^{13}C c.p./m.a.s. n.m.r. study on the miscibility and phase separation of a polystyrene/poly(vinyl methyl ether) blend

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We investigate the miscibility of a polystyrene/poly(vinyl methyl ether) (PS/PVME) blend using nuclear magnetic resonance spectroscopy. We examine ^{1}H spin-lattice relaxation times in both the laboratory ($T_{1\text{H}}$) and rotating ($T_{1\rho\text{H}}$) frames at various temperatures. At temperatures lower than the glass transition temperature (T_g) of the blend, the observed ^{1}H relaxation time of PS is equal to that of PVME, showing that the 5/5 PS/PVME blend is miscible on a scale of 20–30 Å. At temperatures much higher than T_g, the observed ^{1}H relaxation curve ($T_{1\rho\text{H}}$) of PS apparently differs from that of PVME. They are not single exponentials. The non-exponential decays are analysed taking into account spin diffusion; the ^{1}H spin diffusion rate between PS and PVME is found to be $\sim 1000\,\text{s}^{-1}$ at 38°C. This spin diffusion rate is too slow for the $T_{1\rho\text{H}}$ values of PS and PVME to coincide with each other. This is attributed to the fast molecular motion of PVME. The ^{1}H relaxation curve of the phase-separated blend formed by heating above the lower critical solution temperature is markedly different from that of the homogeneous blend. On the assumption that ^{1}H spin diffusion does not occur between phase-separated domains, we analyse the ^{1}H relaxation curve of each component polymer and obtain the stoichiometry of the phase-separated domains. We conclude that the phase separation of the 5/5 PS/PVME blend is initiated by spinodal decomposition; the phase separation rate is $0.5\,\text{min}^{-1}$ at 140°C.

(Keywords: polystyrene; poly(vinyl methyl ether); polymer blend)

INTRODUCTION

Recent developments in high-resolution solid-state nuclear magnetic resonance (n.m.r.) techniques have enabled us to characterize the heterogeneity in solid polymers[1]. The miscibility and phase separation of polycarbonate/ poly(methyl methacrylate) (PC/PMMA) blends have been studied by examining the ^{1}H relaxation of PC and PMMA through well resolved ^{13}C signals[2]. Analysis of the ^{1}H relaxation curve provides information on the homogeneous domain size, the phase diagram and the fluctuation of composition during phase separation[2].

Differential scanning calorimetry and dielectric relaxation studies of polystyrene/poly(vinyl methyl ether) (PS/PVME) blends prepared from toluene (or benzene) solution indicate that the blends consist of a single phase, suggesting that the two polymers are microscopically mixed[3,4].

N.m.r. studies have, however, presented diverse views on miscibility. Caravatti *et al.* examined the interpolymer ^{1}H spin diffusion for PS/PVME blends using two-dimensional (2D) ^{1}H exchange n.m.r. spectroscopy[5] and one-dimensional (1D) ^{1}H saturation transfer n.m.r. experiments[6]. They concluded that the blends consist of mixed, pure PS and pure PVME domains. Chu *et al.*[7] examined ^{1}H spin-lattice relaxation times in the rotating frame ($T_{1\rho\text{H}}$) at −5°C. They showed that PS-rich blends are homogeneous but PVME-rich blends are microscopically heterogeneous.

On the basis of the results of $T_{1\rho\text{H}}$ and Goldman–Shen[8] experiments, Kaplan[9] concluded that the PS/PVME blend is homogeneous on a scale of 6–20 Å. Gobbi *et al.*[10] and others[11] have examined at −33°C the cross-polarization transfer from PVME protons to ^{13}C nuclei of deuterated PS (d-PS) in a 5/5 d-PS/PVME blend which was prepared by mechanical mixing. The results[10,11] suggest that 5/5 d-PS/PVME is homogeneous on a scale less than 20 Å. More recently, White and Mirau[12] indicated a specific intermolecular interaction between the phenyl group of PS and the methoxy group of PVME on the basis of the results of a nuclear Overhauser effect (NOE) experiment in the solid state at −60°C.

The NOE has also been observed between the aromatic protons of PS and the methoxy protons of PVME in toluene solution[13,14]. The results indicate that the distance between the phenyl ring of PS and the ether group of PVME can be less than 5 Å in solution[13,14].

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Kwei *et al.*[15] found a long ^{1}H spin–spin relaxation time (T_{2H}) component at temperatures higher than 25°C for PS/PVME blends prepared by solvent casting. They suggested microheterogeneity on a segmental scale. An electron spin resonance study of a poly(styrene-*co*-maleic anhydride)/PVME blend prepared by solvent casting indicates that the blend is inhomogeneous on a molecular scale ($\leqslant 50$ Å)[16]. ^{13}C linewidth studies show that the molecular motions of PS and PVME in blends are not cooperative, indicating motional heterogeneity[17,18].

These previous n.m.r. results seem to suggest that the blend is heterogeneous at temperatures higher than the glass transition temperature (T_g) and homogeneous at temperatures lower than T_g. Therefore, we carefully took into account the effect of molecular motion on the relaxation process at various temperatures. In this work, we measured the ^{1}H spin relaxation curves for PS and PVME through well resolved ^{13}C signals to re-examine the confusing views on the miscibility of PS/PVME blends.

