Composition Dependence of the Miscibility and Phase Structure of Amorphous/Crystalline Polymer Blends As Studied by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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ABSTRACT: The composition dependence of the miscibility and the phase structure of poly(vinylphenol) (PVPh) and poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG) blends is studied by high-resolution solid-state ^{13}C NMR spectroscopy. ^{1}H T_1, $T_{1\rho}$, and T_2 and proton spin diffusion are observed indirectly through the ^{13}C resonance. The results indicate that an intermolecular hydrogen-bonding interaction causes the blends to be miscible. The miscibility and the phase structure of the blends show a significant compositional dependence. When PVPh is rich, the two polymers are miscible and form an amorphous phase homogeneous on the 20–30-Å scale as well as the 200–300-Å scale; the crystalline phase of PEO does not exist. The motion of PEO in the miscible phase is restricted by "hard" PVPh. At a PEO composition of about 50 wt %, the amorphous PEO phase appears and coexists together with the miscible phase. The size of this phase is on the order of 10 Å. The blend is miscible on the 200–300-Å scale. The motion of PEO in the amorphous phase is not free as in the amorphous phase of pure PEO. When PEO is rich, the blends appear to be partially miscible. The whole blend consists of the amorphous and the crystalline phases of pure PEO and the miscible phase.

Introduction

The blending of polymers is a simple and economic method to produce new technically important material from two different polymers. The properties of the polymer blend depend on the miscibility and the morphology. A convenient way for improving the impact strength, toughness, and ductility properties is to blend an amorphous polymer with a crystalline one. Generally, crystalline, glassy, or even rubbery phases may coexist in amorphous/crystalline blends.

A pair of poly(vinylphenol) (PVPh) and poly(ethylene oxide) (PEO) is a typical amorphous/crystalline polymer blend. It has been reported that the intermolecular hydrogen-bonding interaction between the two polymers is stronger than the self-association of the phenolic group in PVPh[1,2] and that the blend is miscible in the amorphous phase.[2]

High-resolution solid-state NMR spectroscopy has proven to be a powerful method for characterizing polymer solids. Detailed information about the miscibility, intermolecular interaction, and morphology of polymer blends can be obtained through examining NMR parameters such as the chemical shift, line width, and relaxation parameters.

In this paper, we concentrate our attention on the composition dependence of the miscibility and the morphology of the PVPh/PEO blend. ^{13}C CP/MAS spectra are measured to study the intermolecular interaction. ^{1}H T_1, T_2, and $T_{1\rho}$ relaxation times are used to characterize the phase structure and the miscibility of the blends. The Goldman–Shen experiment combined with the CP/MAS technique[3-7] is also applied to study the morphology of the blend.

Experimental Section

Samples. Poly(vinylphenol) with a molecular weight of 1500–7000 was obtained from Polysciences, Inc. Poly(ethylene oxide) with a molecular weight of 900 000 is a product of Janssen Chimica Co. Poly(ethylene glycol) (PEG) was kindly provided by Asahi-Denka Co., and its molecular weight is 20 000. The glass transition temperature of PVPh is 393 K; the melting temperatures of PEO and PEG are about 333 and 338 K, respectively.

PVPh/PEO and PVPh/PEG blends were prepared by mixing the two polymers in tetrahydrofuran (THF; 1% (w/v)) at 328 K. The mixed solutions were stirred for 3 h. The blends were obtained by evaporating the solvent at room temperature for 3 days in the form of a film. The obtained blend films were dried at 328 K for a week under vacuum and further heated at 393 K for 1 h.

