of PVC overlap with the signals of the backbone quaternary carbons and the methylene carbons, respectively.

The dependence of the signal intensity on the delay time for PVC and PPMA homopolymers was examined from the intensities of the  $^{13}C$  peaks at 57 and 151 ppm, respectively (Figure 6). In the 1:1 (w/w) blend, only the PPMA component was analysed using the  $^{13}C$  signal at 151 ppm. The measured  $T_{1\rho}(^1H)$  values from the slopes of the straight lines in Figure 7 for PVC and PPMA homopolymers and their 1:1 (w/w) blend, as well as the expected  $T_{1\rho}(^1H)$  value for the blend calculated from the linear relaxation model<sup>21,22</sup>, are given in Table 1.

In the  $T_{1\rho}(^1H)$  experiments, the scale of mixing is calculated using<sup>19</sup>

$$L^2 \approx (t/T_2)d^2 \quad (1)$$

where  $L^2$  is the mean distance over which the spin diffusion is effective,  $d$  is the interproton distance (typically 0.1 nm),  $t$  is the measured relaxation time (in the present case  $T_{1\rho}(^1H)$ ) and  $T_2$  is the spin-spin

**Table 1** The  $T_{1\rho}(^1\text{H})$  values for PVC, PPMA and the PPMA component in the 1:1 (w/w) blend

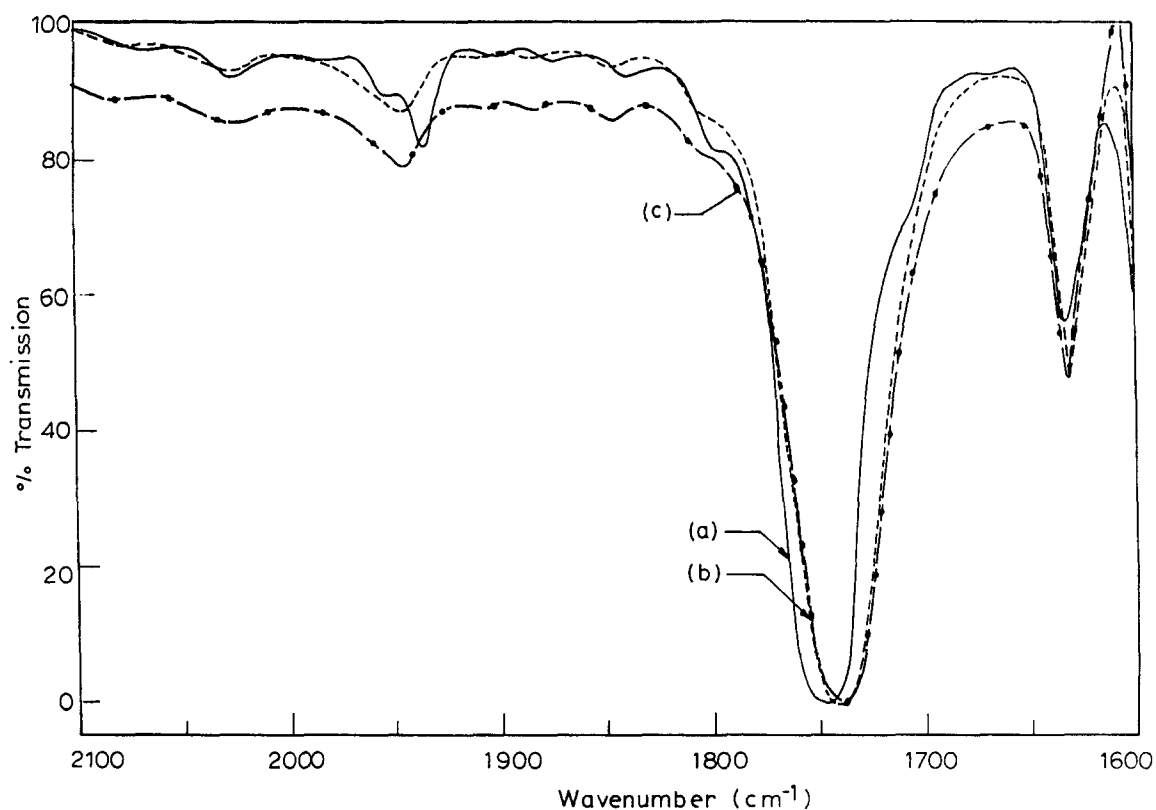
System	$T_{1\rho}(^1\text{H})$ (ms)		
	PVC	PPMA	Theory <sup>a</sup>
Pure PVC	9.2		
Blend (1:1)	Not determined	6.9	7.7
Pure PPMA		6.8	