The phase separation of PS/PVME blends has been studied by light scattering[19,20] and fluorescence emission[21,22]. Nishi *et al.*[23] analysed the ^{1}H relaxation curves of phase-separated PS/PVME blends observed directly from the ^{1}H n.m.r. signals. They pointed out that the direct ^{1}H observation has some difficulty in detecting the minor domain. Indirect observation of the ^{1}H relaxation curve provides information about compositional changes in the minor domain as well as the major domain. The phase separation behaviour is also studied in this paper.

EXPERIMENTAL

Materials

The PS used was commercial PS-666 from Dow with a viscosity average molecular weight (M_v) of 93 000. PVME ($M_v = 87\,000$) was obtained from Aldrich. The average molecular weight was determined by the conventional intrinsic viscosity method. A transparent PS/PVME film was obtained at room temperature by casting a benzene solution of both polymers mixed at a weight ratio of 5/5 (5/5 PS/PVME). The film was further dried under vacuum at 60°C for at least a week. Phase separation was achieved by heat treating the single-phase film for various time intervals in an oven controlled at 140°C. After heating, the film was quickly cooled in liquid nitrogen to quench the phase separation.

N.m.r measurements

^{13}C n.m.r. measurements were made using a JEOL JNM-GX270 spectrometer operating at 67 MHz. The high-resolution solid-state ^{13}C n.m.r. spectra were obtained by the combined use of cross-polarization (c.p.) and magic-angle spinning (m.a.s.)[24,25]. The radio frequency field strength for both ^{1}H and ^{13}C was 55 kHz. The spinning frequency was about 5.5 kHz. The ^{1}H spin-lattice relaxation time in the laboratory frame (T_{1H}) was indirectly measured from well resolved ^{13}C signals enhanced by c.p. applied after the 180° pulse to ^{1}H nuclei[26]. Similarly, $T_{1\rho H}$ was indirectly obtained from the ^{13}C signals by the combined use of c.p. and spin locking of ^{1}H nuclei[27]. The contact time for the c.p. signal enhancement was 500 μs for the $T_{1\rho H}$ measurement and 2 ms for the T_{1H} measurement. The temperature calibration[17,28] was done using the proton signals of methanol under spinning at 5.5 kHz.

RESULTS AND DISCUSSION

T_{1H} and $T_{1\rho H}$ experiments

Figure 1 shows the solid-state ^{13}C n.m.r. spectra of PS, PVME and the 5/5 PS/PVME blend at 38°C and −45°C. The methine carbon peak for PVME in the blend broadens noticeably at 38°C. This is ascribed to the motional broadening effect[17].

The observed relaxation curves are single exponential except for $T_{1\rho H}$ at 38°C. *Tables 1* and *2* list the observed ^{1}H relaxation times T_{1H} and $T_{1\rho H}$, respectively, for pure PS, pure PVME and the 5/5 PS/PVME blend at −45°C, −10°C and 38°C. The values of $T_{1\rho H}$ at 38°C were obtained from the initial slopes. The calculated values were obtained from the molar average relaxation rates of the respective pure polymers[2,29–31]. Such calculations were based on the assumption that the motional state is not altered by blending.

The observed T_{1H} for PS in the blend at −45°C is in good agreement with that for PVME. Agreement is also found at 38°C. These data indicate that averaging of ^{1}H relaxation rates by spin diffusion occurs, suggesting that the 5/5 PS/PVME blend is homogeneous on a scale of 200–300 Å[2,29–31]. Furthermore, the T_{1H} observed at −45°C agrees with the calculated value. This indicates that the motional state is not affected by blending.

On the other hand, the T_{1H} observed at 38°C is different from the calculated value. This suggests that the motional states of PS and PVME in the blend at 38°C are affected by blending.

Table 1 Observed[a] and calculated (average) T_{1H} values (in seconds) for the 5/5 PS/PVME blend at two temperatures

	−45°C	38°C
Pure		
PS	16.2 ± 0.5	1.70 ± 0.01
PVME	1.64 ± 0.03	1.42 ± 0.03
Blend		
PS	2.8 ± 0.1	2.2 ± 0.1
PVME	2.7 ± 0.1	2.1 ± 0.1
Calculated	2.7	1.5

[a] In each case the error is σ

Table 2 Observed[a] and calculated (average) $T_{1\rho H}$ values (in milliseconds) for the 5/5 PS/PVME blend at three temperatures

	−45°C	−10°C	38°C
Pure			
PS	24 ± 1	11.8 ± 0.2	5.35 ± 0.03
PVME (OCH_3)	28 ± 1	2.8 ± 0.1	1.05 ± 0.02[b]
PVME (CH)	29 ± 1	2.9 ± 0.1	0.44 ± 0.01[b]
Blend			
PS	25 ± 1	12.3 ± 0.3	1.91 ± 0.06[b]
PVME (OCH_3)	26 ± 1	11.2 ± 0.9	0.91 ± 0.03[b]
PVME (CH)	26 ± 1	12.5 ± 0.4	0.56 ± 0.03[b]
Calculated	26	4.2	–

