Molecular Motion in a Blend of Poly(vinylphenol) and Poly(ethylene oxide) As Studied by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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ABSTRACT: Molecular motion in a poly(vinylphenol) (PVPh)/poly(ethylene oxide) (PEO) blend (PVPh/PEO) is studied by examining the temperature dependence of the line width of high-resolution solid-state ^{13}C NMR spectra. PEO molecules in the crystalline phase undergo motion in the vicinity of room temperature. The motion is governed by an activation energy and correlation time similar to those related to the glass transition of amorphous polymers. For PVPh/PEO, the onset of backbone chain motion of amorphous PEO and PVPh in the blend reflects on the temperature dependence of ^{13}C line width. The molecular motions of the two polymers in the miscible amorphous phase affect each other strongly although the chain dynamics of the two polymers still have a different characteristic temperature dependence.

Introduction

Recently, we studied the composition dependence of the miscibility and the phase structure of poly(vinylphenol)/poly(ethylene oxide) (PVPh/PEO) blends by solid-state high-resolution ^{13}C NMR spectroscopy.[1] The results indicated that at lower PEO compositions the two polymers are intimately mixed on the 20–30 Å scale as well as the 200–300 Å scale through the intermolecular hydrogen-bonding interaction and form a single miscible amorphous phase. At a PEO content of about 50 wt %, the blend consists of two phases: a miscible amorphous phase and an amorphous pure PEO phase with a size of the order of 10 Å; the blend is miscible on the 200–300 Å scale. At higher PEO contents the blends are partially miscible, consisting of an amorphous and a crystalline phase of pure PEO and the miscible phase. Such various mixing states will affect the molecular motion of the two component polymers.

The effect of blending on molecular motion associated with the glass transition has been studied for a few polymer blends by examining the temperature dependence of the line width of ^{13}C spectra under conditions of proton dipolar-decoupling/magic-angle sample spinning (DD/MAS).[2-4] The ^{13}C line width of DD/MAS spectra consists of four parts.[3] The first is the temperature-independent line width due to the inhomogeneous static field, misalignment of the magic angle, etc. The second is the dispersion of isotropic chemical shift arising from a variety of local conformations in the solid state. The dispersion is insensitive to temperature below the glass transition temperature (T_g). Above T_g, the chemical-shift dispersion is averaged to zero by fast molecular motion, resulting in line-narrowing. The third is the line width arising from the residual ^{13}C–^{1}H dipolar interaction under the DD/MAS conditions. Below T_g, this part is very small because of the proton dipolar-decoupling and is temperature-insensitive. Above T_g, the coherent modulation of the dipolar interaction by the proton decoupling interfers with the random modulation by molecular motion. The interference is most pronounced when the rate of molecular motion is close to the strength of radio-frequency field of proton decoupling (ca. 50 kHz), reducing the efficiency of dipolar-decoupling. This brings about line-broadening in DD/MAS spectra.[5,6] The fourth is the line width due to the residual chemical-shift anisotropy under the DD/MAS conditions. If the rate of molecular motion approaches that of magic-angle sample spinning (ca. 5 kHz), interference occurs. This also brings about line-broadening.[7] This effect is, however, small as compared with the dipolar interaction and can be neglected, in particular, for anisotoropic motion.

The line width of protonated ^{13}C for most polymers is, therefore, temperature-insensitive below T_g; with increasing temperature, line-broadening occurs above T_g, and a line-narrowing follows. Such a temperature dependence can also be expected for a semicrystalline polymer if the polymer in the crystalline phase undergoes motion with a large amplitude.

Poly(ethylene oxide) (PEO) is a semicrystalline polymer. The conformation of PEO in the crystalline phase is a seven-residue/two-turn helix.[8,9] It has been reported that the PEO chain in the crystal undergoes rotational oscillation about the helical axis below the melting temperature. It may be expected that the onset of molecular motion of PEO is detected by the ^{13}C line width.

In this paper, we study the temperature dependence of the ^{13}C line width of PEO and its blend with an amorphous polymer, poly(vinylphenol) (PVPh). We focus our attention, firstly, on the motion of PEO in the crystalline phase, and secondly on the motions of amorphous PEO and PVPh in the PEO/PVPh blend. We apply various NMR techniques to observe the ^{13}C high-resolution solid-state spectra. The low natural abundance of ^{13}C nuclei eliminates the spin-diffusion coupling interaction and facilitates the distinction between motional dynamics of individual polymers. The activation energy and the characteristic temperature associated with the onset of molecular motion are determined. Effects of blending upon molecular motion are discussed.