<sup>a</sup> The linear relaxation model<sup>21,22</sup> based on complete miscibility

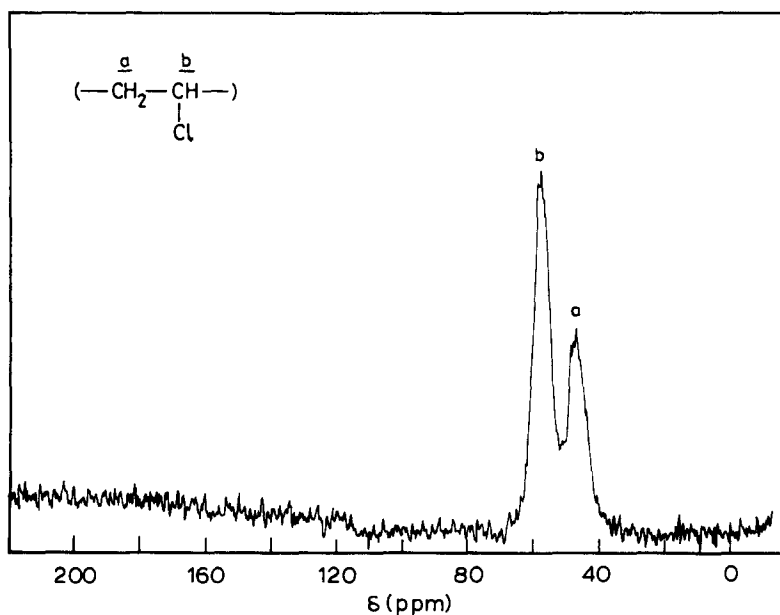
relaxation time, which below  $T_g$  is around  $10\ \mu\text{s}$ . Equation (1) thus reduces to

$$L \approx T_{1\rho}^{1/2} \quad (2)$$

with  $L$  in nanometres and  $T_{1\rho}$  in milliseconds. If we substitute the higher value of  $T_{1\rho}(^1\text{H})$  of 9.2 ms for PVC in equation (2),  $L$  can be calculated to be 3 nm. Thus, the upper limit for the sensitivity of the  $T_{1\rho}(^1\text{H})$  experiment is 3 nm.



**Figure 3** FTIR spectra of 2% phenyl acetate solutions in (a) carbon tetrachloride, (b) 1,2-dichloroethane and (c) dichloromethane



**Figure 4** Solid state CP/MAS <sup>13</sup>C n.m.r. spectrum of PVC

The  $T_{1\rho}(^1\text{H})$  value of the PPMA component in the blend is essentially equal to that of the unblended PPMA homopolymer (Table 1). Thus, there is no mixing on the scale over which the spin diffusion proceeds in the time characterized by the measured  $T_{1\rho}(^1\text{H})$  value of the PVC component, i.e. on a scale of 3 nm. The 1 : 1 blend of PVC and PPMA is miscible at a level of less than 15 nm, as indicated by d.s.c. measurements (Figure 1). However, the blend exhibits microheterogeneity at the 3 nm level, as indicated by  $T_{1\rho}(^1\text{H})$  experiments (Table 1).