[a] In each case the error is σ

[b] Obtained from several initial data points

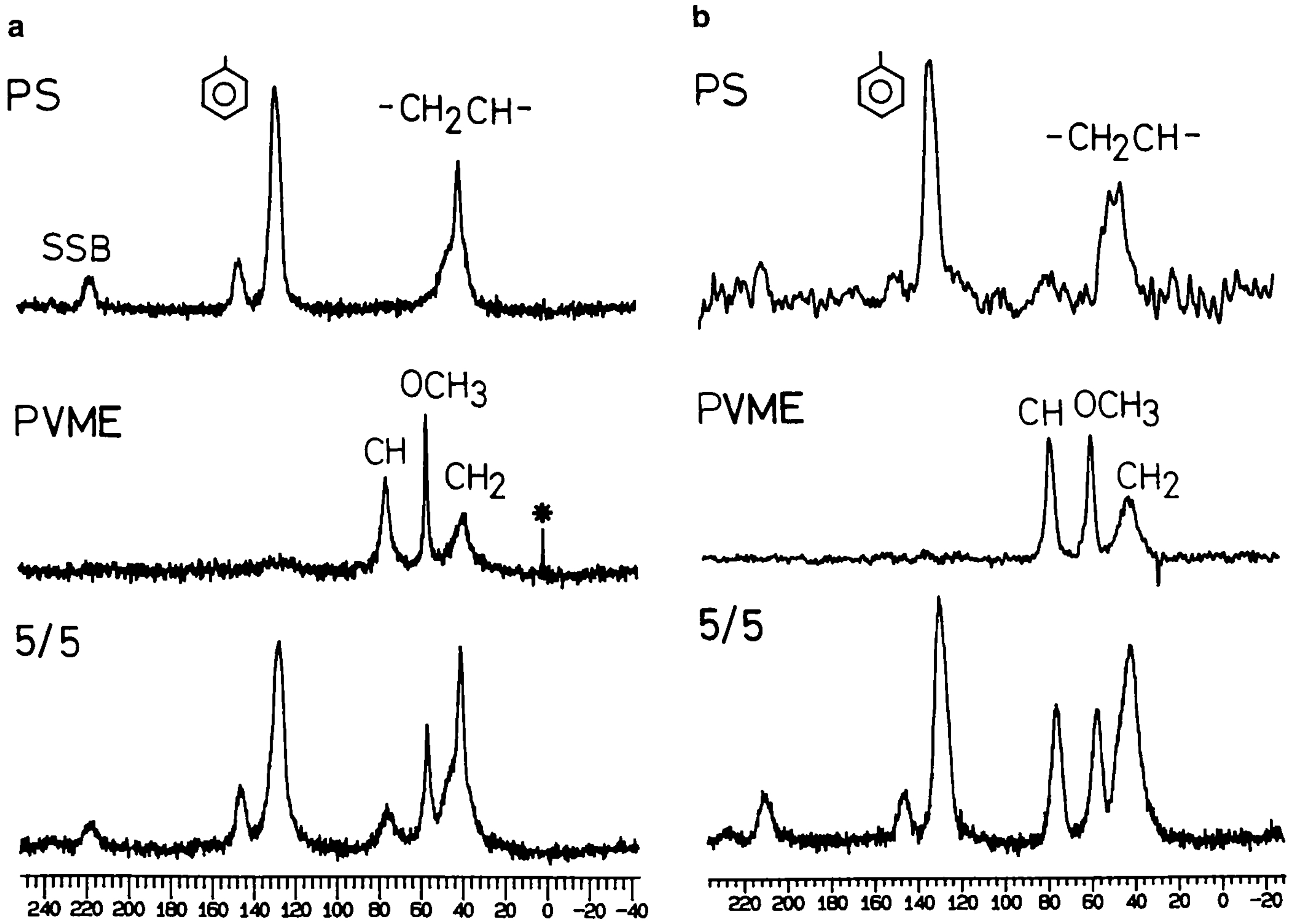

Figure 1 ^{13}C c.p./m.a.s. spectra for pure PS, pure PVME and the 5/5 PS/PVME blend at 38°C (a) and −45°C (b). Peak assignments are also depicted. The asterisk (*) in (a) indicates a peak corresponding to some silicon rubber from the stopper of the sample tube. SSB denotes a spinning side band. The chemical shifts are measured relative to tetramethylsilane

The $T_{1\rho H}$ values for PS in the blend observed at −45°C and −10°C are in good agreement with those for PVME. This indicates that the blend is homogeneous on a scale of 20–30 Å as well as a scale of 200–300 Å. Although the $T_{1\rho H}$ rates for PS and PVME in the blend at −10°C are averaged by spin diffusion, the observed $T_{1\rho H}$ values are not in agreement with the calculated ones. The $T_{1\rho H}$ process is governed by motion at frequencies of ~50 kHz. Chu *et al.*[7] have reported that a $T_{1\rho H}$ minimum for the 5/5 blend occurs at ~0°C. This indicates that such motion occurs at −10°C. The blending affects motions at frequencies of ~50 kHz. A ^{13}C linewidth study has also shown that the motion which governs the $T_{1\rho H}$ process is affected appreciably by blending[17].