NMR Experiments. High-resolution solid-state ^{13}C NMR experiments were carried out on a JEOL JNM-GX270 spectrometer operating at resonance frequencies of 270 and 67.8 MHz for ^{1}H and ^{13}C, respectively. The radio-frequency (rf) field strength for both ^{1}H and ^{13}C was about 56 kHz. The ^{1}H decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS). The ^{13}C CP/MAS spectra were measured by the normal cross-polarization pulse sequence and the magic angle sample spinning (MAS) of 5.5 kHz. The chemical shifts of ^{13}C spectra are reported in ppm relative to TMS by taking the methine carbon of solid adamantane (29.5 ppm) as an external reference standard. ^{1}H T_1 and $T_{1\rho}$ relaxation times were indirectly measured through ^{13}C resonance by methods reported elsewhere.[8] The pulse sequence for ^{1}H T_2 measurement and the Goldman–Shen pulse sequence combined with the CP/MAS technique[3-7] are shown in parts a and b of Figure 1, respectively. The fixed waiting time t_1 of the Goldman–Shen pulse sequence is 40 μs for all samples. The Torchia pulse sequence for ^{13}C T_1 measurement is shown in Figure 1c, which we used to discriminate the ^{13}C resonances by the ^{13}C T_1 difference. All the experiments are carried out at room temperature. The real temperature inside the spinner is about 310 K, at which temperature the ^{1}H $T_{1\rho}$ values of the crystalline phase of PEO and PEG are very short (see below). A short contact time of the cross-polarization of 100 μs was, therefore, used for all samples.

Results and Discussion

^{13}C CP/MAS Spectra. The ^{13}C CP/MAS spectra of PEO and PEG measured by the normal CP/MAS method are shown in Figure 2. The spectrum of pure PEO which is semicrystalline consists of narrow and broad components. As has been reported, the narrow component corresponds to the amorphous phase and the broad one to

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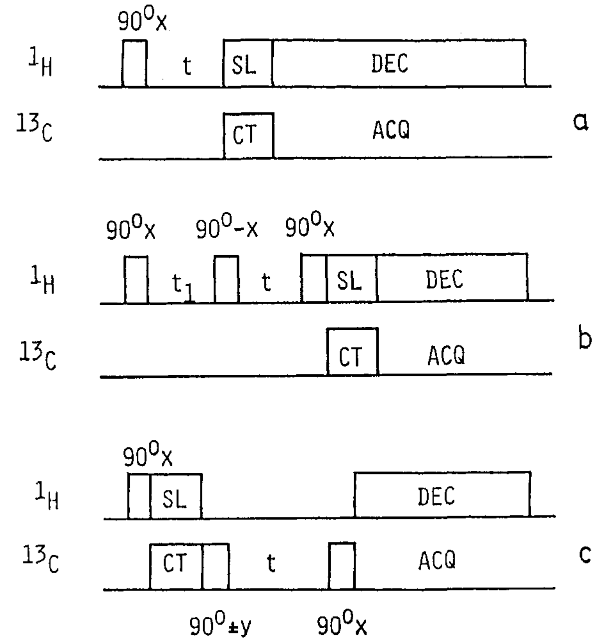

Figure 1. Pulse sequences used in the experiment: (a) sequence for ^{1}H T_2 measurement with CP; (b) Goldman–Shen pulse sequence for spin-diffusion measurement with CP; (c) Torchia pulse sequence.

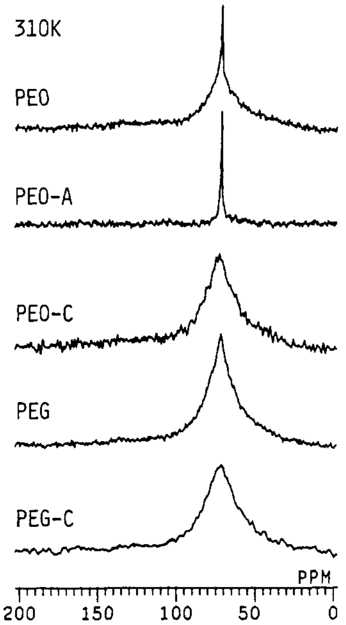

Figure 2. ^{13}C CP/MAS NMR spectra of PEO, the amorphous component of PEO (PEO-A), the crystalline component of PEO (PEO-C), PEG, and the crystalline component of PEG (PEG-C) at 310 K.

the crystalline phase.[9-11] The amorphous phase of PEO has much longer ^{1}H T_2 and shorter ^{13}C T_1 values than the crystalline phase.[9] These differences in relaxation behavior make it possible to observe the spectra of each phase separately.