The effect of the bulky group in the polymethacrylate on the miscibility behaviour with PVC has been studied by Parmer *et al.*<sup>12</sup> with poly(cyclohexyl methacrylate)

(PCHMA) and poly(benzyl methacrylate) (PBzMA) using  $T_g$  and  $T_{1\rho}(^1\text{H})$  measurements. Table 2 summarizes their results, as well as our results on the miscibility of PVC/PPMA blends. From Table 2, it is clear that the miscibility in the PVC/polymethacrylate blends in terms of molar volume does not follow any perceptible trend according to the size of the bulky group in the monomer unit, and therefore the steric effect has no role in explaining the miscibility trend. Hence, the interactions of the polymethacrylates with PVC were examined to see whether electronic effects were involved. It is well known that polymethacrylates interact with PVC through weak hydrogen bonding between the carbonyl groups of the

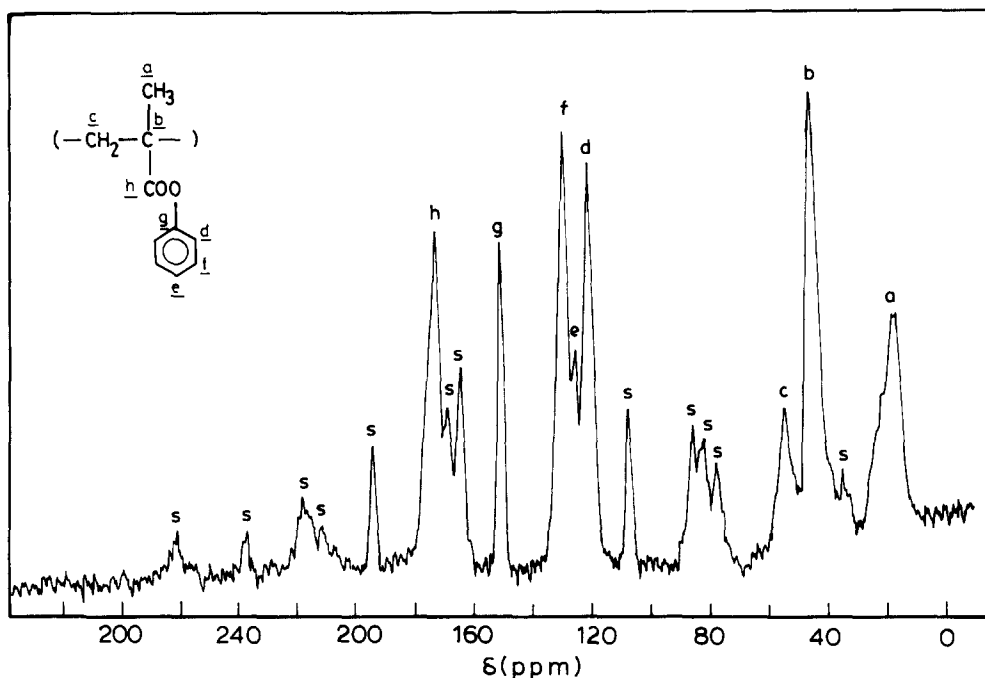


Figure 5 Solid state CP/MAS  $^{13}\text{C}$  n.m.r. spectrum of PPMA. The peaks denoted by 's' are the spinning side-bands