Experimental Section

Samples. PVPh was obtained from Polysciences Inc. Its molecular weight was reported to be 1500–7000. PEO with a nominal molecular weight of 900 000 is a product of Janssen Chimica Co. The glass transition temperature of PVPh is 393 K. The melting temperature of PEO is about 333 K; the glass transition temperature of PEO is in a range of 158–200 K.

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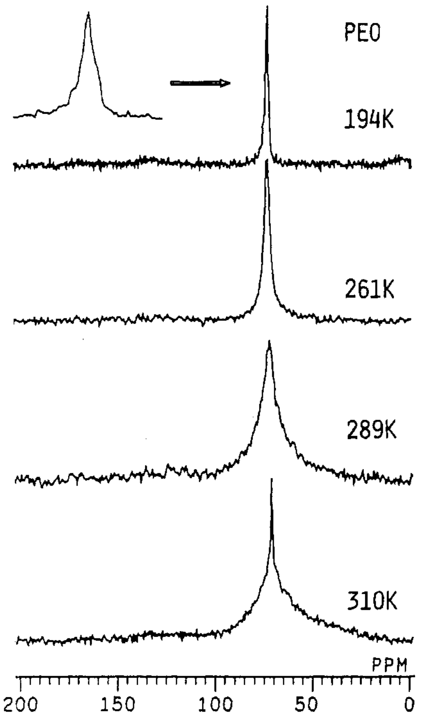

Figure 1. ^{13}C spectra of PEO at various temperatures. The cross-polarization, proton dipolar-decouling, and magic-angle sample spinning method was used. The top spectrum was taken on 8K complex data points, and the others on 4K complex data points. No window function is applied. At the left top, the expanded spectrum at 194 K is shown.

PVPh/PEO blends were prepared by mixing tetrahydrofuran (THF) solutions of the two polymers (1% (w/v)) at 328 K. The solutions were stirred for 3 h. Films of the blends were obtained by evaporating the solvent at room temperature for 3 days and drying under reduced pressure at 328 K for 1 week. The films were further heated at 393 K for 1 h.

NMR Experiments. The 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 ^1H and ^{13}C, respectively. The strength of the radio-frequency field for both ^1H and ^{13}C was about 56 kHz. The chemical shift of ^{13}C spectra is reported in ppm relative to TMS by taking the methine carbon of solid adamantane (29.5 ppm) as an external reference standard. The ^1H decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS).

The variable-temperature measurement was carried out using a JEOL MVT temperature controller. The temperature was calibrated using methanol proton signals under the magic-angle spinning conditions.

The ^{13}C spectra were measured, unless otherwise noted, by the normal cross-polarization (CP) pulse sequence with the proton dipolar-decoupling (DD) and the magic-angle sample spinning (MAS) at a rate of 5.5 kHz. The contact time of cross-polarization signal enhancement was either 0.5 or 0.1ms; the repetition time of accumulation was 2 s.

At high temperatures, where molecular motion is significant, the conventional 90° pulse method with the proton dipolar-decoupling was used at a repetition time of 30 s, because the cross-polarization was ineffective. The pulse saturation transfer (PST)/MAS method was also used to observe the ^{13}C spectra at high temperatures; the ^{13}C magnetization enhanced by saturated protons through the nuclear Overhauser effect (NOE) was created by a single 90° pulse.

Results and Discussion

Molecular Motion of PEO. Figure 1 shows the ^{13}C spectra of PEO at various temperatures measured by the CP-DD/MAS method. The main peak observed at 194 K at about 72 ppm is assigned to the CH_2 carbon of PEO in the monoclinic crystal form, in which the polymer chain has a seven-residue/two-turn helix conformation.[8,9] Above room temperature, the spectrum consists of a narrow component superimposed on a broad one. The line width of the broad component increases with increasing temperature, whereas the narrow one changes little. At 310 K, the two-component feature is most noticeable. The narrow and broad components of PEO at room temperature have been assigned to the amorphous phase and the crystalline phase, respectively.[9,12]

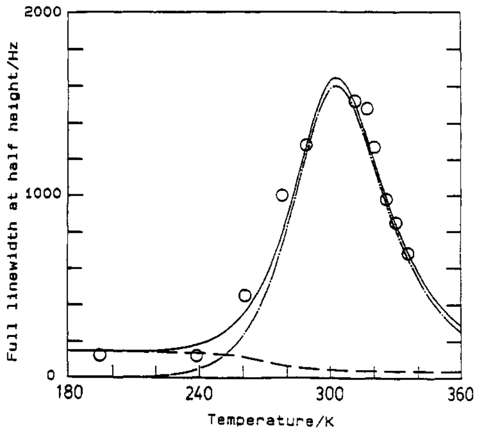

Figure 2. Temperature dependence of the ^{13}C line width of PEO CH_2. The solid curve is the best fit described by the parameters in Table I. The broken line and the dash-dotted line represent, respectively, the first two terms and the third term of eq 1.