To eliminate the ^{1}H signal with a short T_2 value, we applied the pulse sequence shown in Figure 1a. After a delay time t of 50 μs, the ^{1}H transversal magnetization of the crystalline phase has relaxed to zero. On the other hand, there remains a considerable amount of magnetization of the amorphous phase. This remaining ^{1}H magnetization is used to enhance the ^{13}C signal via cross-polarization; the ^{13}C spectra of the amorphous phase of PEO can be observed (shown in Figure 2 (PEO-A)). To observe the crystalline phase, the difference in the ^{13}C T_1 between the crystalline phase (15 s) and the amorphous phase (0.1 s) is utilized. During a fixed delay time t of 1.5 s in the Torchia sequence the magnetization of the amorphous phase relaxes to its equilibrium value; only the enhanced ^{13}C signal of the crystalline phase is accumulated. The spectrum is shown in Figure 2 (PEO-C). The results are similar to those observed by utilizing the difference in the cross-polarization ability between the two phases.[10] Since PEG is highly crystalline, the spectrum PEG-C in Figure 2 observed by the Torchia sequence with the delay time t of 1.5 s is similar to that observed by the normal cross-polarization sequence.

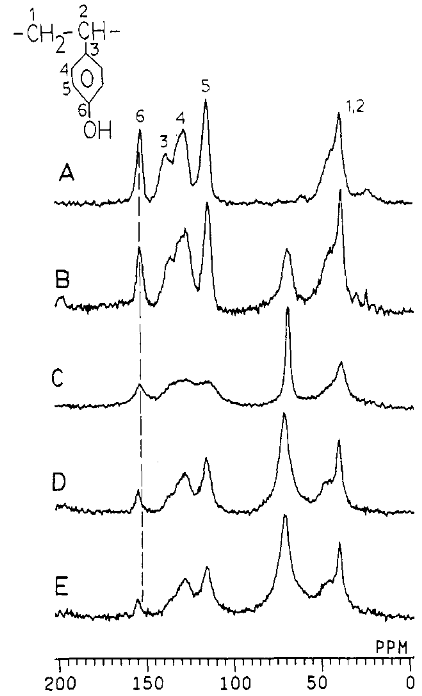

Figure 3. ^{13}C CP/MAS NMR spectra at 310 K: (A) pure PVPh; (B) PVPh/PEO = 73/27; (C) PVPh/PEO = 58/42; (D) PVPh/PEO = 40/60; (E) PVPh/PEO = 31/69.

The ^{13}C CP/MAS spectra of PVPh/PEO and PVPh/PEG blends are shown in Figures 3 and 4, respectively. The assignments are referred to the previous results.[11,12]

Comparison of spectra between the blends and pure PVPh indicates that the phenolic C–OH carbon resonance appears at lower fields for the blends than for pure PVPh; the resonance is observed at 153.7 ppm for pure PVPh and at 155–156 ppm for PVPh/PEO and PVPh/PEG blends. The chemical shift of the CH_2 carbon resonance of PEO and PEG shows little change. The downfield shift of the phenolic C–OH resonance due to the blending is indicative of the intermolecular hydrogen-bonding interaction between PVPh and PEO (PEG). Such downfield shifts have also been reported for other hydrogen-bonding blends.[6,12]

The spectra measured by the Torchia pulse sequence (with 1.5-s delay time) for the blends are shown in Figure 5. The CH_2 peak of PEO in the crystalline phase is not observed for PVPh/PEO (PEG) = 58/42 blends but is observed for PVPh/PEO (PEG) = 40/60 blends. These results indicate that the crystalline phase of PEO (PEG) remains for blends of PVPh composition lower than 50 wt %. At higher PVPh composition, the crystalline phase of PEO (PEG) is destroyed.

