

Determination of Microphase Structure and Scale of Mixing in Poly- ϵ -caprolactone (PCL)/Poly(vinyl chloride) (PVC) Blend by High-Resolution Solid-State ^{13}C -NMR Spectroscopy with Magic Angle Spinning and Cross Polarization

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SYNOPSIS

High-resolution solid-state, pulsed Fourier-transform (FT) ^{13}C -nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS) and cross polarization (CP) was applied to a mechanical blend of poly- ϵ -caprolactone (PCL) and poly(vinyl chloride) (PVC) with 50/50 weight ratio (%) whose composition results in very complex morphology and phase structure in the solid state. Proton spin-lattice relaxation times, $T_1(^1\text{H})$ and $T_{1\rho}(^1\text{H})$, were used as a probe to determine the microphase structure, the degree of homogeneity in terms of the domain size, and the state of mixing of the blend. In particular, $T_{1\rho}(^1\text{H})$ was shown to be able to distinguish the separated domains at a level of a few nanometers; the scale of mixing was evaluated from the approximation based on spin-diffusion phenomenon to be ~ 4.7 nm below which two polymers were partially mixed and above which they were homogeneously mixed. Treatment of the $T_{1\rho}(^1\text{H})$ data with two exponential decay functions resulted in a resolution of individual $T_{1\rho}(^1\text{H})$ into rigid and mobile components, from which more detailed information on the phase structure and state of mixing were obtained.

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INTRODUCTION

A polymer blend is generally a physical mixture of two, or sometimes more, different polymers whose chains are not covalently bonded together. Recognizing that most polymer blends find their actual end-use in the solid state, the ultimate phase structure and morphology in terms of homogeneity (or heterogeneity) are of practical importance because they govern the solid-state physical/mechanical properties of the given blends.¹ In fact, most solid blends are neither completely homogeneous nor completely heterogeneous; it is a matter of degree of homogeneity. If the interaction between the component polymers is attractive, being large enough to overcome the cohesive force of individual polymers,

the resulting blend may exhibit a high degree of homogeneity although microscopic domains of component polymers often exist. On the other hand, if the interaction is very weak or repulsive, the resulting blend may be heterogeneous even in a macroscale. Since the degree of homogeneity is a relative term, the domain size is often used to indicate the extent of homogenization.

Numerous methods including differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and light scattering have been employed to measure the degree of homogeneity and to determine the microscopic heterogeneous structures of the polymer blends in the solid state.² These methods vary widely in the applicability, sensitivity, and information that they yield; a given system that appears to be miscible by one technique may be shown to be immiscible by another. The DSC method is based on the measurements of the glass transition temperature (T_g) of the given blend. Since the T_g is related to the cooperative motions of 30–

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100 backbone chain carbons,³⁻⁵ when the domain size is sufficiently small, the thermal response may be no longer sensitive to the details of the microheterogeneous structures. As for TEM, the principal difficulty is ensuring that sufficient contrast exists when the electron density of the component is similar. Although a staining procedure has been developed to overcome the above difficulty, it is not widely applicable. Furthermore, a quantitative evaluation for the microheterogeneity is rather difficult and inaccurate. The difficulties of the application of the light-scattering method to the solid blends are associated with multiple scattering and sample transparency. Also, the blend components must have a sufficiently different refractive index for observable scattering.

One of the more generally applicable and sensitive techniques at the molecular level, providing both qualitative and quantitative information, is the high-resolution solid-state, pulsed Fourier transform (FT) ¹³C-nuclear magnetic resonance (NMR) spectroscopy capable of magic angle spinning (MAS)⁶ and cross polarization (CP).⁷ The CP/MAS ¹³C spectra enable one to measure the spin-relaxation times of individual specific sites in solid blends and then to analyze the details of the microscopic phase structures in terms of the difference in the molecular mobility.⁸ In addition, spatial dimensions of the microheterogeneous structures can be estimated quantitatively through the process known as spin diffusion.⁹

Two useful spin-relaxation times obtained from solid-state NMR spectroscopy are the spin-lattice relaxation time in the laboratory frame, T_1 , and in the rotating frame, $T_{1\rho}$. From MAS and CP techniques, the resonance of chemically different types of carbons can be resolved⁸ and the transfer of the magnetization from ¹H spins to ¹³C spins take place.¹⁰ Consequently, obtained are separate T_1 's and $T_{1\rho}$'s for protons attached to the different types of carbons, providing a considerably detailed insight. Typical values of the proton spin-lattice relaxation time, $T_1(^1\text{H})$, and the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho}(^1\text{H})$, for most polymers are in hundreds of millisecond and millisecond ranges, respectively. Those values can be translated into the maximum diffusive path lengths (i.e., spatial dimensions) by a simplified approximate approach^{11,12} based on the spin-diffusion phenomenon. The maximum diffusive path length obtained from $T_1(^1\text{H})$ is a few tens of nanometers, an order of magnitude longer than that from $T_{1\rho}(^1\text{H})$, which is a few nanometers. Thus, depending on the relaxation times being used, existence of distinct domains

and their characteristic size can be probed at two different scale levels.

