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Miscibility and Molecular Motion of PMAA/PVAc Blends Investigated by High-Resolution Solid-State CPMAS ^{13}C NMR

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ABSTRACT: The miscibility of poly(methacrylic acid) (PMAA) and poly(vinyl acetate) (PVAc) blends was investigated by the CPMAS ^{13}C NMR. The ^{1}H spin−lattice relaxation time in the laboratory frame (T_1^H) showed that the PMAA/PVAc blends are homogeneous on a scale of 20−50 nm, and the ^{1}H relaxation time in the rotating frame ($T_{1\rho}^H$) revealed that the PMAA/PVAc-rich blends are partially inhomogeneous on a scale of 2−5 nm, while the PMAA-rich/PVAc blends, including the PMAA/PVAc = 1/1 blend, are completely miscible on the scale. The domain size of the PMAA/PVAc = 1/1 blend was also estimated from the Goldman−Shen experiment. The obtained maximum domain size of 2.5 nm is consistent with the results of $T_{1\rho}^H$. The decomposition of ^{13}C NMR spectra for the carboxyl (COOH) and carbonyl (COO) regions and the ^{13}C spin−lattice relaxation time in the laboratory frame (T_1^C) suggested the existence of an interpolymer interaction between PMAA and PVAc: the interaction is most likely a hydrogen bond and acts an important role for a great miscibility. The dependence of T_1^C on the PMAA molar ratio indicates that the molecular motion of PVAc is largely affected by PMAA.

Introduction

The good miscibility of the blends composed with poly(methyl acrylate) (PMA: $-\{CH_2CH(COOCH_3)\}_n-$) and poly(vinyl acetate) (PVAc: $-\{CH_2CH(OCOCH_3)\}_n-$) is known to be attained by an advantage of entropy for mixing not by a specific interaction, because the free volume difference in those polymers is extremely small.[1] Takegoshi et al.[2] showed that the molecular motion of both PMA and PVAc in the solid state is largely affected by blending and the motional anisotropy increases in the blend, although no specific interaction exists.

In the case that a free volume difference between component polymers is relatively small and an exothermic specific interaction further exists among them, polymer blends are thought to have a great homogeneity, and both the molecular motions will be influenced cooperatively. Poly(methacrylic acid) (PMAA) has a carboxylic acid functional group (COOH) in the side chain instead of $COOCH_3$ for PMA. The OH group of the COOH residue can interact with another OC=O group via a hydrogen bond. We can, hence, expect that the mixing of PMAA and PVAc produces the excellent homogeneous polymer blends because the free volume difference between PMAA and PVAc is predicted to be rather small, and the functional groups of both polymers can interact with each other via an interpolymer hydrogen bond.

In this study, we examined the miscibility of PMAA/PVAc blends at various mixing ratios by both ^{1}H spin−lattice relaxation times in the laboratory (T_1^H) and the rotating ($T_{1\rho}^H$) frames. The domain size is also estimated from the Goldman−Shen[3] experiment. The molecular motion of both polymers is investigated by the ^{13}C spin−lattice relaxation time in the laboratory frame (T_1^C).

Experimental Section

Sample Preparation. PMAA (relative weight-average molecular weight M_w is 150 000 and the glass-transition temperature T_g is 491 K) was obtained from Scientific Polymer Products, Inc., and PVAc (M_w = 167 000 and T_g = 292 K) from Aldrich Chemical Co. They were used without further purification. PMAA and PVAc were dissolved in methanol at a concentration of 10% w/v and mixed at molar unit ratios ([MAA]/[VAc] = χ_{PMAA}) of 3/1, 2/1, 1/1, 1/2, and 1/3. The transparent films of PMAA/PVAc blends were obtained from casting the respective methanol solutions on a Teflon plate at 60 °C and further dried under vacuum at 90 °C for 4 days.

NMR Measurements. ^{13}C NMR measurements were made using a Bruker DMX500 spectrometer operating at 125.76 MHz for ^{13}C and 500.13 MHz for ^{1}H. High-resolution solid-state ^{13}C NMR spectra were obtained by the combined use of cross-polarization (CP) and magic-angle spinning (MAS) with ^{1}H high-power dipolar decoupling (CPMAS). The radio-frequency field strengths for both ^{13}C and ^{1}H were 55.6 kHz. The ^{1}H decoupling frequency was chosen to be 3 ppm downfield from $(CH_3)_4Si$ (TMS), and the TPPM decoupling method[4] is used. The MAS frequency is chosen to obtain a clear spectrum at the aliphatic region without overlapping of the artificial spinning sidebands of the CO carbons. The MAS frequency of 8 kHz did not show the sidebands on the peaks at the aliphatic region. At a much higher speed, the efficiency of CP enhancement between ^{1}H and ^{13}C nuclei was steeply getting worse. The MAS frequency is thus set at 8 kHz, and the CP contact time of 1 ms is used. ^{13}C chemical shifts were measured relative to TMS using the methine carbon signal at 29.5 ppm for solid adamantane as an external standard.