^{1}H T_1 and $T_{1\rho}$ Relaxation Times. ^{1}H T_1 and $T_{1\rho}$ relaxation times of PVPh/PEO and PVPh/PEG blends at 310 K are summarized in Tables I and II.

For pure PEO, a single ^{1}H T_1 value is observed; the relaxation rate is averaged out by the spin-diffusion

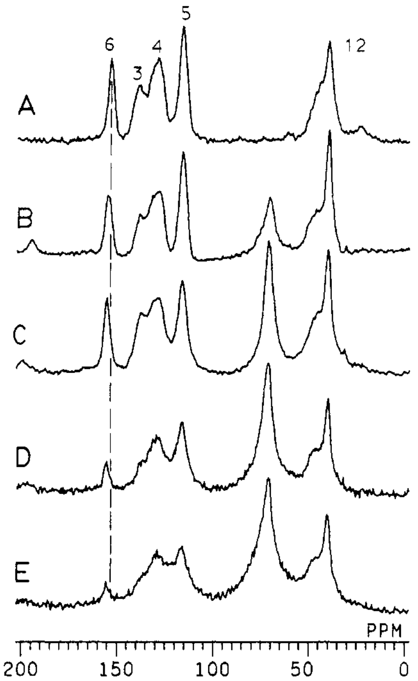

Figure 4. ^{13}C CP/MAS NMR spectra at 310 K: (A) pure PVPh; (B) PVPh/PEG = 73/27; (C) PVPh/PEG = 58/42; (D) PVPh/PEO = 40/60; (E) PVPh/PEG = 31/69.

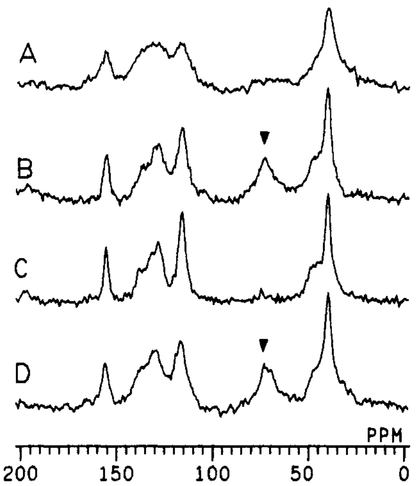

Figure 5. ^{13}C CP/MAS NMR spectra observed by the Torchia pulse sequence with a delay time t of 1.5 s at 310 K: (A) PVPh/PEO = 58/42; (B) PVPh/PEO = 40/60; (C) PVPh/PEG = 58/42; (D) PVPh/PEG = 40/60.

Table I
^{1}H T_1 Values (s) of PVPh/PEO (PEG) Blends at 310 K

	PVPh C-4	PVPh C-5	PVPh C-1,2	PEO (PEG) C-1
PVPh	1.5	1.5	1.5	
PVPh/PEO = 73/27	1.5	1.5	1.5	1.5
PVPh/PEG = 73/27	1.4	1.5	1.5	1.5
PVPh/PEO = 58/42	0.73	0.73	0.74	0.71
PVPh/PEG = 58/42	0.95	0.96	0.96	0.95
PVPh/PEO = 40/60	0.98	1.0	1.0	1.2
PVPh/PEG = 40/60	0.96	0.99	1.4	1.0
PVPh/PEO = 31/69	1.2	1.3	1.3	1.6
PVPh/PEG = 31/69	1.6	1.7	1.9	2.3
PEO				2.0
PEG				4.9