Blends of poly- ϵ -caprolactone (PCL) and poly(vinyl chloride) (PVC) have been of academic interest and interpreted to be compatible throughout the entire composition range of 10–90 wt % PCL.¹³ At the condition of mechanical (melt) mixing, PCL is in an amorphous, molten state and its melt is completely miscible with PVC. However, it crystallizes upon cooling in blends with 40 wt % or more PCL content¹⁴; spherulites containing PVC, which is confined to the interlamellar region,¹⁵ are formed. Furthermore, the pure phase of PVC is present as microcrystallites in the blends.¹⁶ In addition to the microdomains of the pure components, the blends contain domains of the mixed phase. Thus, the resulting blends show very complex morphology and microphase structures in their solid state. However, the detailed phase information of the solid blend at the molecular level has not been satisfactorily achieved yet and many studies have dealt only with the amorphous blend composition (i.e., PCL < 40 wt %), in which the complications caused from the crystalline PCL are usually avoided.

The present work is concerned with the crystalline blend composition, 50/50 wt %, of the mechanically prepared PCL/PVC blend. Its structural heterogeneity and state of mixing in the solid state are investigated in detail, the domain dimensions being quantitatively evaluated; the spin-relaxation times, $T_1(^1\text{H})$ and $T_{1\rho}(^1\text{H})$ measured from CP/MAS ¹³C-NMR spectra are used as a tool. Measurements of $T_1(^1\text{H})$ and $T_{1\rho}(^1\text{H})$ for the pure blend components are also included in order to have a better interpretation and understanding of the blend.

EXPERIMENTAL

Materials and Sample Preparation

The poly- ϵ -caprolactone (PCL) used was PCL-700 (Union Carbide Co.). Its melting point is about 60°C and glass transition temperature is about -60°C. Its number-average molecular weight, M_n , is 13,000 and the weight-average molecular weight, M_w , is 41,000.¹⁷ Poly(vinyl chloride) (PVC), supplied by B.F. Goodrich Co., was Geon 103 EP F-76 and has molecular weights of $M_n = 44,000$ and $M_w = 89,000$.¹⁸

Blending of PCL and PVC with a weight ratio of 50/50 was carried out on a batch, Banbury-type internal mixer (1.57 Farrel Banbury mixer); 1% thermal stabilizer (Therm-Chek 1827 of Ferro Corp.) was added. The fill factor in the mixing chamber of

the mixer was around 0.7, which is typical in the commercial operation. The temperature of the chamber was first set at 65°C, PCL was charged, and the rotors were rotated until the complete melting of PCL. Then, PVC was charged and mixed with the rotor speed of 80 rpm. At 450 s, the mixing was considered to be completed, and the whole mixing process was terminated. The observed temperature during mixing was shown to go over a maximum (160°C) and then decrease to a constant value. After the mixing, the mixture was taken out and sheeted out through a two-roll laboratory mill in order to turn the large chunks into easily handled sheets. After 2 weeks of aging at ambient temperature, the sheets were cut into squares of about 1 × 1 mm for the solid-state ¹³C-NMR experiments.

NMR Measurements

The solid-state ¹³C-NMR experiments were performed with a Chemagnetic Inc. Model CMX-300 spectroscopy equipped with a magic angle probe at ¹H frequency of 299.6 MHz. The samples were packed inside the rotor, being positioned at the center of the magnet, and then spun at the rate of about 3.5 KHz. A ¹H 90° pulse width of 4.25 μm was employed with FDI signal accumulations.

Proton spin-lattice relaxation times, $T_1(^1\text{H})$'s, were measured by observing the ¹³C spectra after a π - τ - $\pi/2$ pulse sequence followed by the cross polarization (CP) as shown in Figure 1(a). Proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}(^1\text{H})$'s, were measured via carbon signal intensities using a ¹H spin-lock- τ pulse sequence prior to cross polarization [Fig. 1(b)]. A contact time of 1 ms was generally used. In all experiments, recycled delays (waiting time) of $5 \times T_1$ were used in order for the net magnetization to be completely relaxed, and all the spectra were obtained at 21°C.