The $T_{1\rho H}$ values of the blend at −10°C are larger than the calculated value. This implies that the motions of PVME at frequencies of ~50 kHz are much affected at −10°C by blending.

As mentioned before, the $T_{1\rho H}$ decays of the blend are not single exponential at 38°C, i.e. much higher than the T_g of the blend (−14°C)[3]. Even for pure PVME, the methoxy and methine groups have different $T_{1\rho H}$ decays at 38°C. A ^{13}C linewidth study has shown that the main chain of PVME undergoes rapid motion at this temperature[17]. The motion partially averages the ^1H dipole–dipole interactions, resulting in slow spin diffusion.

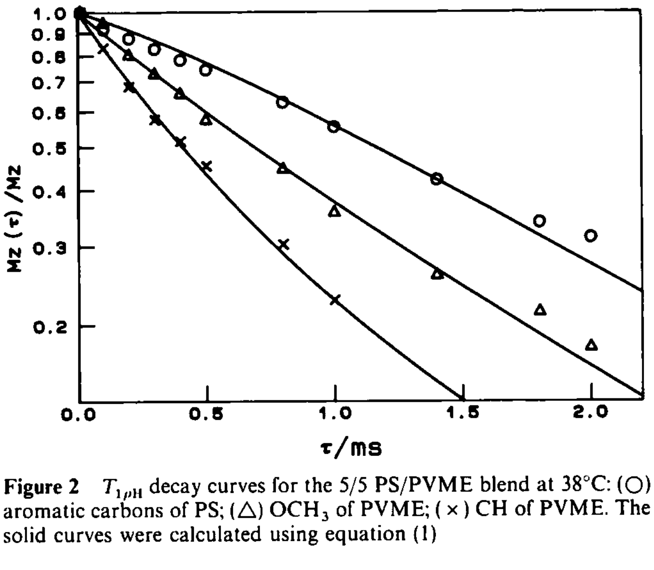

Figure 2 $T_{1\rho H}$ decay curves for the 5/5 PS/PVME blend at 38°C: (○) aromatic carbons of PS; (△) OCH_3 of PVME; (×) CH of PVME. The solid curves were calculated using equation (1)

Effects of molecular motion on ^1H relaxation curves

Figure 2 shows the $T_{1\rho H}$ decay curves for PS and PVME in the blend at 38°C. All $T_{1\rho H}$ decay curves are not single exponential.

We will treat the effect of slow spin diffusion on the relaxation curve more quantitatively. We assume that the

^{1}H spin system of the blend consists of three species: the protons of PS, the side chain protons of PVME and the main chain protons of PVME. The three proton species exchange the magnetization via spin diffusion. The equation of the spin system can be given as

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} M_A \\ M_B \\ M_C \end{pmatrix} = \begin{pmatrix} -\xi_A & f_A k_{AB} & f_A k_{CA} \\ f_B k_{AB} & -\xi_B & f_B k_{BC} \\ f_C k_{CA} & f_C k_{BC} & -\xi_C \end{pmatrix} \begin{pmatrix} M_A \\ M_B \\ M_C \end{pmatrix} \quad (1)$$

with

$$\xi_A = K_A + f_B k_{AB} + f_C k_{CA}$$
$$\xi_B = K_B + f_A k_{AB} + f_C k_{BC}$$
$$\xi_C = K_C + f_A k_{CA} + f_B k_{BC}$$

where M_i, f_i and K_i (i = A, B and C) denote, respectively, the magnetization, the proton molar fraction and the intrinsic relaxation rate of species i. The quantity k_{ij} (i, j = A, B and C; $i \neq j$) is the spin diffusion rate between species i and j ($k_{ij} = k_{ji}$). Here, A, B and C denote PS, the side chain of PVME (OCH$_3$) and the main chain of PVME (CH and CH$_2$), respectively.

We solved this equation numerically with the initial magnetizations $M_A^0 : M_B^0 : M_C^0 = f_A : f_B : f_C$. The 'best-fit' lines in *Figure 2* were calculated using $K_A = 0.40 \times 10^3\,\mathrm{s}^{-1}$, $K_B = 1.06 \times 10^3\,\mathrm{s}^{-1}$, $K_C = 1.85 \times 10^3\,\mathrm{s}^{-1}$, $k_{AB} = 1.0 \times 10^3\,\mathrm{s}^{-1}$, $k_{CA} = 1.1 \times 10^3\,\mathrm{s}^{-1}$ and $k_{BC} = 100\,\mathrm{s}^{-1}$. The K_i values are in good agreement with the observed initial rates (*Table 2*). Analysis of the $T_{1\rho H}$ curves for pure PVME indicates that the spin diffusion rate between the main chain and side chain of pure PVME is $\sim 100\,\mathrm{s}^{-1}$.

Note that k_{AB} and k_{CA} are larger than k_{BC}, indicating that the ^{1}H spin diffusion operates more effectively between the protons of PS and PVME than between the main chain and side chain protons of PVME. The combination of motions of the main chain and OCH$_3$ of PVME averages more effectively the dipole interaction between the two, resulting in a smaller k_{BC} value. The larger intermolecular spin diffusion rate between PVME and PS is caused by the rigidity of the PS chain at 38°C.