The ^{1}H spin−lattice relaxation time in the laboratory frame (T_1^H) was indirectly measured from well-resolved ^{13}C signals enhanced by CP of 1 ms applied after the ^{1}H π pulse. Similarly, the indirect measurement was applied for detecting the ^{1}H spin−lattice relaxation time in the rotating frame ($T_{1\rho}^H$) by combined use of CP of 500 μs and spin-locking of ^{1}H nucleus. The ^{13}C spin−lattice relaxation time in the laboratory frame (T_1^C) was measured by the Torchia[5] pulse sequence.

DSC Measurements. Glass-transition temperatures (T_g) were measured by means of temperature-modulated differential scanning calorimetry method[6] using a Perkin-Elmer 7 system at temperature increasing and decreasing ratios of

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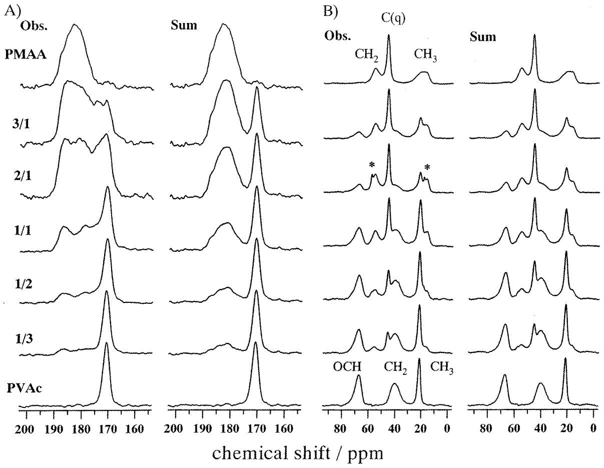

Figure 1. Observed CPMAS ^{13}C NMR spectra of PMAA, PVAc, and the PMAA/PVAc blends: (A) carboxyl regions of PMAA and carbonyl regions of PVAc; (B) aliphatic region. The sum of the ^{13}C NMR spectra of pure PMAA and pure PVAc at the respective molar unit ratio is also depicted on the right of the observed spectra.

20 K/min from T to $T + 4$ K and 10 K/min from $T + 4$ K down to $T + 2$ K.

Results and Discussion

CPMAS ^{13}C NMR Spectra. Figure 1 shows the observed and the simulated CPMAS ^{13}C NMR spectra of PMAA, PVAc, and the PMAA/PVAc blends at molar ratios of 3/1, 2/1, 1/1, 1/2, and 1/3. The carboxyl (COOH) and carbonyl (COO) regions (afterward we also use CO for representing both COOH and COO carbons) are shown in (A) and the aliphatic regions in (B). The simulated spectra for blends are obtained from the simple sum of each observed ^{13}C NMR spectrum of pure PMAA and pure PVAc at the respective molar ratio, and they are displayed in each right side. The spectrum depicted as a sum on the right side of PMAA or PVAc is entirely the same as the observed pure one itself.

The broad COOH line of pure PMAA is observed at 183 ppm, and the narrower COO peak of PVAc is at 171 ppm. Figure 1A clearly shows that the observed spectra of the PMAA/PVAc blends are different from the simulated spectra. The observed spectra have a much more complicated envelope. The line shape of the CO region in the blends seems to be divided into apparently five peaks. Two peaks at around 187 and 180 ppm of those five peaks are clearly seen, especially in the spectrum of the PMAA/PVAc = 1/1 blend. A peak at around 175 ppm can be also clearly seen in the spectrum of the PMAA/PVAc = 3/1 blend, while the peak at 175 ppm for the other blends disappeared behind the broad envelope.

On the contrary, the observed spectra for the aliphatic regions in Figure 1B are in accord with the simulated spectra. This indicates that there is no interaction, which influences the ^{13}C NMR spectra, between the main chain of PMAA and PVAc in the blends. These ^{13}C NMR measurements show that the environment of the side-chain functional groups is significantly influenced, but for the main-chain groups the circumstance is little affected by blending.