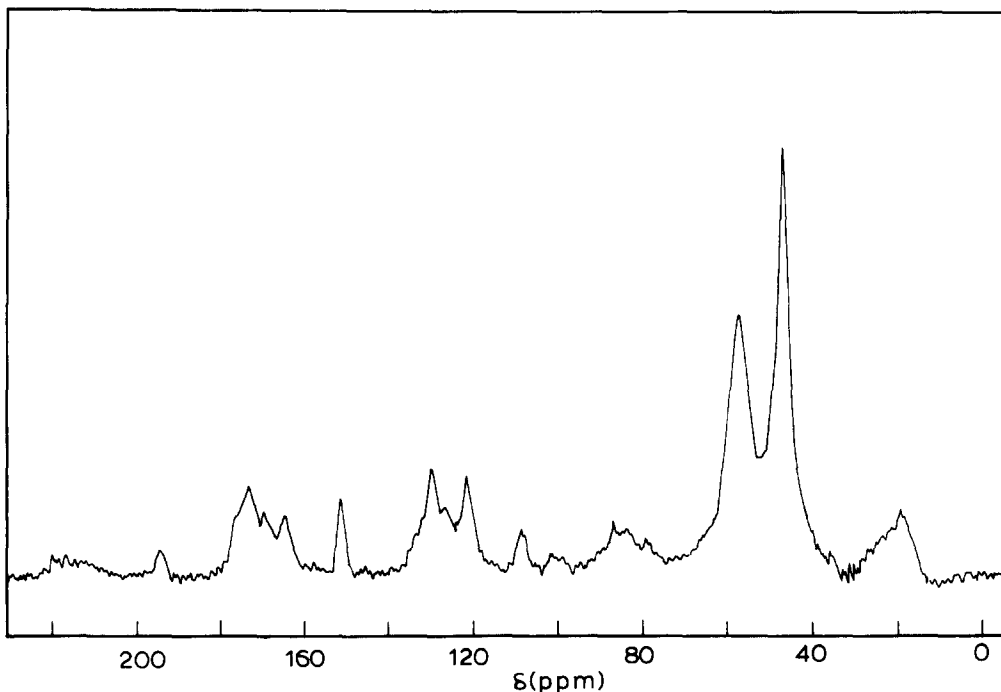
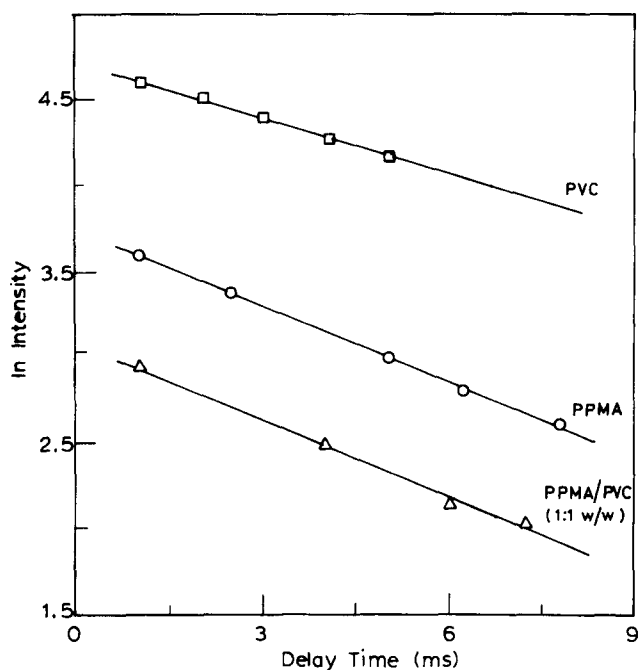


Figure 6 Solid state CP/MAS  $^{13}\text{C}$  n.m.r. spectrum of the 1 : 1 (w/w) PVC/PPMA blend

**Table 2** Miscibility behaviour in some PVC/polymethacrylate blends

System	Molar volume of the polymethacrylates <sup>23</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	Miscibility determination		Charge on the carbonyl oxygen
		$T_g$	$T_{1\rho}(^1\text{H})$	
PVC/PCHMA	153	Miscible	Miscible	-0.3619
PVC/PPMA	149	Miscible	Immiscible	-0.3447
PVC/PBzMA	134	Immiscible	Immiscible	-0.3312

**Figure 7** Plots of the logarithm of the signal intensity vs. delay time for PVC and PPMA homopolymers and their 1:1 (w/w) blend

methacrylate and the methine protons of PVC. The charges on the carbonyl oxygens were calculated for the model compounds of the corresponding polymethacrylates using the modified neglect of diatomic overlap method<sup>24</sup>. The results presented in Table 2 show a similarity between the miscibility trend and the trend in the charge on the carbonyl oxygen. This emphasizes that exothermic interactions between the polymethacrylates and PVC are responsible for their miscibility.

