¹H Spin–Spin Relaxation and Spin-Diffusion of Poly(vinyl phenol)/Poly(methyl acrylate) Blends

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ABSTRACT: ¹H spin–spin relaxation time (T_2) and ¹H spin-diffusion of poly(4-vinyl phenol)/poly(methyl acrylate) (PVPh/PMA) blend are measured indirectly by observing well-resolved ¹³C CP/MAS resonance. The results indicate that at 310 K the molecular motion of the whole chain of PMA in the blends is hindered by mixing with PVPh. At 361 K, the blending hinders only the main-chain motion of PMA; the CH_3 group in the side-chain still undergoes more or less free rotation. The spin-diffusion from the CH_3 protons of PMA to the protons of PVPh occurs in the blend. It is concluded that PVPh and PMA are intimately mixed in the blend.
        KEY WORDS   ¹H Spin–Spin Relaxation / Spin-Diffusion / ¹³C CP/MAS
        NMR / Poly(vinyl phenol)/Poly(methyl acrylate) / Polymer Blend /

In a recent paper,[1] we reported high-resolution solid-state ¹³C NMR studies of poly(4-vinyl phenol)/ poly(methyl acrylate) (PVPh/PMA) blend. The results indicated that the intermolecular hydrogen-bonding interaction is responsible for the two polymers to be intimately mixed on a scale of 20—30 Å. The intimate mixing is expected to bring about significant change in the molecular motion of the two polymers.

¹H spin–spin relaxation time (T_2) is a sensitive parameter for studying molecular motion of polymer.[2] It reflects the large-scale segmental motion related to the glass transition. It also reflects local motions of the main-chain and side-chain.[3] Even a slight change in motion induced by blending would alter the relaxation time. The purpose of this paper is to obtain information about molecular motion of the PVPh/PMA blend. We can measure the ¹H spin–spin relaxation

time by ¹H spin-echo experiment. It is, however, difficult to measure ¹H T_2 of each polymer in blend separately, becasue ¹H spectra of solid polymers are broad. The ¹³C spectra observed by the magic-angle sample spinning and ¹H dipolar decoupling method are well resolved. We take this advantage to measure the ¹H T_2 indirectly by observing the high-resolution spectra of ¹³C that directly attaches to the proton

Proton spin-diffusion provides information about the miscibility of polymer blend. Much work has been done on the spin-diffusion from theoretical and experimental view-points.[4–14]

Another purpose of this paper is to obtain information about the miscibility of the blend. We utilize the Goldman-Shen pulse sequence combined with cross polarization/magic-angle sample spinning (CP/MAS) to measure the spin diffusion between PMA and PVPh.

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EXPERIMENTAL

PVPh was obtained from Polysciences Inc. The molecular weight was 1500—7000. PMA was obtained from Aldrich Chemical Company Inc. The number- and weight-average molecular weights of PMA were 10600 and 30700, respectively.

The PVPh/PMA blend was prepared by the solution-cast method using tetrahydrofuran (THF) as a solvent. PVPh and PMA were separately dissolved in THF at a concentration of 1% (w/v). The two solutions were mixed together at room temperature at given weight ratios. After stirring the mixed solutions for 3 h, the solvent was allowed to evaporate at room temperature for several days. The resulting samples were further dried under reduced pressure at 333 K for two weeks. We prepared five blend samples; the composition of blend is expressed in weight ratio of the two polymers. Pure PVPh and PMA samples were prepared in the same way.

^{13}C CP/MAS NMR experiments were carried out on a JEOL JNM-GX270 spectrometer operating at 270 and 67.8 MHz for ^{1}H and ^{13}C, respectively. The radio-frequency field strength for both ^{1}H and ^{13}C was about 56 kHz. A double-bearing aluminum oxide rotor was used. The magic angle was adjusted by monitoring the ^{79}Br NMR spectrum of KBr incorporated in the rotor. The ^{1}H decoupling frequency was set 3 ppm downfield from tetramethylsilane (TMS). The ^{13}C CP/MAS spectra were measured by the normal CP/MAS pulse sequence at a magic-angle sample spinning rate of about 6 kHz. The CP contact time was 1.2 ms at 310 K and 0.6 ms at 361 K. The chemical shift of ^{13}C spectra was measured in ppm relative to the methine resonance of solid adamantane as 29.5 ppm. Variable-temperature measurements were made using a JEOL MVT temperature controller in an accuracy of 1 K. Temperature calibration was done by the conventional methanol method.
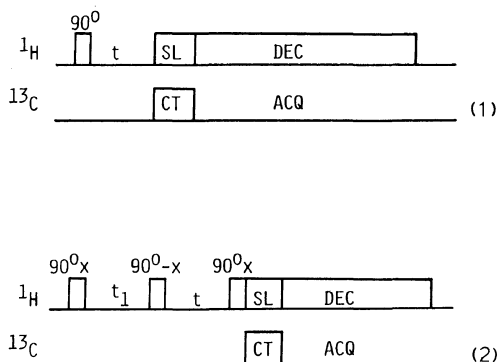
^{1}H T_2 measurement was made by the pulse