To investigate the complicated line shape of the CO region, we fitted the observed spectra by a sum of five Gaussian curves. Figure 2 shows the observed (A) and the decomposed (B) ^{13}C NMR spectra for the CO region of the PMAA/PVAc blends. In the PMAA−COOH region, the observed ^{13}C NMR spectra apparently show the two peaks at around 187 and 180 ppm. A similar envelope for the COOH region had been observed in the our previous study of a dehydration process for pure PMAA.[7] Our previous 2D exchange ^{13}C NMR and IR studies suggested that the COOH residues are mainly divided into three groups of the intermolecular acid dimers at 187 ppm, disordered carboxylic acids at 183 ppm, and free carboxylic acids at 178 ppm. The results give us the consideration that the COOH residue of PMAA can be taken three states at least. To fit the current observed ^{13}C NMR spectra of the CO region in the blends, we adopted those parameters of the three peaks for the PMAA−COOH region as the initial parameters for least-squares fitting. Furthermore, to reproduce the observed CO region, two peaks at 175 and 171 ppm are also adopted; the peak at 171 ppm is the original peak of the COO carbon for pure PVAc. Thus, the three peaks at 187, 178, and 175 ppm are added to the original peaks of pure PMAA (183 ppm) and pure PVAc (171 ppm) as the initial peak parameters for fitting. The observed spectra are successfully fitted by the sum of five Gaussian curves. Each Gaussian curve is depicted by a broken line in Figure 2B. The solid line in Figure 2B represents the sum of each broken line.

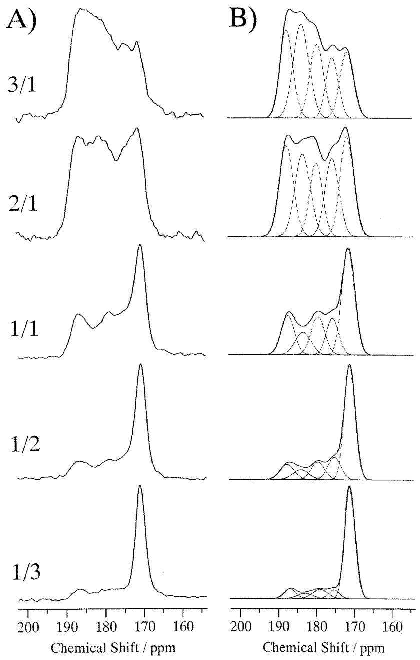

Figure 2. Expanded observed CPMAS ^{13}C NMR spectra (A) and the decomposed simulated spectra using five Gaussian curves (B) of the CO region in the blends: each decomposed peak is depicted by a broken line, and the sum of each line is drawn by a solid line.

The fitted spectra are in good agreement with the observed ones. The chemical shift and the relative area values of each decomposed peak are summarized in Table 1. The chemical shift values of the initial peak at 178 ppm changes to 179 ppm after fitting, while those of the other peaks is the same as the initial values. The chemical shift values of the five Gaussian peaks are the same among the blends. Furthermore, the values of the line width at half-width are mostly the same except for the peak of the PVAc−COO peak at 171 ppm. The line width at half-height for the PVAc−COO peak altered gradually from 380 Hz for the pure state to 530 Hz for the PMAA/PVAc = 3/1 blend with increment of PMAA

Table 1. Relative Areas (in %) of the Carboxyl Peak (COOH) for PMAA and the Carbonyl Peak (COO) for PVAc Obtained from Decomposed ^{13}C Spectra of Figure 2B[a]

	PMAA (183 ppm)[b]			PVAc (171 ppm)[b]	
χ_{PMAA}	187 ppm	183 ppm	179 ppm[c]	175 ppm[c]	171 ppm
3/1	22	28	19 (27)	14 (45)	17
2/1	22	21	16 (27)	18 (44)	23
1/1	17	11	16 (36)	14 (25)	42
1/2	10	7	11 (39)	13 (18)	58
1/3	7	5	9 (43)	6 (8)	73

[a] The peaks at 187, 183, and 179 ppm are attributed to PMAA and those at 175 and 171 ppm to PVAc. [b] The values in parentheses represent the chemical shifts of each homopolymer. [c] The values in parentheses (in %) are the relative values against the respective polymers, e.g., for 3/1, 27 = 19/(22 + 28 + 19) × 100.