## CONCLUSIONS

It has been shown that PCHMA is miscible with PVC by both  $T_g$  and  $T_{1\rho}(^1\text{H})$  measurements, whereas PBzMA is immiscible with PVC according to both types of measurement. This indicates that PCHMA is highly miscible with PVC, with domain sizes of less than 3 nm. PPMA shows an intermediate behaviour, exhibiting

miscibility with PVC only by  $T_g$  measurements and not by  $T_{1\rho}(^1\text{H})$  measurements. This reveals that the phase sizes here are between 3 and 15 nm. Finally, it may be concluded that the PVC/polymethacrylate blends are largely controlled by the exothermic interactions between the ester groups of the methacrylate and the methine protons of PVC.

## REFERENCES

- Walsh, D. J. and Sham, C. K. *Macromolecules* 1989, **22**, 3799
- Walsh, D. J. and McKeown, J. G. *Polymer* 1980, **21**, 1330
- Schurer, J. W., de Boer, A. and Challa, G. *Polymer* 1975, **16**, 201
- Vorenkamp, E., ten Brinke, G., Meijer, J. G., Jager, H. and Challa, G. *Polymer* 1985, **14**, 1725
- Perrin, P. and Prudhomme, R. E. *Polymer* 1991, **32**, 1468
- Shen, S. and Torkelson, J. M. *Macromolecules* 1992, **25**, 721
- Tremblay, C. and Prudhomme, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1857
- Walsh, D. J. and Cheng, G. L. *Polymer* 1984, **25**, 499
- Bosma, M., ten Brinke, G. and Ellis, T. S. *Macromolecules* 1988, **21**, 1465
- Varnell, D. F., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Polym. Eng. Sci.* 1983, **23**, 658
- Fowkes, F. M., Tischler, D. O., Wolfe, J. A., Lannigan, L. A., Ademu-John, C. M. and Halliwell, M. J. *J. Polym. Sci. Polym. Phys. Edn* 1984, **22**, 547
- Parmer, F. F., Dickinson, L. C., Chien, J. C. W. and Porter, R. S. *Macromolecules* 1989, **22**, 1078
- Chong, Y. F., Lee, S. Y. and Goh, S. H. *Eur. Polym. J.* 1990, **26**, 1207
- Wandelt, B. and Szumilewicz, A. *Polymer* 1987, **28**, 1791
- Schafer, J., Sefcik, M. D., Stejskal, E. O. and McKay, R. A. *Macromolecules* 1981, **14**, 275
- Assink, R. A. *Macromolecules* 1978, **11**, 1233
- Paul, D. R. and Newman, S. 'Polymer Blends', Vol. I, Academic Press, New York, 1978, Ch. 5
- Kaplan, D. S. *J. Appl. Polym. Sci.* 1986, **20**, 2615
- Dickinson, L. C., Yang, H., Chu, C. W., Stein, R. S. and Chien, J. C. W. *Macromolecules* 1987, **20**, 1757
- Masson, J. F. and Manley, R. St. J. *Macromolecules* 1992, **25**, 589
- McBrierty, V. J. and Douglass, D. C. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 295
- Simmons, A. and Natansohn, A. *Macromolecules* 1990, **23**, 5127
- Van Krevelen, D. W. and Hoftyzer, P. J. 'Properties of Polymers: Their Correlation With Chemical Structure; Their Numerical Estimation and Prediction Additive Group Contributions', Elsevier, Amsterdam, 1990, Ch. 4
- Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 1979, **99**, 4899