Various relaxation parameters are different in the two phases; the amorphous phase has much longer ^1H T_2 and shorter ^{13}C T_1 values than the crystalline phase.[12] The difference in the relaxation behavior between the two phases helps us to observe the spectrum of each phase separately. One can observe the spectrum of PEO in the amorphous phase selectively by the delayed CP method.[1] The Torchia pulse sequence yields selectively the spectrum of PEO in the crystalline phase.[13] The ^{13}C spectra of PEO in the amorphous phase and the crystalline phase were shown in Figure 2 of ref 1.

The temperature dependence of the line width of PEO in the crystalline phase is different from that of amorphous PEO. At 239 K, the line width of crystalline PEO is about 120 Hz. This value is similar to that of amorphous PEO observed by the delayed CP method (delay time of 30 μs). With an increase in temperature, the line width of crystalline PEO increases and reaches a maximum at room temperature. A further increase of temperature, however, decreases the line width.

The temperature dependence of the line width of PEO in the crystalline phase is shown in Figure 2. The data above room temperature were measured by the single 90° pulse method at a repetition time of 30 s, because the motional modulation of ^{13}C–^1H dipolar interaction deteriorates the efficiency of cross-polarization.

The ^{13}C line width δ can be given as a function of temperature T by the following empirical equation:[3]

$$\delta = \delta_0 + \delta_1(2/\pi)\arctan(\alpha(T_0 - T)) + \lambda M_2 J(\omega_1,\tau) \quad (1)$$

where the first term δ_0 represents the intrinsic line width accounting for various static line-broadenings. The second represents the normal motional-narrowing process with an assumption of arctangent dependence on temperature. δ_1 accounts for the line width due to the dispersion of isotropic chemical shifts; α describes the steepness of the dependence, and T_0 is a characteristic temperature of the onset of motion. The third represents the interference term. M_2 is the powder average of the second moment of

Table I
Best Fitting Parameters of the CH_2 Line Width of PEO in PVPV/PEO Blends

samples	E_a/kcal mol^{-1}	$10^{13}\tau_0$/s	λ	δ_0/Hz	δ_1/Hz	T_0/K
PEO (crystalline)	9.6	3.3	0.43	90	60	273
PVPh/PEO = 73/27	9.2	9.0	0.14	222	201	285
PVPh/PEO = 58/42	11	11	0.17	247	227	272

the $^{13}C-^{1}H$ dipolar interaction. λ ($0 < \lambda < 1$) is a reduction factor of the second moment; for isotropic motion $\lambda = 1$, and λ decreases as the motion becomes more anisotropic. $J(\omega_1, \tau)$ is the spectral density of motion of the internuclear vector between C and H at a correlation time τ and at a decoupling strength ω_1.

$$J(\omega_1,\tau) = \tau/(1 + \omega_1^2\tau^2) \qquad (2)$$

This is the motional-broadening term and shows a maximum broadening at $\omega_1\tau = 1$ when τ is varied. Maximum broadenings for CH and CH_2 carbons are, respectively, estimated to be 1852λ and 3704λ Hz for $\omega_1/2\pi$ of 55.6 kHz and r of 1.1 Å. A more detailed description of this equation is found in ref 3. The correlation time τ is assumed to have the Arrhenius-type dependence on temperature,

$$\tau = \tau_0 \exp(E_a/RT) \qquad (3)$$

where E_a is the activation energy, τ_0 is the correlation time at infinite temperature, and R is the gas constant. The observed line width can be least-squares fitted to eqs 1–3.

The best fitting parameters for the line width of PEO in the crystalline phase (Figure 2) are summarized in Table I. The characteristic temperature of the onset of motion is 273 K and the maximum line width occurs at 300 K. The other parameters are approximately the same as those found for other glassy polymers.[3]

Molecular motion of PEO in the crystalline phase has been studied by the broad-line proton NMR method.[10,11] It was found that the rotational oscillation of the PEO molecule around the helical axis in the crystalline phase causes ^1H line-narrowing at about 270 K. This temperature is in agreement with the characteristic temperature of the onset of motion observed in the ^{13}C line width (Table I).

We found that the maximum of the ^{13}C line width occurs at 300 K. The maximum broadening occurs at $\omega_1\tau = 1$, which is the same as the ^1H $T_{1\rho}$ minimum condition. The very small ^1H $T_{1\rho}$ of 160 μs at 310 K reported in the previous paper[1] is probably the minimum of $T_{1\rho}$.