Figure 1. Pulse sequences used in the work. (1) pulse sequence for ^{1}H T_2 measurement with CP; (2) pulse sequence of Goldman–Shen spin-diffusion measurement with CP.

sequence shown in Figure 1(1).[12] The first ^{1}H 90° pulse creates a proton transversal magnetization. It decays with T_2. The decayed magnetization at a delay time t is transferred to ^{13}C. Then we observe the ^{13}C resonance by the magic-angle spinning and broad-band ^{1}H decoupling technique. The delay time t was varied from 1 μs to 100 μs.

The ^{1}H spin diffusion was measured using the Goldman–Shen pulse sequence[4] combined with the CP/MAS technique shown in Figure 1(2).[11,12] For a constant delay time t_1 (22 μs), a shorter T_2 component of ^{1}H transveral magnetization ($T_2 < 22 \mu$s) vanishes, and only a longer T_2 component remains. The second 90°$_{-x}$ pulse, therefore, flips only the longer T_2 magnetization back in the z-direction. An inhomogenous distribution of ^{1}H magnetization is created in the sample. For time t, the magnetization gradually approaches a uniform distribution through the spin-diffusion. We measure the ^{1}H magnetization at a time t by observing ^{13}C resonances using the CP/MAS technique.

RESULTS AND DISCUSSION

Figure 2 shows the ^{13}C CP/MAS spectra at 310 K of pure PVPh(A), PVPh/PMA = 1/1 blend(B), and pure PMA(C). The resonances
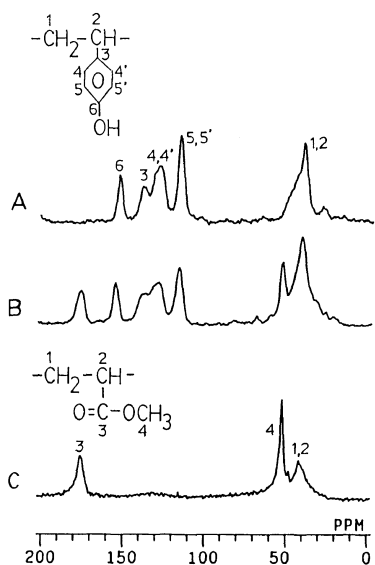
Figure 2. ^{13}C CP/MAS NMR spectra of PVPh/PMA blends at 310 K: A, pure PVPh; B, PVPh/PMA = 1/1; C, pure PMA.

of two polymers in the blend are well-resolved. We can, therefore, measure the [1]H T_2 of each polymer in the blend separately. Table I lists [1]H T_2 values at 310 K and 361 K of pure PVPh, five PVPh/PMA blends with different weight ratios, and pure PMA.

[1]H T_2 decay of pure PVPh shows a fast Gaussian decay with a small T_2 value of about 13 μs for all PVPh carbon resonances at 310 and 361 K.

[1]H T_2 values of the main-chain of pure PMA observed through the C-1 and C-2 resonances are also small (14 μs) at 310 K. On the other hand, neither single Gaussian decay nor single Lorentzian decay can represent the [1]H T_2 decay observed through the CH$_3$ (C-4) resonance of the side-chain as shown in Figure 3. The solid line represents the superposition of two types of decay: a slow Lorentzian with a T_2 value of 89 μs and a fast Gaussian with a T_2 value of 17 μs. At 361 K, the decay is a single Lorentzian with a larger T_2 value of 155—210 μs for all

Table I. [1]H T_2 (μs) of PVPh/PMA blends at 310 and 361 K[a]