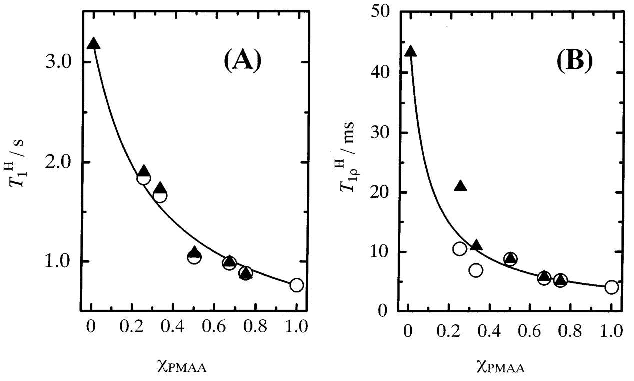

Figure 3. Observed ^{1}H spin−lattice relaxation times in the laboratory (T_1^H, A) and in the rotating ($T_{1\rho}^H$, B) frames against the molar unit ratio of PMAA/PVAc blends (χ_{PMAA}): ○, CH$_2$ carbon of PMAA; ▲, OCH carbon of PVAc. Each solid line represents the calculated curve from eq 1.

content (Figure 2). This line width change shows that the molecular motion of PVAc is affected by PMAA-rich matrix and becomes slow in the blends. We will discuss molecular motion later.

There is an argument that the complicated line shape is not due to each symmetrical peak like a Gaussian or a Lorentzian but due to a few asymmetric complicated peaks. However, the line shape of the pure PVAc−COO carbon is symmetric, and the divided peak intensity changed independently during the measurements of T_1^C; the spectra are not shown, but each T_1^C value is plotted in Figure 5A. This indicates that the divided peaks really exist in this region. We, hence, conclude that the decomposition by the five symmetrical peaks is suitable for this ^{13}C NMR line shape.

Another argument is about the relative intensity among the five CO carbons after the CP experiment. We checked the efficiency of CP enhancement by comparing the conventional dipolar decoupling (DD) with the MAS spectrum for the PMAA/PVAc = 1/1 blend on behalf of the other blends. There is a possibility that the signal envelope of the CO carbons changes by CP due to the difference in the efficiency of the enhancement. We, however, did not observe the difference for the signal shape and the relative intensity for the CO carbons between the CPMAS and the DDMAS spectra. Since the measurement temperature is below T_g, the CP enhancement from ^{1}H to ^{13}C works widely and rapidly during the contact time into the polymers so that the efficiency for the five CO carbons is the same.

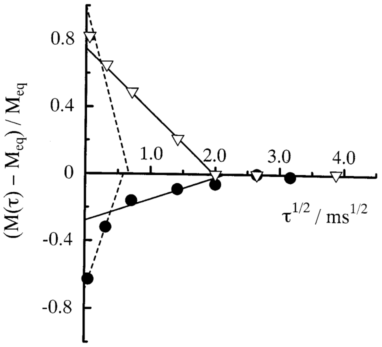

Figure 4. Plots of ^{1}H normalized magnetization change (●, C(q) signal of PMAA; ▽, CH$_3$ signal of PVAc) vs square root of ^{1}H spin-diffusion time $\tau^{1/2}$ for the PMAA/PVAc = 1/1 blend. Solid straight lines are drawn without the initial point to determine the intercept time t_e. Broken lines are drawn through the initial and the second data points. M_{eq} represents the quasi-equilibrium magnetization after long mixing period but much shorter than T_1^H.

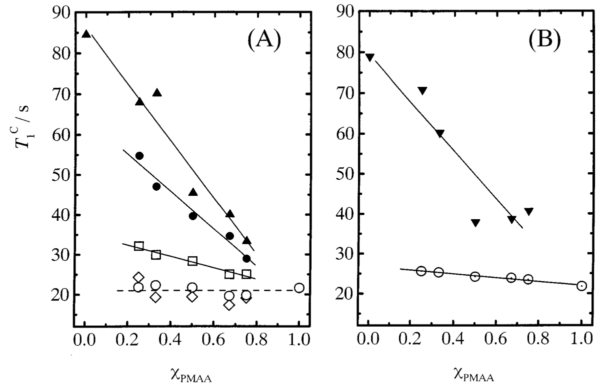

Figure 5. Observed ^{13}C spin−lattice relaxation times in the laboratory frame (T_1^C) plotted against the molar unit ratios (χ_{PMAA}): (A) side-chain COOH carbon of PMAA (◇, 187 ppm; ○, 183 ppm; □, 179 ppm) and side-chain COO carbon of PVAc (●, 175 ppm; ▲, 171 ppm); (B) main-chain CH$_2$ carbon of PMAA (⊙) and main-chain OCH carbon of PVAc (▼). The solid lines are least-squares fitted to the observed data points, and the broken line is drawn to guide the reader's eyes.

Table 1 shows that the ratio between the sum of the relative areas at 187, 183, and 179 ppm and that at 175 and 171 ppm is comparable to each molar ratio of the blends. For example, for 3/1, the sum of the relative areas at 187, 183, and 179 ppm is 69% and that at 175 and 171 ppm is 31%. The value of 69/31 is close to the molar ratio of 3/1 (75/25). Taking the fitting error of area (approximately 5%) into account, the difference is negligible. Therefore, the decomposed peak at 175 ppm is assigned to the carbonyl group of PVAc, showing that the group is affected by blending to cause a change in the chemical shift.