A similar analysis has been reported for a 75/25 poly(2,6-dimethyl-p-phenylene oxide) (PPO)/PS blend[32]; the ^{1}H spin diffusion rate between PPO and PS is $135\,\mathrm{s}^{-1}$, about one eighth of that obtained for the 5/5 PS/PVME blend. The slower spin diffusion rate for the 75/25 PPO/PS blend does not, however, come from motional averaging of the ^{1}H dipole–dipole interactions, but from the microheterogeneity on a scale of 20–30 Å.

Caravatti *et al.*[6] measured the spin diffusion rate of a 59/41 PS/PVME blend by the selective inversion recovery method. They obtained a value of $154 \pm 17\,\mathrm{s}^{-1}$ for the blend, which is one order of magnitude smaller than our value of $k_{AB} = k_{CA} \approx 1000\,\mathrm{s}^{-1}$. They carried out experiments at 67°C, which is higher than our experimental temperature of 38°C. This is one reason for their smaller value.

The spin diffusion rate between PS and PVME ($k_{AB} = k_{CA} \approx 1000\,\mathrm{s}^{-1}$) is not fast enough to average the $T_{1\rho H}$ process of the blend. In order to realize the single-exponential decay curve, the spin diffusion rate must be 10–100 times larger than the fastest intrinsic relaxation rate. However, if the spin diffusion rate is four to 10 times slower than the slowest relaxation rate, the relaxation curve is not single exponential.

The spin diffusion rate under the T_{1H} experimental conditions is larger than that under the ^{1}H irradiation conditions of the $T_{1\rho H}$ experiment[33]. The spin diffusion rate of $\sim 1000\,\mathrm{s}^{-1}$ obtained from the $T_{1\rho H}$ experiments is fast enough to average the T_{1H} process ($\sim 0.5\,\mathrm{s}^{-1}$) of PS and PVME in the blend. Even for pure PVME, a spin diffusion rate of $100\,\mathrm{s}^{-1}$ is fast enough to average the two T_{1H} processes of OCH$_3$ and CH.

Kwei *et al.*[15] observed two T_{2H} components, long and short, for the blend above T_g, suggesting more or less independent segmental motions of PS and PVME. Such different segmental motions of PS and PVME have been reported[17,18].

We conclude that the PS/PVME blend is homogeneous, but from the viewpoint of molecular motion it is microscopically heterogeneous. The microheterogeneity of the PS/PVME blend suggested by several groups[5–7,15,16] may be as a result of ineffective spin diffusion through heterogeneous molecular motion above T_g.

Compositional change during phase separation

Since the PS/PVME blend exhibits a lower critical solution temperature (*LCST*) phase diagram, the blend undergoes phase separation when heated above 100–120°C: the binodal point is at a 5/5 composition[4,23]. The heterogeneity of the phase-separated blend will affect the relaxation process. We studied the compositional change of the 5/5 PS/PVME blend during phase separation by analysing the $T_{1\rho H}$ decay curve.

Figures 3 and *4* show the observed $T_{1\rho H}$ decay curves of the blend after heat treatment for 1 min and 2 min, respectively, at 140°C. In order to minimize the effects of molecular motions on the $T_{1\rho H}$ process, we carried out the measurements at −10°C. After heat treatment, the $T_{1\rho H}$ curves of PS and PVME become double exponential. The decay curves of PS in *Figures 3* and *4* become different from those of PVME. The difference between the two becomes more significant as the heat treatment time increases. These results are clearly brought about by the phase separation.

To analyse the $T_{1\rho H}$ curve of the phase-separated blend, we assumed that the phase-separated blend consists of two spatially separated domains between which spin

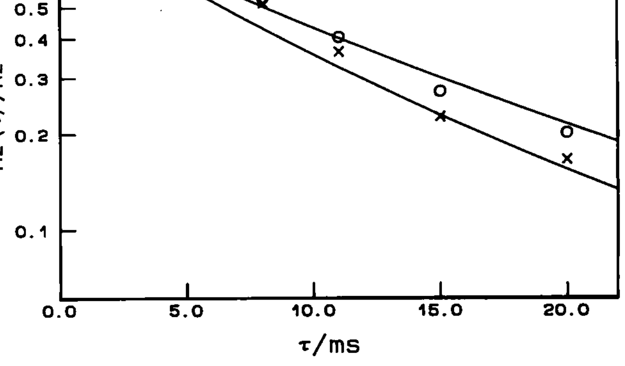

Figure 3 Observed $T_{1\rho H}$ decay curves for PS (○) and PVME (×) in the 5/5 PS/PVME blend after 1 min of heating at 140°C. These decay curves were obtained at −10°C. The solid lines are the 'best-fit' curves from equations (2)