RESULTS

Measurements of Proton Spin-Lattice Relaxation Time, $T_1(^1\text{H})$

Figure 2 shows magic-angle spun, cross-polarized (CP/MAS) ¹³C spectra of PVC, PCL, and the PCL/PVC blend recorded at 21°C. The top spectrum is for PVC and two resonance peaks are shown, each being assigned to methylene (CH₂) and methine (CH) carbons of PVC, respectively. For the PCL spectrum in the middle, peaks are assigned to (i) carbonyl (C=O) carbons, (ii) methylene (CH₂)

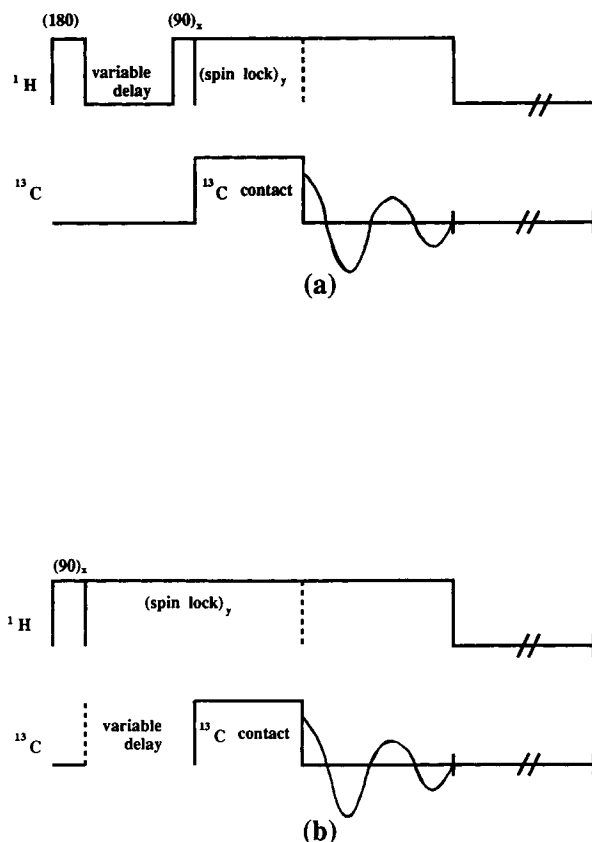


Figure 1 Pulse sequences for measuring (a) $T_1(^1\text{H})$ relaxation times and (b) $T_{1\rho}(^1\text{H})$ relaxation times.

carbons adjacent to carbonyl group, and (iii) methine (CH) carbons that are overlapped. The bottom peak in the figure is the ¹³C spectrum of the PCL/PVC blend, showing that it is a merely a superposition of the individual spectra of the component polymers. It is noted that the height of these peaks (i.e., peak intensity) changes as the delay time (τ) in the pulse sequence varies. When the changes in the peak height are monitored as a function of τ , the relaxation times can be measured.

Figure 3 represents the series of ¹³C spectra (namely, stack spectra) for PVC, which were generated from the pulse sequence of the $T_1(^1\text{H})$ experiment [Fig. 1(a)] with variable delay times, τ . Figure 4 is the plot of the changes of intensity at individual chemical shift positions (i.e., CH carbons and CH₂ carbons) in the stack spectra as a function of τ . These relaxation data were further analyzed by the computer fitting based on a nonlinear least-squares fitting program whereby the $T_1(^1\text{H})$ values for the individual peaks are obtained. The form of the fitted equation with a single exponential decay function for the intensity $I(\tau)$ is