On the basis of our previous study,[7] the peaks at 187 and 183 ppm are related to the intramolecular acid dimers and the disordered acids, respectively. The chemical shift value of 179 ppm is similar to the free carboxyl carbon peak at 178 ppm, which we observed previously in the course of dehydration of pure PMAA. Generally, since the hydrogen bonding causes the lower-field shift, we can recognize that the regularly aligned acid dimers are observed at 187 ppm, which is lower field (higher frequency) than the disordered acids of 183 ppm, and the free COOH carbons without a hydrogen bond appear in the upper field of 179 ppm. However, in this case, it is difficult to convince us that the free COOH carbons exist in the normal state of the blends. The free COOH carbon was caused by the pentad configuration of *meso*−*racemic*−*racemic*−*meso* for PMAA. Since the intramolecular six-membered anhydrides of PMAA easily form in the *meso* configuration after heating, the residual one COOH group in the *racemic*−*racemic* configuration becomes free.[7]

On the other hand, the hydrogen bonding does not always make the chemical shift value toward the lower field. This shift depends on the relative strength of the hydrogen bonding. For PMAA/poly(ethylene oxide) (PEO) or poly(acrylic acid) (PAA)/PEO systems, Miyoshi et al.[8,9] observed the upper-field shift due to the interpolymer hydrogen bond between the PMAA or PAA and PEO. This suggests that the strength of the hydrogen bond between the PMAA (or PAA) and PEO is weaker than that of the intramolecular hydrogen bond for PMAA; therefore, the chemical shift of the COOH carbon interacted with the oxygen of PEO changes to the upper field. A similar criterion holds on the current PMAA/PVAc system. Furthermore, the dependence of T_1^{C} values on the molar ratio of PMAA for the peaks at 175 and 179 ppm shows a similar tendency, while those of the peaks at 187 and 183 ppm are rather constant (details are discussed later; see Figure 5A), suggesting that both the functional groups are affected by each other.

The observations mentioned above have led us to conclude that the peak at 179 ppm for PMAA is attributed to the COOH carbon interacted with the oxygens of the COO group of PVAc. The strength of the interpolymer hydrogen bond between the COOH of PMAA and the COO of PVAc is weaker than that of the intramolecular interaction within a PMAA. On the other hand, for PVAc, the COO carbon without a hydrogen bond observed at 171 ppm changes to the lower field at 175 ppm, owing to the interpolymer interaction.

Miscibility (T_1^{H} and $T_{1\rho}^{\mathrm{H}}$). Figure 3 shows the plots of the ^{1}H spin−lattice relaxation times in the laboratory (T_1^{H}, A) and in the rotating ($T_{1\rho}^{\mathrm{H}}$, B) frames against the molar ratio of PMAA (χ_{PMAA}). The ^{1}H relaxation times are indirectly observed from the well-resolved ^{13}C peaks via CP. The fast ^{1}H spin diffusion averages the spin temperatures of almost all protons in a polymer, resulting in each ^{1}H relaxation time obtained from every well-resolved ^{13}C peak having the same value in the solid state. We obtained the ^{1}H relaxation times from CH$_2$ (○) and OCH (▲) carbons for PMAA and PVAc, respectively, because these two carbons are observed separately even in the blends (Figure 1), so that we can obtain each ^{1}H relaxation time for PMAA or PVAc in the blends independently.

Figure 3A shows that both the original T_1^{H} values of pure PMAA and pure PVAc alter in the blends and the obtained T_1^{H} values of PMAA are in excellent agreement with those of PVAc. This indicates that the complete averaging of the T_1^{H} rates by ^{1}H spin diffusion occurs, suggesting that PMAA and PVAc are in close proximity with each other and the PMAA/PVAc blends are homogeneous on a scale of 20−50 nm[10] for all compositions. Similarly, Figure 3B shows that the $T_{1\rho}^{\mathrm{H}}$ values of PMAA in the PMAA-rich/PVAc blends, which are the PMAA/PVAc = 3/1, 2/1, and 1/1 blends, are fully consistent with those of PVAc. For the PMAA-poor (PMAA/PVAc-rich) blends, which are the PMAA/PVAc = 1/2 and 1/3 blends, however, the $T_{1\rho}^{\mathrm{H}}$ values of PMAA are different from those of PVAc, although the values of PMAA or PVAc alter toward each other and become close from those of pure ones. This exhibits that the partially averaging of $T_{1\rho}^{\mathrm{H}}$ rates by ^{1}H spin diffusion occurs in the PMAA/PVAc-rich blends. These results show that the PMAA-rich/PVAc blends are homogeneous on a scale of 2−5 nm as well as 20−50 nm, but the PMAA/PVAc-rich blends are inhomogeneous on the scale. The PMAA/PVAc-rich blends are probably homogeneous on a 5−10 nm scale, because the $T_{1\rho}^{\mathrm{H}}$ values are affected largely by ^{1}H spin diffusion.