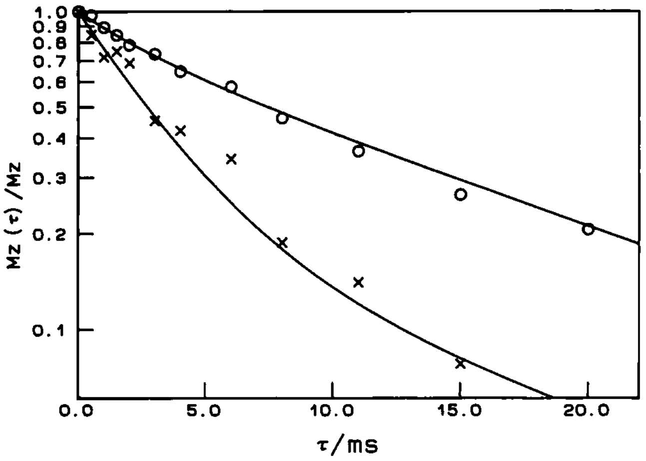

Figure 4 Observed $T_{1\rho H}$ decay curves for PS (○) and PVME (×) in the 5/5 PS/PVME blend after 2 min of heating at 140°C. These decay curves were obtained at −10°C. The solid lines are the 'best-fit' curves from equations (2)

Table 3 Observed^a and calculated (average) $T_{1\rho H}$ values (in milliseconds) for each domain during phase separation at 140°C

Heat treatment time	$T^{E}_{1\rho}$	Calculated	$T^{S}_{1\rho}$	Calculated
20 s	7.3 ± 0.3	3.8	19.7 ± 0.2	3.9
40 s	7.0 ± 1.0	3.7	20.2 ± 0.5	4.1
1 min	6.7 ± 0.2	3.5	17.8 ± 0.2	4.4
1.5 min	5.3 ± 0.8	3.3	17.2 ± 0.1	4.3
2 min	3.1 ± 0.2	3.0	15.3 ± 0.6	6.0

^{a} In each case the error is σ

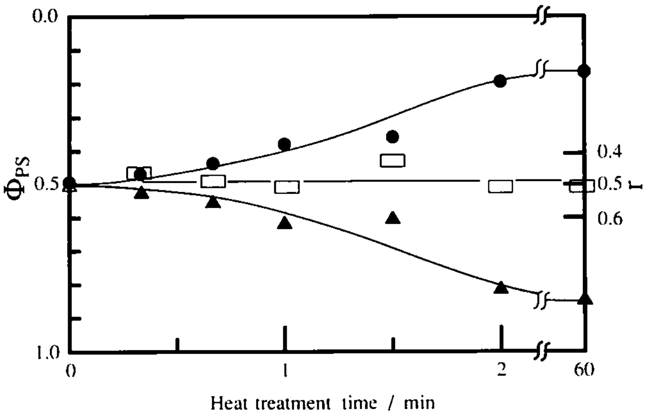

Figure 5 Compositional changes during phase separation of the 5/5 PS/PVME blend: (●) PS in the PVME-rich domain; (▲) PS in the PS-rich domain; (□) fraction of the PVME-rich domain *r*. The solid lines are for guidance only

diffusion does not occur. Within a domain, there occurs fast spin diffusion between PS and PVME.

The normalized ^{1}H magnetization $M_{PS}(\tau)$ of PS is expressed by a double-exponential function which reflects the two relaxation rates of two domains. PS in the PVME-rich domain (E domain) has $T^{E}_{1\rho}$ and that in the PS-rich domain (S domain) has $T^{S}_{1\rho}$. The $T_{1\rho H}$ decays can be written as

$$\begin{aligned} M_{PS}(\tau) &= \chi^{E}_{PS}\exp(-\tau/T^{E}_{1\rho}) + \chi^{S}_{PS}\exp(-\tau/T^{S}_{1\rho}) \\ M_{PVME}(\tau) &= \chi^{E}_{PVME}\exp(-\tau/T^{E}_{1\rho}) + \chi^{S}_{PVME}\exp(-\tau/T^{S}_{1\rho}) \end{aligned} \qquad (2)$$

Here, χ^{i}_{PS} denotes the proton molar fraction of PS in domain i (i = E or S; $\chi^{E}_{PS} + \chi^{S}_{PS} = 1$) and $T^{i}_{1\rho}$ is the $T_{1\rho H}$ of domain i. A similar description applies for PVME.

At the initial stage of phase separation, spin diffusion at the interphase of the domains may be significant when the scale of the domains is small and the fraction of the interphase is relatively high. If spin diffusion occurs to a significant extent, the observed $T_{1\rho H}$ curve probably does not become double exponential in such an initial stage. A domain on a scale of 20–30 Å is distinguishable by $T_{1\rho H}$. However, the observed curves are clearly double exponential: the initial stage in which the domain size remains unchanged lasts for several minutes[15,21,23]. Therefore, we recognize that the domain size is larger than 20–30 Å; thus, we can ignore the effect of spin diffusion at the interphase.

We fitted the two decay curves observed for PS and PVME to equations (2). The adjustable parameters are χ^{E}_{PS}, χ^{E}_{PVME}, $T^{E}_{1\rho}$ and $T^{S}_{1\rho}$. The solid lines shown in *Figures 3* and *4* are the 'best-fit' curves. The 'best-fit' values of χ^{E}_{PS}, χ^{E}_{PVME}, $T^{E}_{1\rho}$ and $T^{S}_{1\rho}$ in *Figure 3* are 0.40 ± 0.05, 0.62 ± 0.06, 6.7 ± 0.2 ms and 17.8 ± 0.2 ms, respectively (the error being standard deviation σ).