Table II
^{1}H $T_{1\rho}$ Values (ms) of PVPh/PEO (PEG) Blends at 310 K

	PVPh C-4	PVPh C-5	PVPh C-1,2	PEO (PEG) C-1
PVPh	7.1	7.2	7.2	
PVPh/PEO = 73/27	3.1	3.2	3.2	3.0
PVPh/PEG = 73/27	2.8	2.6	2.9	2.0
PVPh/PEO = 58/42	1.3	1.2	1.5	1.1
PVPh/PEG = 58/42	1.7	1.6	2.2	0.65
PVPh/PEO = 40/60	1.4	1.4	1.2	1.1 (75%) 0.18 (25%)
PVPh/PEG = 40/60	1.6	1.3	1.9	1.2 (60%) 0.17 (40%)
PVPh/PEO = 31/69	1.4	1.3	1.9	1.0 (57%) 0.19 (43%)
PVPh/PEG = 31/69	1.1	1.1	1.1	1.0 (62%) 0.17 (38%)
PEO				5.4 (43%) 0.16 (57%)
PEG				0.23

coupling between the crystalline and the amorphous phases. This observation suggests that the domain sizes of PEO crystalline/amorphious phases are less than the ^{1}H T_1 measuremental scale of 200–300 Å.[13] Two $T_{1\rho}$ components are observed. The shorter component with a $T_{1\rho}$ value of 160 μs corresponds to the crystalline phase and the longer one (5.4 ms) to the amorphous phase. This result combined with the T_1 result suggests that the domain size of amorphous/crystalline phases is between 20–30 and 200–300 Å. Pure PEG which is highly crystalline shows a single ^{1}H T_1 value of 4.9 s and a single ^{1}H $T_{1\rho}$ value of 230 μs. These values are different from those of pure PEO.

The single ^{1}H T_1 and $T_{1\rho}$ are observed for pure PVPh as reported previously;[12] this polymer is amorphous.

For PVPh-rich blends (PVPh/PEO (PEG) = 73/27 and 58/42), single ^{1}H T_1 and $T_{1\rho}$ values are observed and the short ^{1}H $T_{1\rho}$ component of pure PEO (PEG) disappears. The T_1 and $T_{1\rho}$ values observed through PVPh are identical to those observed through PEO (PEG). The results indicate that for these blends the crystalline phase of PEO (PEG) disappears and that the two polymers are miscible on the scale of 200–300 Å as well as the scale of 20–30 Å.[13]

For PEO (PEG)-rich blends (PVPh/PEO (PEG) = 40/60 and 31/69), although a single ^{1}H T_1 value is observed for PEO (PEG) in the blends, the value is different from those observed for PVPh. Furthermore, the two-component ^{1}H $T_{1\rho}$ is observed through PEO (PEG). The longer values (1.0–1.2 ms) are different from the values of the amorphous phase of either pure PEO (5.4 ms) or PVPh (7.2 ms). The results suggest that the two polymers are not phase-separated completely but are miscible to some extent. The shorter value (170–190 μs) corresponds to that of the PEO crystalline phase, indicating that the crystalline phase of PEO (PEG) exists in the blends; the blends are not completely miscible.

^{1}H Spin–Spin Relaxation. The ^{1}H T_2 values of PVPh/PEO and PVPh/PEG blends observed at 310 K are shown in Table III.

The ^{1}H T_2 decay of pure PVPh observed through each PVPh carbon resonance is Gaussian with a short T_2 value of about 13 μs. This is consistent with the fact that the motion of PVPh is frozen in the glassy state (T_g = 393 K). The ^{1}H T_2 decay of pure PEO has two components. One is Gaussian with a T_2 value of 20 μs and the other Lorentzian with a T_2 of 350 μs. These two components correspond respectively to the crystalline and the amorphous phases of PEO. For highly crystalline polymer PEG, only a single short T_2 (16 μs) is observed.