Table 2. Observed and Calculated Relative Ratios (%) against Whole and the Respective Polymers on the Assumption that the Interpolymer Interaction Is Formed at the Molar Unit Ratio [MAA]/[VAc] of 3/2[a]

χ_{PMAA}	whole	PMAA (179 ppm) respective	PVAc (175 ppm) respective
3/1 (12/4)			
obs	33	27	45
cal	31	25	50
2/1 (10/5)			
obs	34	27	44
cal	33	30	40
1/1 (8/8)			
obs	30	36	25
cal	31	38	25
1/2 (7/14)			
obs	24	39	18
cal	24	43	14
1/3 (7/21)			
obs	15	43	8
cal	18	43	9

[a] The values in the parentheses in the χ_{PMAA} column represent the minimum numbers of units for PMAA and PVAc for calculation. The observed values in the "whole" column are the sum of the ratio at 179 and 175 ppm listed in Table 1. The observed values in the "respective" column are the same as the values in the parentheses listed in Table 1.

To investigate the effect of the interpolymer interaction, which is most likely a hydrogen bond, on the miscibility, we estimate the fraction of the interaction. Table 1 shows that the sums of areas at 179 and 175 ppm are 33, 34, 30, 24, and 15%, respectively, from the 3/1 to the 1/3 blends. Table 1 also lists the relative area ratios for the respective polymer in the parentheses: e.g., for the PMAA/PVAc = 1/1 blend, the ratio of 179 ppm is calculated to 36% (= 16/(17 + 11 + 16) × 100) and that of 175 ppm is 25%. We can estimate the PMAA/PVAc unit ratio ([MAA]/[VAc]) at the interpolymer interacted portion in order to reproduce the above-mentioned values. All the values for whole blends can be obtained on the simple assumption that the interpolymer interaction is made at the unit ratio of [MAA]/[VAc] = 3/2. For example, in the case of the PMAA/PVAc = 1/1 blend, here we consider simply that the blend is composed of an eight-unit PMAA chain and an eight-unit PVAc chain; the three-unit of PMAA becomes 38% against the eight PMAA units, and the two-unit of PVAc is 25% against the eight PVAc units. The relative area ratio for whole polymers becomes 31% (= 5/16 × 100). These values are consistent with the above-mentioned 36% and 25% and the sum of areas at 179 and 175 ppm (30%). All values calculated are listed in Table 2 with the observed values. Table 2 shows that the calculated values are in excellent agreement with the observed ones. This indicates that the interacting portion is formed with [MAA]/[VAc] = 3/2. The fraction of the interacting portion is over 30% for PMAA-rich/PVAc blends and about 20% for PMAA/PVAc-rich blends. Over 30% interacting portion against whole polymer chains works the bridge between PMAA and PVAc in the

PMAA-rich/PVAc blends, resulting in the superior miscibility. The decrease of only 10% causes the poorer miscibility on a scale of 2−5 nm for the PMAA/PVAc-rich blends compared to the PMAA-rich/PVAc blends.

If the ^{1}H spin diffusion affects entirely during a period less than the shortest ^{1}H relaxation time among the mixed polymers, the ^{1}H relaxation rate is averaged by ^{1}H mole fraction as follows:[10−12]

$$1/T_1^{\mathrm{Ave}} = f_{\mathrm{PMAA}} \times 1/T_1^{\mathrm{PMAA}} + (1 - f_{\mathrm{PMAA}}) \times 1/T_1^{\mathrm{PVAc}} \quad (1)$$

where T_1^{Ave} is the averaged ^{1}H relaxation time and f_{PMAA} the ^{1}H mole fraction of PMAA in the respective blend. T_1^{PMAA} and T_1^{PVAc} are the ^{1}H relaxation times for pure PMAA and PVAc, respectively. In a case of no significant change of molecular motion between the pure and the mixed states, the observed ^{1}H relaxation times for the blends equal to the calculated values obtained from eq 1.[10,11]

The solid lines in Figure 4A,B represent the calculated values from eq 1. The observed T_1^{H} values are in good agreement with the estimated values. The observed $T_{1\rho}^{\mathrm{H}}$ values for PMAA-rich blends are also in good agreement with the calculated ones. These agreements indicate that the molecular motions of both polymers in the blends are not changed drastically with each other compared with those before mixing, and the fast ^{1}H spin diffusion is not hindered by the molecular motions. These results are reasonable by taking account of the high T_g for these blends.