We can determine the weight fraction *r* of the E domain in the whole blend and the coexistent composition (ϕ^{E}_{PS} and ϕ^{S}_{PS}) of the phase-separated blend[2] from χ^{E}_{PS} and χ^{E}_{PVME}. Values of *r*, ϕ^{E}_{PS} and ϕ^{S}_{PS} calculated from the 'best-fit' values of χ^{E}_{PS} and χ^{E}_{PVME} in *Figure 3* are 0.51 ± 0.05, 0.39 ± 0.05 and 0.62 ± 0.05, respectively (the error being standard deviation σ).

Table 3 summarizes the 'best-fit' $T_{1\rho H}$ values at −10°C for the samples heat treated for various times. The average $T_{1\rho H}$ value was calculated from the ϕ^{E}_{PS} and ϕ^{S}_{PS} values obtained at each heat treatment time. The $T_{1\rho H}$ values of the PVME-rich domain ($T^{E}_{1\rho}$) is shorter than that of the PS-rich domain ($T^{S}_{1\rho}$). This is because PVME has the shorter $T_{1\rho H}$. The $T_{1\rho H}$ value of the PVME-rich domain changes gradually from 7.3 ms to 3.1 ms with increasing heat treatment time. This is because of increasing PVME content in the PVME-rich domain. The $T_{1\rho H}$ value of the PS-rich domain is less sensitive to a decrease in PVME content. This tendency has also been reported by Chu *et al.*[7]. At present, we cannot explain this. In addition, the $T_{1\rho H}$ values of the PS-rich domain are larger than those of pure PS (*Table 2*). This shows that the characteristic motion of PS is restricted by the neighbouring PVME. The restriction may be more effective when the domain size is smaller; the microstructure established by the compositional fluctuation in the early stages of phase separation may influence the mobility of PS. The predicted values are different from the observed ones, as in the case of the homogeneous blend (*Table 2*). This suggests that the molecular motions of PS and PVME in the phase-separated domains are affected by blending.

The changes in composition during the phase separation process at 140°C are summarized in *Figure 5* for the 5/5 PS/PVME blend. Further heat treatment for more than 2 min does not cause any appreciable change in $T_{1\rho H}$. Heat treatment for more than 2 min would cause a morphological change on a scale larger than 20–30 Å.

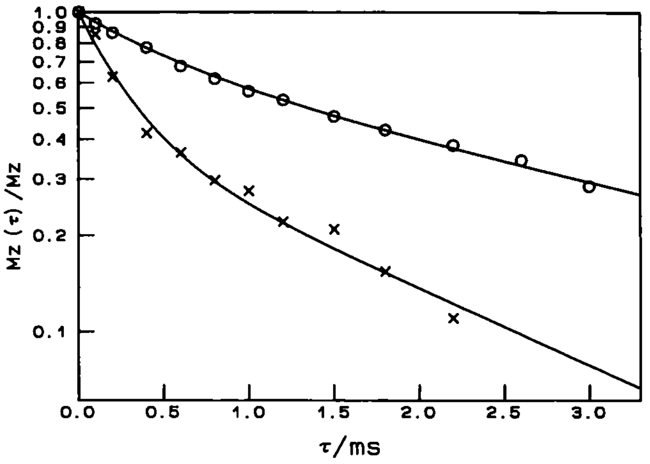

Figure 6 Observed $T_{1\rho H}$ decay curves for PS (○) and PVME (×) in the 5/5 PS/PVME blend after 1 min of heating at 140°C. These decay curves were obtained at 38°C. The solid lines are the 'best-fit' curves from equations (3)

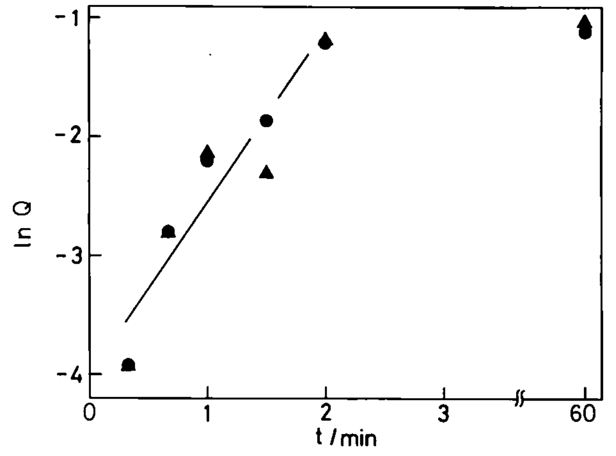

Figure 7 Plots of ln Q *versus* heat treatment time: (●) PVME-rich domain; (▲) PS-rich domain. Q is the total reduction in the composition. The initial slope is three times the phase separation rate R

Figure 6 shows the $T_{1\rho H}$ decay curves of the 5/5 PS/PVME blend observed at 38°C. Fast molecular motion of PVME in the blend averages the ^{1}H dipole–dipole interactions between PS and PVME; the spin diffusion within each domain is slow at 38°C. Even in the same domain, the $T_{1\rho H}$ value of PS is different from that of PVME. Equations (2) should be rewritten as

$$\begin{aligned} M_{PS}(\tau) &= \chi^E_{PS}\exp(-\tau/T^E_{1PS}) + (1-\chi^E_{PS})\exp(-\tau/T^S_{1PS}) \\ M_{PVME}(\tau) &= \chi^E_{PVME}\exp(-\tau/T^E_{1PVME}) \qquad (3) \\ &\quad + (1-\chi^E_{PVME})\exp(-\tau/T^S_{1PVME}) \end{aligned}$$