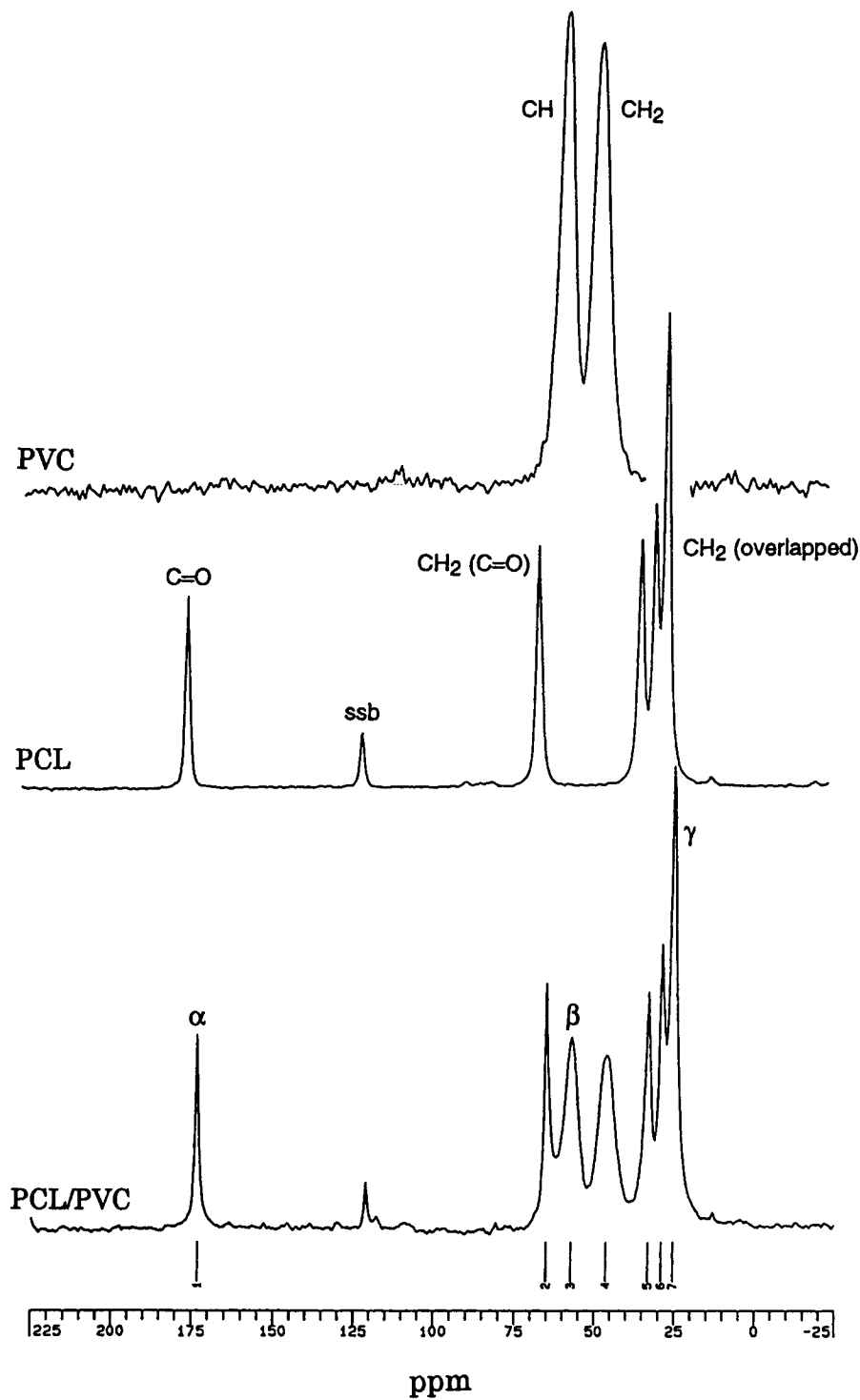


Figure 2 CP/MAS ^{13}C spectra of PVC, PCL, and the PCL/PVC blend. The spinning side band is labeled ssb.

$$I(\tau) = I_{\infty}[1 - \alpha \exp(-\tau/T_1)] \quad (1)$$

where T_1 , I_{∞} , and α are treated as adjustable parameters. As was summarized in Table I, $T_1(^1\text{H})$

obtained from the methine carbon peak is 2.62 s and that from methylene carbon peak is 2.55 s. Considering that the slight difference in the T_1 values may indicate an experimental error, the average of them,

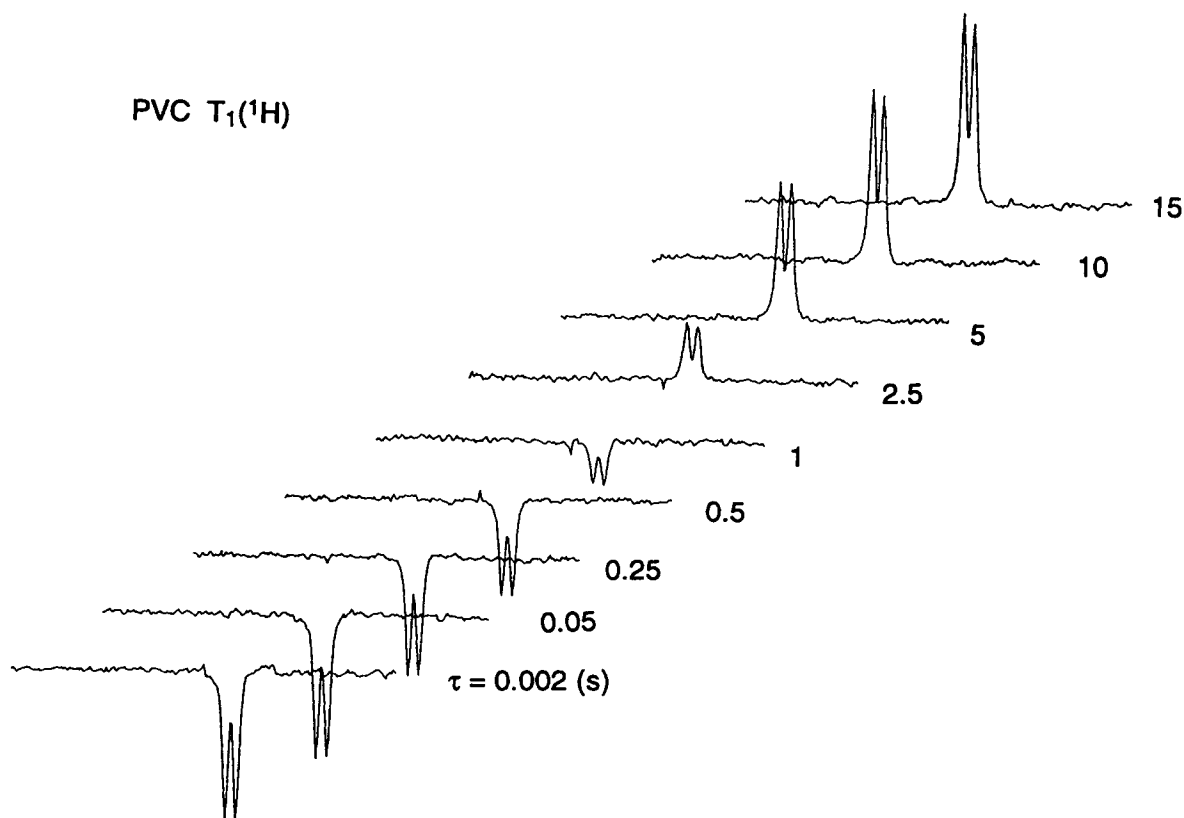


Figure 3 ^{13}C stack spectra of PVC in the $T_1(^1\text{H})$ experiment.