		PMA C-3	PVPh C-6	PVPh C-4	PVPh C-5	PMA C-4		PVPh,PMA C-1,2 C-2
PVPh	310 K		13	13	13			14
	361 K		13	13	13			13
PVPh/PMA = 4/1	310 K	13	15	15	14		16	13
	361 K		14	14	13	14 (76%) 55 (24%)L		14
PVPh/PMA = 2/1	310 K	14	15	15	15	15		14
	361 K	14	13	14	14	14 (65%) 51 (35%)L		13
PVPh/PMA = 1/1	310 K	14	15	15	15	14		14
	361 K	14	15	15	15	14 (62%) 56 (38%)L		14
PVPh/PMA = 1/1.5	310 K	13	12	13	13	12		12
	361 K	19	22	18	22	16 (27%) 53 (73%)L		16
PVPh/PMA = 1/3	310 K	14	16	16	14	13(82%) 86(18%)L		14
	361 K	—	—	—	—	—		—
PMA	310 K	20				17 (52%) 89 (48%)L		14
	361 K	155L				210L		180L

[a] "L" denotes Lorentzian [1]H T_2 decay and all others, Gaussian decay. The value in parenthesis represents proton-number percentage of the two components.
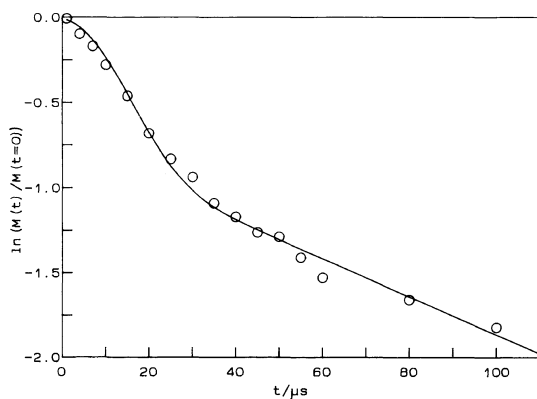
Figure 3. The normalized decay curve of ^{1}H magnetization of C-4 proton of pure PMA at 310 K. The solid line represents the superposition of a slow Lorentzian with a T_2 value of 89 μs and a fast Gaussian with a T_2 value of 17 μs.

resonances of PMA.

The fast Gaussian decay with small T_2 observed for pure PVPh indicates that PVPh is in the glassy state at 310 and 361 K. This is consistent with the fact that the glass transition temperature T_g of PVPh is 393 K. The Lorentzian decay with the larger T_2 value observed for pure PMA at 361 K is in accord with the fact that PMA is in the rubbery state at this temperature.

Pure PMA is in a more complicated motional state at 310 K than PVPh. The main-chain motion of PMA is not fully excited at 310 K. The temperature of 310 K is not high enough to activate the main-chain motion on the NMR time scale. On the other hand, the CH$_3$ group of side-chain undergoes rotation rather freely.

Since the cross-polarization occurs through dipolar interaction, a large part of ^{13}C polarization is brought about by directly-bonded rigid protons. ^{13}C resonance of the PMA main-chain is, therefore, enhanced by the main-chain rigid protons, showing small ^{1}H T_2 at 310 K as seen in Table I. On the other hand, there is no proton that makes a major contribution to the ^{13}C polarization of the CH$_3$ group of PMA (C-4), because the directly-bonded CH$_3$ protons undergo rotation, and

the rigid main-chain protons are distant. It seems that the main-chain protons and CH$_3$ protons make a contribution to the ^{13}C polarization in a similar degree. There appear, therefore, two components: a fast Gaussian decay with T_2 of 17 μs (52%) and a slow Lorentzian decay with T_2 of 89 μs (48%). At 361 K, we only obtain a longer Lorentzian component with T_2 of 155—210 μs for both the main-chain and the CH$_3$ carbons, indicating that rapid segmental motion occurs.

All PVPh/PMA blends studied here show a fast Gaussian component with a ^{1}H T_2 value of about 13—16 μs at 310 K. The longer T_2 component of the CH$_3$ resonance of PMA is detected in a small fraction (18%) only for PV Ph/PMA = 1/3 blend. At 361 K, the CH$_3$ resonance of PMA in the blends shows the fast Gaussian component, though the CH$_3$ of pure PMA does not. The T_2 value of the slow Lorentzian component of the CH$_3$ resonance of PMA in the blend is 51—56 μs, smaller than that of pure PMA (210 μs).

These results suggest that PMA and PVPh are intimately mixed and that neighboring "hard" PVPh chains hinder the main-chain motion of PMA in the blend. The rotation of CH$_3$ group of PMA is not so greatly influenced by blending. This is comparable to poly-styrene/poly(vinyl methyl ether) blend.[15]

Goldman–Shen experiments were performed to examine spin-diffusion in PVPh/PMA = 1/1.5 blend at 361 K. The CH$_3$ protons of PMA have long T_2 as compared to other protons. Immediately after the second 90°$_{-x}$ pulse, an inhomogeneous distribution of magnetization is created. For delay time t, the magnetization of CH$_3$ protons declines and those of other protons recover by spin diffusion.