The ^{1}H T_2 decays of PVPh in the blends are described by a Gaussian component with a value of 13–16 μs. The ^{1}H T_2 value of PEO (PEG) in the blends depends significantly on the composition. For PVPh/PEO (PEG) = 73/27 blends, the T_2 values of PEO (PEG) are rather short (22 and 17 μs) and the longer T_2 component cannot be observed. As the PEO (PEG) composition increases to

Table III
^{1}H T_2 (μs) of PVPh/PEO (PEG) Blends at 310 K[a]

	PVPh C-4	PVPh C-5	PVPh C-1,2	PEO (PEG) C-1
PVPh	13	13	14	
PVPh/PEO = 73/27	13	14	11	22
PVPh/PEG = 73/27	15	15	13	17
PVPh/PEO = 58/42	17	17	14	25 (20%) 185 (80%)L
PVPh/PEG = 58/42	14	14	11	18 (28%) 78 (72%)L
PVPh/PEO = 40/60	17	15	12	17 (43%) 81 (57%)L
PVPh/PEG = 40/60	16	16	12	15 (40%) 90 (60%)L
PVPh/PEO = 31/69	13	14	12	13 (58%) 81 (42%)L
PVPh/PEG = 31/69	13	15	12	12 (54%) 86 (46%)L
PEO				20 (52%) 353 (48%)L
PEG				16

[a] L denotes the Lorentzian ^{1}H T_2 decay, and all others are Gaussian decays. The value in parentheses represents the proton number percentage of the two components.

42 wt %, the longer T_2 component becomes observable. At the composition of PEO (PEG) of 69 wt %, the longer T_2 component of PEO (PEG) amounts to 42% (46%).

The results of ^{1}H T_2 can be interpreted in terms of the effects of motion and phase structure. For the PVPh/PEO (PEG) = 73/27 blend, the observed single short T_2 of PEO (PEG) cannot be attributed to the crystalline phase, because the crystalline phase does not exist. This is, therefore, due to slow motion of PEO (PEG) restricted by "hard" PVPh. The two polymers associate with each other so strongly that there is no remarkable difference in mobility between the two. This is similar to the case of polystyrene/poly(vinyl methyl ether)[14] and poly(vinylphenol)/poly(methyl acrylate)[6] blends at low temperatures. The appearance of the longer T_2 component at the PEO (PEG) composition of 42 wt % indicates that some PEO (PEG) molecules in the blend become mobile. Although these PEO (PEG) molecules are not as free as in the amorphous phase of pure PEO (PEG), they possibly form a similar amorphous phase in the blend. At higher PEO (PEG) compositions of 60 and 69 wt %, the crystalline phase of PEO (PEG) exists; hence, a large part of the short T_2 component is attributed to the crystalline phase and the rest to the miscible phase.

Goldman–Shen Experiment. The Goldman–Shen experiment[3] makes it possible to differentiate protons with different ^{1}H T_2 values. We combine the Goldman–Shen pulse sequence with the CP/MAS technique to observe the ^{1}H spin diffusion by the ^{13}C resonance. Since the ^{1}H T_2 of PEO (PEG) in the amorphous phase is longer (>80 μs) than those of PVPh (11–17 μs), it is possible to differentiate the CH$_2$ protons of amorphous PEO (PEG) from the others in the blends.

We choose 40 μs as the delay time t_1 of the Goldman–Shen experiment. After t_1 of 40 μs, the transversal magnetization of PVPh with the shorter T_2 values created by the first 90°(x) pulse fades out to zero while the magnetization of amorphous PEO (PEG) remains nonzero because of the longer ^{1}H T_2. The remaining transversal magnetization of the amorphous PEO (PEG) is then transformed to the longitudinal magnetization by the second 90°($-x$) pulse. During the diffusion time t, the ^{1}H magnetization will diffuse from the CH$_2$ protons of amorphous PEO (PEG) to the PVPh protons through the ^{1}H–^{1}H dipolar interaction. Then, the ^{1}H magnetization is transferred to the carbon spins through the cross-polarization technique, and thereby the spin-diffusion process during the time t is monitored through the intensity of the carbon resonances. The ^{13}C CP/MAS spectra of the PVPh/PEO = 58/42 blend at various spin-diffusion times are shown in Figure 6.