2.59 s, is regarded as $T_1(^1\text{H})$ of PVC. It should be noted that this value cannot be directly compared to previously published values because the experi-

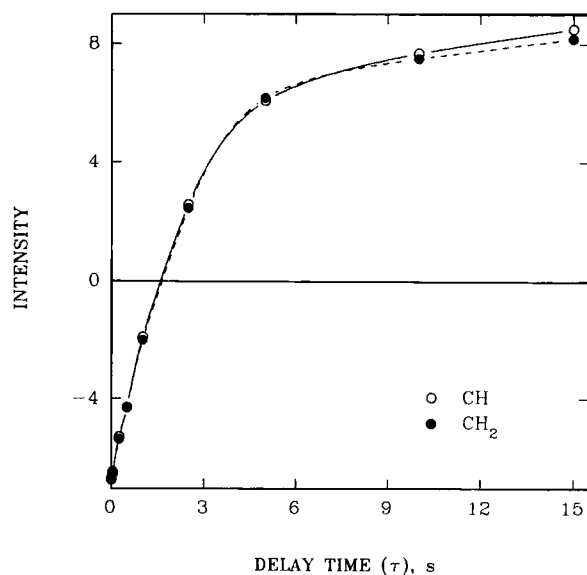


Figure 4 $T_1(^1\text{H})$ relaxation data of PVC at two different chemical shift positions.

mental condition and the instrument being used are not necessarily the same.

$T_1(^1\text{H})$ relaxation data of PCL are represented in Figure 5, where the intensities of the leftmost (i.e., $\text{C}=\text{O}$) and the rightmost (i.e., CH_2) peaks in the middle spectrum of Figure 2 were observed as a function of τ . The data being fitted by eq. (1), $T_1(^1\text{H})$'s result in 0.752 and 0.737 s (see Table I); they are almost identical, considering an experimental uncertainty.

Table I $T_1(^1\text{H})$'s of PCL, PVC, and PCL/PVC Blend

	Peak Position	$T_1(^1\text{H})$ (s)
PCL	$\text{C}=\text{O}$	0.752 ± 0.026
	CH_2 (rightmost)	0.737 ± 0.016
PVC	CH	2.62 ± 0.105
	CH_2	2.55 ± 0.095
PCL/PVC	α ($\text{C}=\text{O}$; PCL)	0.94 ± 0.06
	β (CH; PVC)	0.97 ± 0.07
	γ (rightmost CH_2 ; PCL)	0.94 ± 0.04

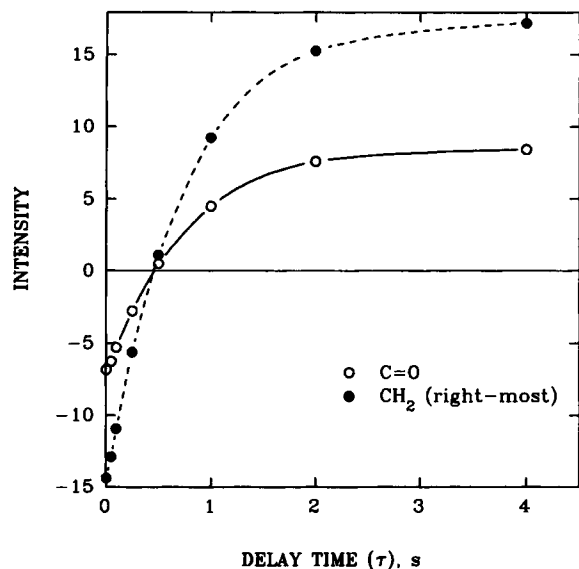


Figure 5 $T_1(^1\text{H})$ relaxation data of PCL at two different chemical shift positions.