To investigate the miscibility, one observes the conventional DSC curve to detect whether a single T_g is observed for a blend. However, the change of the conventional DSC curve due to the glass transition is often hardly measured for a miscible blend. We, hence, adopted the temperature-modulated DSC method[6] to detect the T_g signal for the PMAA/PVAc blends. The glass-transition signals for pure PMAA and pure PVAc are respectively observed at around 490 and 290 K. A single T_g for each blend is observed, and the values are higher than 390 K: the value is obtained from the PMAA/PVAc = 1/3 blend. This high T_g for the PMMA/PVAc blends implies that the molecular motion rate is much less than several tens of kilohertz at a measurement temperature of 300 K, suggesting that the molecular motion does not hinder the fast ^{1}H spin diffusion[11] even if the molecular motion is influenced by the interaction between PMAA and PVAc.

Domain Size (Goldman−Shen Experiment). The observation of ^{1}H relaxation time has easily led us to know the homogeneity on a scale of several nanometers, but the estimated scale is a measure. The Goldman−Shen experiment[3] accompanying with CP gives us more quantitative information on the distance between PMAA and PVAc.

The ^{1}H spin−spin relaxation time (T_2) of CH_3 for PVAc is over 80 μs and that of C(q) for PMAA is 30−40 μs, while that of the other groups for both polymers is shorter than a few tens of microseconds. To retain the CH_3 magnetization and eliminate the other ones, we set the waiting period between first and second ^{1}H 90° pulses in the Goldman−Shen pulse sequence to 45 μs. However, since the quaternary carbon C(q) peak has a longer T_2 than the other peaks for PMAA, we could not eliminate it completely. Thus, the spectrum after the second 90° pulse includes the C(q) of PMAA and the CH_3 of PVAc signals.

To plot the change of signal intensity against the ^{1}H spin-diffusion time, we collected the peak areas of C(q) for PMAA and the CH_3 for PVAc. Figure 4 shows the plots of the normalized ^{1}H magnetization change vs square root of the ^{1}H spin-diffusion time $\tau^{1/2}$ in the Goldman−Shen pulse sequence for the PMAA/PVAc = 1/1 blend. The closed circles represent the observed data points of the main-chain C(q) carbon (●) of PMAA, and the open inverse triangles are the observed data points of the side-chain CH_3 carbon (▽) of PVAc.

It is noted that the C(q) signal of PMAA exists at the initial condition; the ordinate value at $\tau = 0$ is not −1.0. To examine ^{1}H spin diffusion from a domain to the another intermolecular domain, the signals of PMAA have to be eliminated completely; otherwise, the ^{1}H spins diffuse both intra- and intermolecular domains. In this current case, hence, the increase of the C(q) peak includes both the effects of the spin diffusion via the intra- and intermolecular domains. Figure 4 shows that the initial slope obtained from the first and the second data points is steeper than that obtained from the second to the fifth data points, especially for the C(q) of PMAA. This indicates that the ^{1}H spins first diffusive intramolecular domain; after the intramolecular diffusions finish, the interpolymer ^{1}H spin diffusion becomes predominant.

The effective ^{1}H spin diffusion time τ_e and the diffusion coefficient D provide the domain sizes of PMAA and PVAc.[10,13] The straight solid lines obtained from the data points without the initial point are drawn to estimate the effective ^{1}H spin diffusion time and to avoid the effects of the intramolecular ^{1}H spin diffusion. Both the straight lines intercept around $\tau^{1/2} = 2$ ms$^{1/2}$, indicating τ_e equals about 4 ms. It is necessary to subtract the time for intramolecular ^{1}H spin diffusion from the 4 ms to estimate the domain size accurately. From the broken lines through the initial and the second data points, we also obtain the intramolecular τ_e to be about 0.3 ms. On the basis of the T_2 value of 80 μs, we estimate the ^{1}H spin-diffusion coefficient to be 3.4×10^{-16} m^2/s.[14] By using the obtained τ_e of 3.7 ms and D, the sum of the thickness, L, of both the polymer domains is estimated to be about 5.1 nm: each domain size is 2.5 nm, by using the following equation: $L = 2\tau_e^{1/2}D^{1/2}/(\pi^{1/2}\chi_{\mathrm{PMAA}}(1 - \chi_{\mathrm{PMAA}}))$.[15] This estimated domain size of 2.5 nm coincides with the results of $T_{1\rho}^{\mathrm{H}}$.