The activation energy is about 9.6 kcal/mol, and the correlation time τ_0 is about 3.3×10^{-13} s. These values are of the same order of magnitude as those of the glass transition of polymers, although the motion of PEO in the crystalline phase is different from that associated with the glass transition of the amorphous polymer.

The ^{13}C CP/MAS spectra of PEO in the crystalline phase can be observed at 330 K with a good signal-to-noise ratio, but not at 335 K. This means that the molecular motion is not sufficiently fast to average out the dipolar interaction at 330 K; the remaining dipolar interaction yields the cross-polarization. It is fast enough at 335 K.

The ^{13}C spectra of PEO in the amorphous phase at 239, 310, and 327 K were measured by the delayed CP method (delay time of 30 or 40 μs) and are shown in Figure 3. The spectrum at 335 K was obtained by a single 90° pulse with a repetition time of 1 s, and hence only the amorphous mobile phase is observed. The line width of amorphous PEO is 110 Hz at 239 K and decreases to 50 Hz at 335K. Since the T_g of pure amorphous PEO is about 158–200 K, the line-broadening is expected at very low temperatures. The experimental temperatures were not low enough to observe only the line-narrowing part. We cannot determine the characteristic temperature of motion of amorphous PEO.

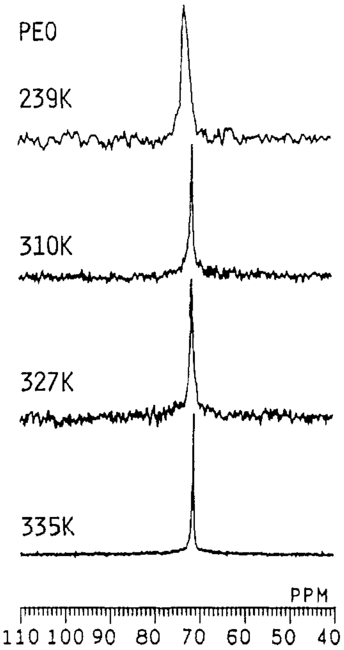

Figure 3. ^{13}C spectra of amorphous PEO at various temperatures. The spectra at 239, 310, and 327 K were observed by the delayed cross-polarization method. The spectrum at 335 K was observed by a 90° pulse with a short repetition time of 1 s.

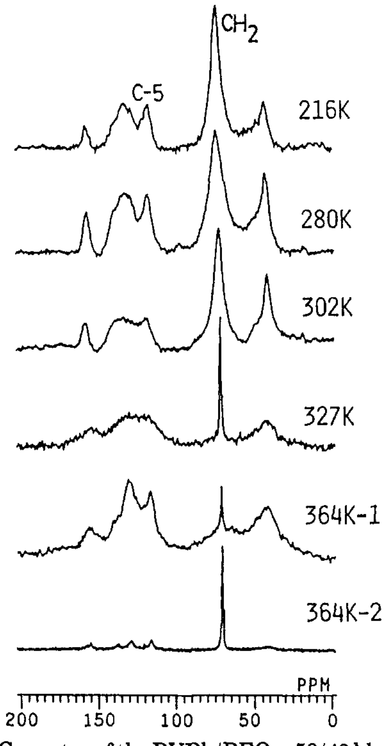

Figure 4. ^{13}C spectra of the PVPh/PEO = 58/42 blend at various temperatures. The spectrum of 364 K-2 was observed by a 90° pulse with a short repetition time of 3 s, and the other spectra were observed by the CP/MAS method.

Molecular Motion of PVPh/PEO Blends. Figure 4 shows the ^{13}C spectra of the PVPh/PEO = 58/42 blend at five different temperatures. The assignment is based on a previous report.[4] At the lowest temperature studied (216 K), the line widths of both PVPh and PEO are small.

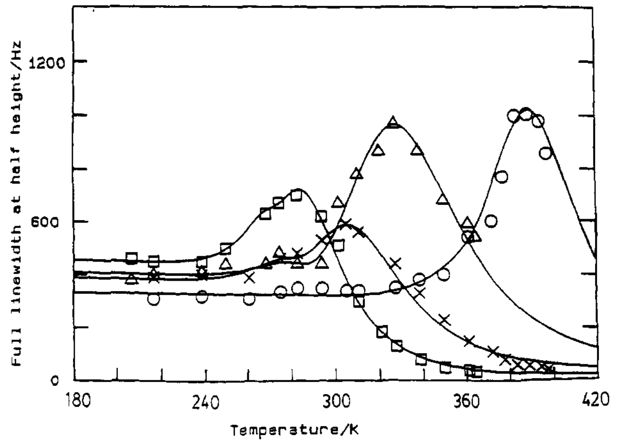

Figure 5. Temperature dependence of the ^{13}C line width of PEO CH_2 and PVPh C-5 in the PVPh/PEO blend: PEO CH_2 (×) and PVPh C-5 (○) in PVPh/PEO = 73/27 and PEO CH_2 (□) and PVPh C-5 (△) in PVPh/PEO = 58/42.