Shown in Figure 6 are the $T_1(^1\text{H})$ relaxation data of the PCL/PVC blend, and the calculated values of $T_1(^1\text{H})$ on the basis of eq. (1) are summarized in Table I. The peak positions designated as α , β , and γ indicate C=O of the PCL fraction, CH of the PVC fraction, and the rightmost CH_2 of the PCL fraction in the blend, respectively. As seen in Table I, individual T_1 values determined from both PCL

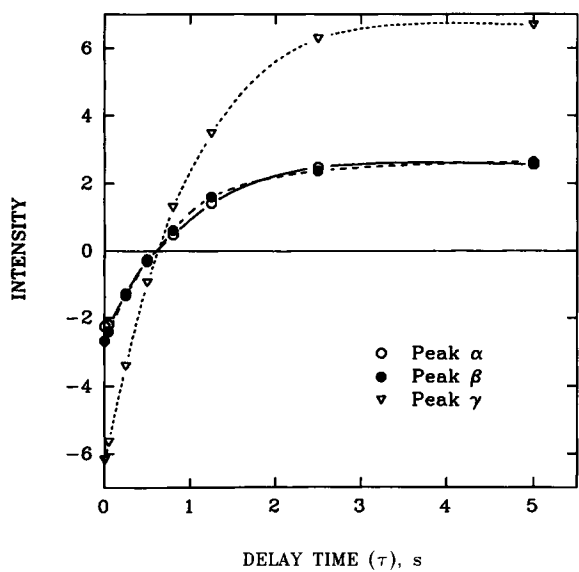


Figure 6 $T_1(^1\text{H})$ relaxation data of PCL/PVC blend at three different chemical shift positions.

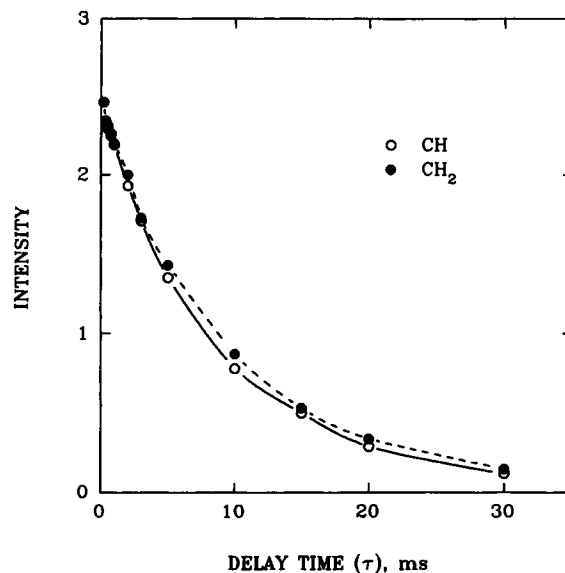


Figure 7 $T_{1\rho}(^1\text{H})$ relaxation data of PVC at two different chemical shift positions.

and PVC fractions in the blend are very close one another.

Measurements of Proton Spin-Lattice Relaxation Time in the Rotating Frame, $T_{1\rho}(^1\text{H})$

Figure 7 represents the $T_{1\rho}(^1\text{H})$ relaxation data of PVC observed with the pulse sequence shown in Figure 1(b). The relaxation took place with variable delays and was monitored by observing the ^{13}C spectra. The data were fitted by a nonlinear least-squares fit based on the following equation:

$$I(\tau) = I_{\infty} \exp(-\tau/T_{1\rho}) \quad (2)$$

The data are often required to be fitted by two exponential decay functions rather than the above single-exponential decay function:

$$I(\tau) = I_{\infty,A} \exp(-\tau/T_{1\rho,A}) + I_{\infty,B} \exp(-\tau/T_{1\rho,B}) \quad (3)$$

The $T_{1\rho}$ values calculated for the two chemical positions of PVC (i.e., methine and methylene carbons) by a single-exponential curve fitting [eq. (2)] are 8.91 and 8.66 ms, respectively (see Table II). When the curve of the methine carbons in Figure 7 were fitted by two exponential decay functions [eq. (3)], the $T_{1\rho}$ relaxation times are resolved into two components, i.e., 4.0 ms (26%) and 11.1 ms (74%),

Table II $T_{1\rho}(^1\text{H})$'s of PCL, PVC, and PCL/PVC Blend

	Peak Position	$T_{1\rho}(^1\text{H})$ (ms)	
		Single-exponential Curve Fit	Double-exponential Curve Fit
PCL	C=O	46.62 ± 0.61 [0.023]	16.99 ± 4.08 [0.014]
			51.02 ± 9.63 [0.014]
	CH2 (rightmost)	36.53 ± 1.74 [0.178]	7.20 ± 0.74 [0.030]
			48.15 ± 1.13 [0.030]
PVC	CH	8.91 ± 0.27 [0.043]	4.0 ± 2.5 [0.030]
			11.0 ± 2.2 [0.030]
	CH2	9.66 ± 0.29 [0.045]	
PCL/PVC	α (C=O; PCL)	32.2 ± 1.0 [0.073]	8.2 ± 2.4 (21%) [0.026]
			40.1 ± 3.1 (79%) [0.026]
		β (CH; PVC)	9.2 ± 0.6 [0.110]
	16.8 ± 1.2 (44%) [0.026]		
	γ (rightmost CH ₂ ; PCL)	37.0 ± 1.5 [0.310]	7.4 ± 0.5 (28%) [0.061]
		47.4 ± 1.0 (72%) [0.061]	

[] indicates standard deviation.

which represent the crystalline and amorphous fractions in PVC, respectively; the value in the parentheses indicates the fraction from the total intensity signal. The standard deviation of the double-exponential curve fitting, 0.030, is not much different from that of the single-exponential curve fitting, 0.043.