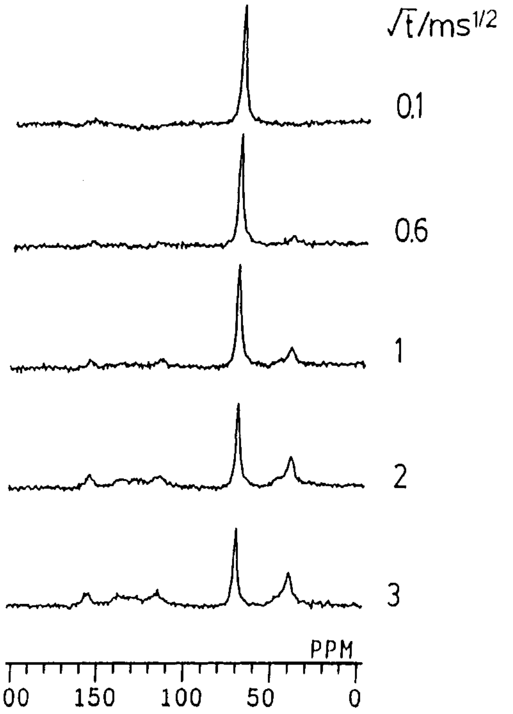

Figure 6. ^{13}C CP/MAS NMR spectra of the PVPh/PEO = 58/42 blend observed by the Goldman–Shen pulse sequence combined with the cross-polarization technique with a fixed delay time t_1 of 40 μs at various spin-diffusion times t at 310 K.

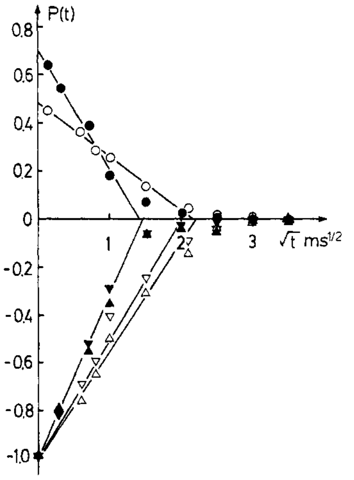

Figure 7. Plots of ^{1}H magnetization change ($P(t)$) vs the square root of the spin-diffusion time $t^{1/2}$ for PVPh/PEO and PVPh/PEG = 58/42 blends at 310 K. ○ and ●, △ and ▲, and ▽ and ▼ express respectively the results observed through CH$_2$ of PEO or PEG, C-1,2, and C-5 of PVPh. Straight lines are drawn through the initial linear portion of the data to determine t_e.

We adopt the method of data treatment suggested by VanderHart[15] and Tekely et al.;[5] $P(t) = (M(t) - M_{eq})/M_{eq}$ is plotted against the square root of the spin-diffusion time for PVPh/PEO (PEG) = 58/42 blends as shown in Figure 7. Here, $M(t)$ is the ^{13}C magnetization at a diffusion time t and M_{eq} is the pseudoequilibrium magnetization at a diffusion time long enough but still shorter than ^{1}H T_1.

From the intercept of the straight line with the abscissa, we obtain an effective diffusion time t_e of 4.4 ms ($t_e^{1/2}$ = 2.1) and 2 ms ($t_e^{1/2}$ = 1.4) for PVPh/PEO = 58/42 and

Table IV
Domain Size of PVPh/PEO (PEG) Blends

sample	$T_{2L}/\mu s$	$D/\mathrm{cm^2\,s^{-1}}$ (10^{-12})	t_e/ms	$\langle x^2\rangle^{1/2}$/Å
PVPh/PEO = 58/42	185	1.5	4.4	9
PVPh/PEG = 58/42	78	3.5	2.0	10
PVPh/PEO = 40/60	81	3.4	4.0	13
PVPh/PEG = 40/60	90	3.0	4.0	12
PVPh/PEO = 31/69	81	3.4	3.2	12
PVPh/PEG = 31/69	86	3.2	2.3	10

PVPh/PEG = 58/42, respectively; t_e represents approximately the time required for the magnetization to reach the local pseudoequilibrium.