Table II
Best Fitting Parameters of the CH (C-5) Line Width of PVPh in PVPh/PEO Blends

samples	E_a/kcal mol^{-1}	$10^{13}\tau_0$/s	λ	δ_0/Hz	δ_1/Hz	T_0/K
PVPh/PEO = 73/27	16	3.0	0.52	180	160	360
PVPh/PEO = 58/42	9.0	2.9	0.50	220	200	285

As the temperature increases, the lines of PVPh in the blend broaden at 327 K, and narrow on further heating. Even at 364 K, the CP ability of PVPh is still so strong that we can observe the CP/MAS spectra (Figure 4, 364 K-1). On the other hand, the line of CH_2 of PEO broadens at 280 K and then narrows with increasing temperature. At temperatures above 360 K, the CP ability of PEO becomes weak; the CP method yields a very weak signal. We, therefore, adopted the 90° pulse method with the proton dipolar decoupling. We obtained a value of 50 Hz for the line width of CH_2 (Figure 4, 364 K-2).

The ^{13}C line widths of CH_2 of PEO and C-5 of PVPh in the PVPh/PEO blend are plotted as a function of temperature in Figure 5. The line width of C-5 of PVPh is affected by both the main-chain motion and the side-chain motion. Nevertheless, the line width of C-5 can be used as a probe of the main-chain motion, because all carbons of PVPh including the main-chain carbons show a similar temperature dependence. The data are successfully fitted to eqs 1–3. The best fitted parameters are summarized in Tables I and II.

As seen in Figure 5 and Tables I and II, we can observe the onset of motion of both amorphous PVPh and amorphous PEO in the PVPh/PEO = 73/27 and 58/42 blends. It has been reported that in PVPh/PEO = 73/27 and 58/42 blends the crystalline phase of PEO disappears completely and that the two polymers are mixed intimately in the amorphous phase.[1] For these blends, the segmental motions of the polymers must affect each other and a single glass transition should be observed at a temperature of weight-averaged T_g's of the two polymers.[14] Because the T_g of PVPh is too high (393 K) and that of PEO in the amorphous phase is too low (158–200 K), we cannot observe the motional onset associated with the respective T_g transitions of the two pure polymers. The appearance of the onset of motion in the blends in the present experimental temperature range suggests that the motions of the two polymers are strongly affected by each other.

For PVPh/PEO = 73/27 and 58/42 blends, the glass transition temperatures were reported to be about 330 and 290 K, respectively.[14] The two polymers have different T_0's. T_0's of PVPh in PVPh/PEO = 73/27 and 58/42 blends are 360 and 285 K, respectively; T_0's of PEO in PVPh/PEO = 73/27 and 58/42 blends are 285 and 272 K, respectively. These results suggest that the chain dynamics of the two polymers have a different characteristic temperature dependence; in the blend the polymer chain of the amorphous PEO is more flexible than the PVPh chain. It is of interest to note that the T_g value is in between the T_0 values of PVPh and PEO for both blends.

The activation energy of C-5 of PVPh of the PHPh/PEO = 58/42 blend is much smaller than that of the PVPh/PEO = 73/27 blend, but the activation energy of PEO is approximately the same for both blends. This implies that the "hard" PVPh is more effectively influenced by the "soft" PEO. Tables I and II show that the reduction factor λ of PEO in the amorphous phase of the blends is smaller than that of PEO in the crystalline phase and PVPh in the blend. This seems to suggest that PEO in the amorphous phase of the blends undergoes more anisotropic motion than PEO in the crystalline phase and PVPh in the blends. This conclusion is, however, not acceptable, because the motion of PEO in the amorphous phase is thought to be more isotropic. It is probable that some motional freedom reduces the dipolar interaction at lower temperatures. The real maximum broadening would, thus, be smaller than the value of 3704 Hz which is used in the present analysis. This is a reason why the reduction factor λ of PEO in the blend is apparently small.

In conclusion, the temperature dependence of the line width of ^{13}C spectra under conditions of proton dipolar-decoupling and magic-angle sample spinning provides useful information on the molecular motion of individual polymers in the polymer blend.

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