In Figure 8, the $T_{1\rho}(^1\text{H})$ relaxation data of PCL are given. The relaxation times are determined the same way as for PVC. By a single-exponential curve fitting [eq. (2)], the $T_{1\rho}(^1\text{H})$'s obtained from carbonyl carbons and the rightmost methylene carbons

are 45.62 and 36.53 ms, respectively (see Table II). When the data are fitted by two exponential decay functions [eq. (3)], the standard deviations decrease significantly and individual $T_{1\rho}(^1\text{H})$ resolves into two components that indicate the crystalline and amorphous fractions of PCL, respectively.

The $T_{1\rho}(^1\text{H})$ relaxation data of the PCL/PVC blend are shown in Figure 9 and the $T_{1\rho}$ values obtained by single- and double-exponential curve fittings are summarized in Table II. Since the values of standard deviation for the double-exponential curve fitting decrease significantly compared to

those for the single-exponential curve fitting, the double-exponential fitting seems to be more desirable.

DISCUSSION

The CP/MAS ^{13}C spectrum of the PCL/PVC blend appears as merely a superposition of the individual spectra of the blend components, i.e., PCL and PVC. To observe distinct changes in the CP/MAS spectrum of a given blend, some mixing must occur on a scale comparable to a few bonds, namely, ~ 1 nm or less, so that electron clouds are disturbed. Consequently, mixing between PCL and PVC did not take place at the atomic level since no outstanding spectral change is observable in the spectrum of PCL/PVC relative to its components.

From the measurements of proton T_1 's, it was shown that the T_1 value of the PVC fraction in the blend (0.97 s) is not the same as that of the pure PVC (2.62 s), which indicates that some mixing must have taken place. Occurrence of mixing is also confirmed by the result of the $T_1(^1\text{H})$ of PCL component in the blend; the T_1 values are not equal to those of pure PCL. The proton T_1 relaxation times of the PVC fraction and the PCL fraction in the blend are identical, within the experimental uncertainty. Hence, the spin-diffusion process across the mixed domains of PVC and PCL occurs quite completely enough to average out the T_1 values of the individual protons. In other words, the blend of the

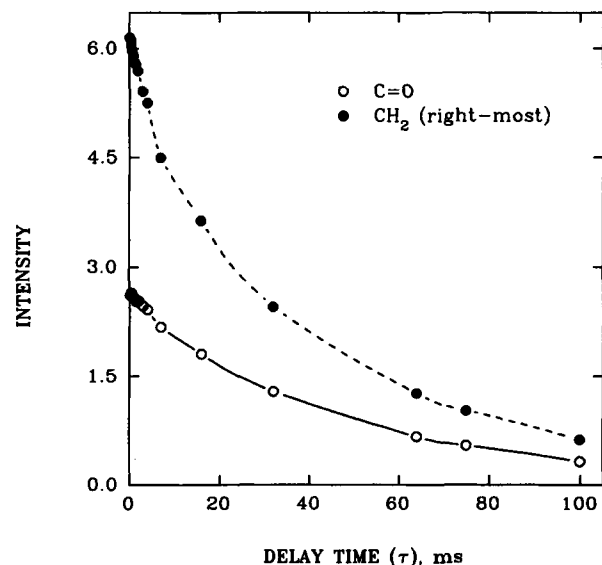


Figure 8 $T_{1\rho}(^1\text{H})$ relaxation data of PCL at two different chemical shift positions.

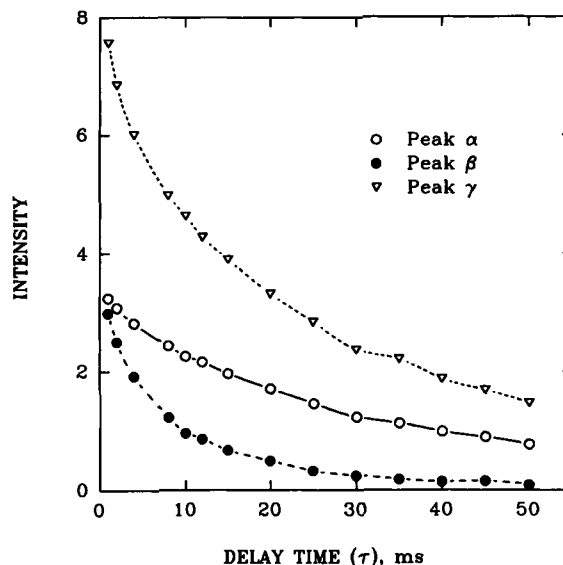


Figure 9 $T_{1\rho}(^1\text{H})$ relaxation data of PCL/PVC blend at three different chemical shift positions.

two polymers is homogeneous on the time scale over which spin diffusion proceeds in times T_1 .