The mean square of the effective diffusive path length $\langle x^2\rangle$ during an effective diffusion time t_e can be given in one-dimension as[15,16]

$$\langle x^2\rangle = 4Dt_e/3 \qquad (1)$$

The spin-diffusion coefficient D can be estimated by the method suggested by Assink[17]

$$D = 2(r_0)^2/T_2 \qquad (2)$$

where r_0 is the proton van der Waals radius of 1.17 Å and T_2 is the spin–spin relaxation time. The D value is calculated to be 1.5×10^{-12} and 3.5×10^{-12} cm^2/s for PVPh/PEO = 58/42 and PVPh/PEG = 58/42 blends, respectively, using the corresponding T_2 values of 185 and 78 μs. These values of spin diffusion are close to those reported for other polymers.[5,15]

We calculated the $\langle x^2\rangle^{1/2}$ value from eq 1 combined with eq 2 using the T_2 values of the Lorentzian decay of PEO (PEG) listed in Table III and the experimental values ov t_e. In Table IV are compiled the results for PVPh/PEO (PEG) = 58/42, 40/60, and 31/69 blends together with the required data. Since the spin diffusion occurs between PEO (PEG) in the mobile amorphous phase and PVPh in the miscible phase, the values of $\langle x^2\rangle^{1/2}$ are interpreted to represent the domain size of the amorphous phase of PEO and the miscible phase of PVPh/PEO. The results show that the domain size is on the order of 10 Å.

The effective diffusion time of 2–4 ms for the blends suggests that the spin-diffusion coupling interaction is not so strong that the $T_{1\rho}$ values are not averaged during the short $T_{1\rho}$ time (about 1–3 ms). This is a reason why the $T_{1\rho}$ values observed through PVPh are not *completely* identical to those observed through PEO (PEG).

Before concluding, we note the effects of magic angle sample spinning. Haeberlen and Waugh[18] reported that magic angle sample spinning has little effect on T_1 but has some effect on T_2 and $T_{1\rho}$. Tekely et al. reported that T_2 of the mobile amorphous component becomes longer by magic angle sample spinning. The T_2 values of the Lorentzian component of PEO (PEG) listed in Table III are probably large as compared with those without sample spinning. Caravatti et al.[19] noted that averaging of the dipolar interaction by molecular motion leads to reduced dipolar couplings which become sensitive to the sample spinning. The sample spinning may reduce spin diffusion. The domain size listed in Table IV may be overestimated. We do not think, however, that the overestimation is serious enough to change the conclusion.

Conclusion

The present results of PVPh/PEO and PVPh/PEG blends indicate that the intermolecular hydrogen-bonding interaction causes the blends to be miscible. The miscibility and the phase structure of the blends show a significant compositional dependence. When PVPh is rich, the blends are completely miscible on a scale of 20–30 Å as well as 200–300 Å and form a single miscible amorphous phase. The motion of PEO (PEG) in the miscible phase is restricted by PVPh. At a PEO (PEG) composition of about 50 wt %, the amorphous PEO (PEG) phase appears and coexists with the miscible phase. The size of the amorphous PEO (PEG) phase is on the order of 10 Å. The blend is, hence, miscible on the 200–300-Å scale. The motion of PEO in the amorphous phase is not free as in the amorphous phase of pure PEO. When PEO (PEG) is rich, the blends appear to be partially miscible. The whole blend consists of the amorphous and the crystalline phases of pure PEO (PEG) and the miscible phase.

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