On the basis of the method suggested by VanderHart,[13] $P(t) = (M(t) - M_{eq})/M_{eq}$ was plotted against $t^{1/2}$ as shown in Figure 4, where $M(t)$ is the magnetization after diffusion time t and M_{eq} is the magnetization in internal equilibrium. We see a linear relationship between $P(t)$ and $t^{1/2}$ at least at the initial stage.
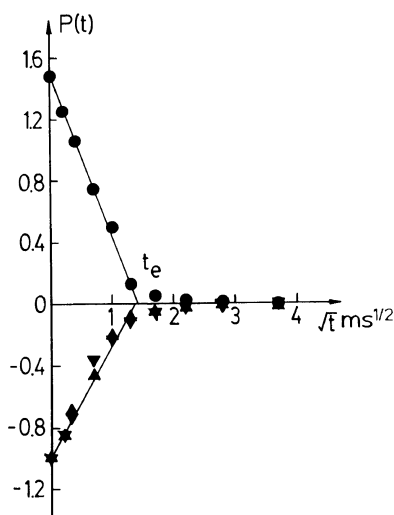
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Figure 4. Plot of $P(t)$ vs. square root of spin-diffusion time $t^{1/2}$ for PVPh/PMA = 1/1.5 blends at 361 K. (●), (▼), and (▲) represent, respectively, data observed through the C-4 resonance of PMA, the C-5,5′ resonances of PVPh, and the C-1, 2 resonance of both PVPh and PMA in the blend. Straight lines are drawn through the linear portion of the data at early stage to determine the intercept time t_e.

The decay rate of the CH_3 protons is comparable to the recovery rate of the C-5,5′ protons of PVPh and those of the main-chain protons of PVPh and PMA. The results indicate that the spin-diffusion occurs from the CH_3 protons of PMA to other protons including the protons of PVPh in the blend in a similar way. This is other evidence for the good miscibility of the blend.

We define an effective spin-diffusion time t_e as the intercept of the straight line with the abscissa: time required for magnetization to reach the internal equilibrium.[13] We obtain t_e of $2ms(t_e^{1/2} = 1.4)$. Because ^1H T_1 of the blend is longer than t_e, we can neglect the T_1 effect in the spin-diffusion process.

In summary, the present study indicates that at 310 K molecular motion of PMA in the blends is considerably hindered by the mixing with PVPh. At 361 K, the blending hinders only the main-chain motion of PMA. The side-chain still undergoes more or less free rotation. The spin-diffusion between the CH_3 protons of the PMA side-chain and the other protons of PVPh occurs. The results obtained here provide additional evidence that PVPh and PMA are intimately mixed in the blend.[1] The two polymers associate each other so closely that they act as a single polymer.

REFERENCES

1. X. Zhang, K. Takegoshi, and K. Hikichi, *Macromolecules*, **24**, 5756 (1991).
2. V. J. McBrierty, *Polymer*, **15**, 503 (1974).
3. M. Andreis and J. Koenig, *Adv. Polym. Sci.*, **89**, 71(1989).
4. M. Goldman and L. Shen, *Phys. Rev.*, **144**, 321 (1966).
5. R. A. Assink, *Macromolecules*, **11**, 1233 (1978).
6. T. T. P. Cheung and B. C. Gerstein, *J. Appl. Phys.*, **52**, 5517 (1981).
7. K. J. Packer, J. M. Pope, and R. R. Yeung, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 589 (1984).
8. J. R. Havens and D. L. VanderHart, *Macromolecules*, **18**, 1663 (1985).
9. P. Caravatti, P. Neuenschwander, and R. R. Ernst, *Macromolecules*, **18**, 119 (1985).
10. P. Caravatti, P, Neuenschwander, and R. R. Ernst, *Macromolecules*, **19**, 1889 (1986).
11. Y. Wang, Q. Chen, and X. Zhang, "Interfaces in Polymer, Ceramic, and Metal Matrix Composites," H. Ishida, Ed., Elsevier Press, New York, N.Y., 1988, p 249.
12. P. Tekely, D. Canet, and J-J. Delpuech, *Mol. Phys.*, **67**, 81 (1989).
13. D. L. VanderHart, *Makromol. Chem. Macromol. Symp.*, **34**, 125 (1990).
14. H. Tanaka and T. Nishi, *Phys. Rev. B*, **33**, 32 (1986).
15. T. Nishi, T. Wang, and T. Kwei, *Macromolecules*, **8**, 227 (1975).