As is the same in $T_1(^1\text{H})$ relaxation times, when a given blend is completely homogeneous on a molecular scale (say, less than a few nanometers), the values of $T_{1\rho}$ of the component polymers in the blend must be identical. However, the $T_{1\rho}$'s fitted with a single-exponential decay function of PVC and PCL components in the blend are quite different from each other, which implies that the spin-diffusion process between PVC and PCL are not efficient enough to average out the $T_{1\rho}$ values. Thus, on the time scale over which the spin diffuses in the times $T_{1\rho}$, the two polymers are not completely but partially mixed. The scale to which the spin diffusion takes place in the times $T_{1\rho}$ can be estimated from the following approximate expression^{11,12}:

$$L \approx (6DT)^{1/2} \quad (4)$$

The above equation relates the maximum diffusive path length L (in nm), i.e., the maximum linear scale over which the diffusion is effective, to the diffusion coefficient D , which is typically taken to be $100 \text{ nm}^2/\text{s}$,¹¹ and the time T (either T_1 or $T_{1\rho}$) over which the spin energy diffuses. From the largest $T_{1\rho}$ value, which is 37.0 ms of rightmost CH_2 carbons of the PCL fraction, the scale is estimated to be ~ 4.7 nm; this approximation, however, depends on the true value of D . So, it is reasonable to suppose that some of the PVC chains are apart from the PCL chains by more than ~ 4.7 nm and the scale of the complete

homogeneous mixing is somewhat larger than this value. The $T_{1\rho}$ value of the PVC component (peak β) in the blend for the single-exponential curve fitting is 9.2 ms and the value is almost the same as that of the pure, unmixed PVC (CH peak). This indicates that PVC has been little mixed with PCL at the scale of ~ 2.3 nm, which was also calculated from eq. (4). The $T_{1\rho}$ value obtained from the rightmost methylene carbon peak of PCL component in the blend is nearly equal to that of pure PCL, whereas the $T_{1\rho}$ value calculated from the carbonyl carbons of the PCL fraction in the blend is different from that of pure PCL. The above observation implies that some mixing must have occurred near the carbonyl carbons rather than near the methylene carbons. This is in good agreement with the known fact that the specific interaction occurring in PCL/PVC blends involves the carbonyl group of the ester.¹⁹⁻²²

Curve fittings on the $T_{1\rho}$ relaxation data by means of two exponential decay functions provide more detailed information on the microscopic phase structures and state of mixing. As seen in Table II, the double-exponential curve fittings result in two $T_{1\rho}$ relaxation times for individual carbon sites resolved into short and long components. Although the short component is due to the more motionally constrained region (i.e., crystalline region), the long component indicates the more mobile phase (i.e., amorphous region). Closer examinations reveal that (i) the $T_{1\rho}$ value for the rigid portion of PVC in the blend (3.8 ms) is similar to that of pure PVC (4.0 ms), but the $T_{1\rho}$ value for the mobile phase of PVC in the blend (16.8 ms) is quite different from that of pure PVC (11.0 ms); (ii) $T_{1\rho}$'s of the rigid and mobile portions from the rightmost methylene carbons of PCL component in the blend are almost same as those of pure PCL, respectively; and (iii) $T_{1\rho}$ values of carbonyl carbons of the PCL component in the blend are quite different from those of pure PCL. From (i), (ii), and (iii), it is believed that, upon mixing, the microcrystallites of PVC have been little affected and only the amorphous chains were interacted with PCL; in the case of PCL, both crystalline and amorphous chains were affected by PVC and the mixing occurred near the carbonyl carbon sites.

CONCLUSIONS

The present article explored the use of two proton spin-lattice relaxation times, one in the laboratory frame $T_1(^1\text{H})$ and another in the rotating frame

$T_{1\rho}(^1\text{H})$, to probe the structural microheterogeneity and domain size of PCL/PVC blend in the solid state. The blend composition was 50/50 by wt %, for which PCL is in an amorphous, molten state during mixing, but it crystallizes upon cooling, forming spherulites; the resulting blend also contains PVC microcrystallites in addition to the spherulites of PCL.

The following conclusions were drawn from the results:

1. From the measurements of $T_1(^1\text{H})$, the blend was shown to be homogeneous on the time scale over which the spin diffusion proceeds in the time characterized by T_1 .
2. The measurements of $T_{1\rho}(^1\text{H})$, however, revealed that on the time scale over which the spin energy diffuses in the times $T_{1\rho}$ the blend was not completely homogeneous.
3. The scale of mixing was estimated to be ~ 4.7 nm, indicating that some of individual polymer chains are apart from each other by more than ~ 4.7 nm.
4. The $T_{1\rho}(^1\text{H})$'s treated with two exponential decay functions provided more detailed information on the state of mixing and microphase structures; the PVC microcrystallites existed almost intact, whereas the crystalline as well as amorphous chains of PCL were shown to be affected, particularly near the carbonyl carbon sites, by the amorphous PVC chains.

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