We assumed that the relaxation curve of each component is single exponential, although a more rigorous treatment like equation (1) should be applied. We adopted six parameters – χ^E_{PS}, T^E_{1PS} and T^S_{1PS} for PS and χ^E_{PVME}, T^E_{1PVME} and T^S_{1PVME} for PVME – to fit the two observed $T_{1\rho H}$ curves to equations (3). In *Figure 6* the 'best-fit' curves are shown by solid lines. It can be seen that the 'best-fit' χ values at 38°C ($\chi^E_{PS} = 0.31 \pm 0.08$ and $\chi^E_{PVME} = 0.6 \pm 0.1$ in *Figure 6*) are in agreement with the values obtained at -10°C ($\chi^E_{PS} = 0.40 \pm 0.05$ and $\chi^E_{PVME} = 0.62 \pm 0.06$ in *Figure 3*) within experimental error. The observed decay curves at various heat treatment times can be described by equations (3) with the χ values obtained at -10°C.

Kinetics of phase separation

It is of interest to study whether the phase separation is governed by spinodal decomposition or a process of nucleation and growth. In the early stages of the spinodal decomposition process, the composition of each domain changes continuously with time[19,20,23,34]. In addition, the fractions of the two domains remain unchanged during the early stages of phase separation. In the nucleation and growth process[23,35], the number of nuclei with a composition close to the binodal increases remarkably with time. The composition of the nuclei remains approximately constant and the fraction of nuclei increases during phase separation.

Figure 5 shows that the ratio r of the PVME-rich domain to the PS-rich domain remains at ~0.5 during phase separation. The PS content of the PVME-rich domain (ϕ^E_{PS}) decreases gradually from 50% to 20% in the first 2 min; the PS content of the PS-rich domain (ϕ^S_{PS}) increases from 50% to 81%. These results clearly indicate that phase separation does not proceed by a process of nucleation and growth, but is initiated by spinodal decomposition. The compositions at 60 min, 17/83 for the PVME-rich domain and 85/15 for the PS-rich domain, are close to the binodal composition. The compositional change during phase separation of the 5/5 PS/PVME blend is almost complete in a few minutes.

Even though the phase separation begins from the 5/5 composition, the r value is not always 0.5. In fact, Nishi *et al.*[23] obtained an r value of 0.35–0.40 from direct ^{1}H observations. The r value reflects the shape of the binodal curve. An r value of ~0.5 implies that the binodal curve is approximately symmetrical.

On the basis of the Cahn theory[34], Nishi *et al.*[23] derived an equation for the total reduction Q of the amount of a minor component in a given phase as follows

$$\ln Q = \text{constant} + 3Rt \qquad (4)$$

where R expresses the growth rate of the amount of component in the phase separation process (phase separation rate) and t is the heat treatment time. If the phase separation process is initiated by spinodal decomposition, R should be positive because the compositional change always increases with time. A negative R is expected for a process of nucleation and growth because the composition of the nuclei does not change significantly[23].

Figure 7 shows plots of $\ln Q$ against heat treatment time t. From the initial slope of $\ln Q$, we found that the R value of the PVME-rich domain is $+8.3 \times 10^{-3}\,\text{s}^{-1}$ ($\sim 0.5\,\text{min}^{-1}$) at 140°C. Similarly, from ϕ^S_{PVME} we found that R in the PS-rich domain is $+7.7 \times 10^{-3}\,\text{s}^{-1}$ ($\sim 0.5\,\text{min}^{-1}$). The two values are close together. That R is positive is consistent with spinodal decomposition. These values are one order of magnitude larger than the value obtained by Nishi *et al.*[23] for PVME in the PS-rich domain ($3.82 \times 10^{-4}\,\text{s}^{-1}$ ($0.02\,\text{min}^{-1}$)) at 130°C. This difference is attributed mainly to the different heat treatment temperature; the phase separation rate at 140°C is 10 times faster than that at 130°C. Gelles and Frank[21] analysed the results of an excimer fluorescence experiment for a phase-separated 1/9 PS/PVME blend at 150°C by assuming spinodal decomposition. They obtained an R value of $0.9\,\mathrm{min}^{-1}$ for the PS-rich domain. This value is slightly larger than the one we obtained, again reflecting the different temperature. The correlation between temperature and phase separation rate has also been shown by Larbi *et al.*[35].

CONCLUSION

We have shown that the diverse results on the miscibility of PS/PVME blends derived from ^1H relaxation measurements are brought about by insufficient spin diffusion because of fast molecular motion. Because the relaxation is affected by molecular motion, one should carefully consider the effects of motion. Otherwise, a wrong conclusion may be reached.

From an analysis of the relaxation curve, we examined the compositional change in the early stages of phase separation. We found that the phase separation is initiated by spinodal decomposition. The phase separation rate was found to be $0.5\,\mathrm{min}^{-1}$ at 140°C.

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