Molecular Motion (T_1^{C}). Figure 5 shows the ^{13}C spin−lattice relaxation time in the laboratory frame (T_1^{C}) for the CO (A) and the main-chain (B) carbons in the blends plotted against the unit molar ratio of PMAA (χ_{PMAA}). The T_1^{C} values are obtained from the decomposed CO peaks at 187 (◇), 183 (○), and 179 (□) ppm for PMMA and at 175 (●) and 171 (▲) ppm for PVAc. For the main-chain carbons, the T_1^{C} values are obtained from the CH_2 peak at 55.5 ppm (⊙) for PMAA and the OCH peak at 67.5 ppm (▼) for PVAc. The observed T_1^{C} values of the COOH carbon for pure PMAA at 183 ppm and of the COO carbon for pure PVAc at 171 ppm are 22 ± 1 and 84 ± 3 s, respectively. For the main-chain CH_2 and OCH carbons of the pure polymers, the observed T_1^{C} values are 22 ± 1 and 79 ± 7 s, respectively.

For both the side-chain and the main-chain carbons of PVAc, the T_1^{C} value depends on the molar ratio of

PMAA. The T_1^C values for PVAc decreases linearly with increasing the molar ratio of PMAA in the blends. From the least-squares fitting to the decreasing observed data points, the change rates of T_1^C values for PMAA content are estimated to be 71 ± 6 s/χ_{PMAA} for the side-chain (▲) carbon and 60 ± 12 s/χ_{PMAA} for the main-chain (▼) carbon. The rate for the PVAc−COO group observed at 175 ppm (●), which interacts with the COOH group of PMAA, is 47 ± 5 s/χ_{PMAA}. This rate is much smaller than the other carbons of PVAc.

On the contrary, the T_1^C values of PMAA COOH carbons at 187 (◊) and 183 ppm (○) do not show such dependence and have a relatively constant value of about 21 s (broken line), and that of the PMAA main-chain CH_2 carbon (⊙) depends slightly on the PMAA molar ratio in the blends; the rate is 4.8 ± 0.4 s/χ_{PMAA}. For the COOH carbon observed at 179 ppm (□), the dependence is greater than the other carbons of PMAA. The change rate of T_1^C values is about 3-fold greater than that of the main-chain CH_2; the rate is 14 ± 1 s/χ_{PMAA}.

These results indicate that the molecular motion of PVAc is affected largely by the coexistence of PMAA and that of PMAA is less sensitive to the mixing with PVAc. A similar phenomenon is also observed on the CPMAS ^{13}C NMR spectra in Figure 2. Only the line width at half-height of PVAc−COO carbon at 171 ppm changes gradually with increment of PMAA content. Because the T_g of 490 K for PMAA is 200 K higher than that for PVAc, PMAA is firm as compared to PVAc, and the movement of PVAc is hindered by PMAA in the blend. The molecular motion of PVAc faster than PMAA is influenced extremely by the rigid PMAA.

Interestingly, the dependence of the COOH carbon observed at 179 ppm is different from that observed at 187 and 183 ppm. The T_1^C values observed from the peak at 179 ppm (□) are longer than those observed from the peaks at 187 and 183 ppm. Similarly, for the PVAc−COO carbons at 175 ppm (●), the T_1^C values are shorter than the another COO carbon at 171 ppm. Furthermore, the T_1^C values for the peak at 179 and 175 ppm decrease with increasing the molar ratio of PMAA in the blends. These decrease rates are different from the other CO carbons and become close to each other. This indicates that both the COOH group at 179 ppm for PMAA and the COO group at 175 ppm for PVAc move cooperatively rather than independently, suggesting again that the COOH group of PMAA observed at 179 ppm is in contact with the COO group of PVAc observed at 175 ppm.

Conclusion

The PMAA/PVAc blends are homogeneous on a scale of 20−50 nm, and especially the PMAA-rich/PVAc blends are intimate on a scale of 2−5 nm. The PMAA/PVAc-rich blends are partially miscible on a scale of 2−5 nm. The homogeneity is achieved by the interpolymer hydrogen bond between the COOH group of PMAA and the COO group of PVAc. To be miscible on a scale of 2−5 nm, the amount of this interaction is needed to be 30% in the blends. For the PMAA/PVAc-rich blends, this amount decreases to 20%. The less amount causes the partial inhomogeneity on a scale of 2−5 nm for the PMAA/PVAc-rich blends. The interaction works as the cross-linked bond between PMAA and PVAc. We clarified that the interaction is the main role of the homogeneity between PMAA and PVAc by means of the dependence of T_1^C values on the molar ratio of PMAA in the blends.

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