

NMR Studies of Molecular Motion and Compatibility in Polymer Blends of Poly(epichlorohydrin)/Poly(methyl methacrylate)

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ABSTRACT: Molecular motion of polymer chains depends on blending and differs in bulk and in polymer blend. In this research the molecular motion of poly(epichlorohydrin) (PECH) was studied by ^{13}C NMR and showed different behavior in bulk from polymer blend. Two types of blend films, PECH/poly(methyl methacrylate) (PMMA) = (60/40) (wt%), were prepared from toluene and tetrahydrofuran (THF) solution; the former is transparent and the latter is opaque film. The line shape and temperature dependence of T_1 and T_2 in PECH indicate that the molecular motion of PECH is inhibited by surrounding PMMA chains and that the decrease in molecular motion depends on miscibility. The slow motion described by T_2 is more influenced by blending than the fast one described by T_1 . Distribution curves of T_2 were obtained for bulk and three types of blend films prepared from toluene, THF, and THF/H₂O solution. The bulk and blend films cast from toluene show sharp distributions are homogeneous in molecular motions. The blend films cast from THF and THF/H₂O have wide distribution in molecular motion, which indicates the existence of the gradient in local concentration. T_1 in PMMA agrees with T_1 and T_2 in PECH.

KEY WORDS ^{13}C Nuclear Magnetic Resonance / Poly(methyl methacrylate) / Poly(epichlorohydrin) / T_1 / T_2 / Distribution / Polymer Blend / Phase Structure / Molecular Motion /

The blending of polymers offers the possibilities of tailoring new technically important materials with specified properties.¹ Some physical properties of polymer blends depend on chemical composition and miscibilities.²⁻⁵ Especially thermal properties, for example glass transition temperature T_g , are studied on many kinds of polymer blends^{1,3-5} and show that molecular motions of polymer chains are different in bulk and in blend.

NMR is one of the suitable methods to study molecular motions of polymer chain.⁶ There have been a lot of studies on the compatibilities of polymer blends by relaxation behavior of pulse NMR.⁷⁻¹⁰ High resolution NMR shows molecular mobilities in line shape and in relaxation time.^{6,11,12} Recently there are many studies on molecular motions of polymer chain at solid state in relation to relaxation time of solid state high resolution NMR.^{13,14} Relaxation time and spin-diffusion are applied to studies on morphology of inhomogeneous polymer system, such as crystalline/amorphous^{13,15} or polymer blend.^{13,18} Especially spin-lattice relaxation time of ^1H and spin diffusion have been applied to many studies on polymer blends.¹⁸⁻²¹ Above the glass transition temperature T_g , ^{13}C high resolution NMR spectra are obtainable for solid polymer even by conventional NMR spectrometers used for liquids. Molecular mobilities of solid polyesters above T_g were studied by F. Horii *et al.* in this method.²²

Poly(epichlorohydrin) (PECH) is a rubber like polymer and poly(methyl methacrylate) (PMMA) is a glassy polymer at room temperature. Their structures are shown in Figure 1. PECH is miscible with PMMA²³ and this mixture shows low critical solution temperature (LCST) behaviors by DSC.²⁴

But the molecular behavior of PECH polymer chain in blend film is unknown. This work studies the differences of molecular motion of PECH polymer chain

for two blend films (transparent film and opaque film) with PMMA and bulk by NMR. We observed the behavior of PMMA polymer chain by solid state ^{13}C NMR. In the case of opaque film we observed the behavior of PECH polymer chain about the blend cast from tetrahydrofuran (THF)/H₂O to know the influence of compatibility by blending poor solvent in cast solvent.

EXPERIMENTAL

Sample Preparation

Blended PECH/PMMA was prepared by solvent casting. Three PECH/PMMA = 60/40 (wt%) blend films were prepared on petri dishes from toluene, THF, and THF/H₂O = 90/10 (wt%) solution containing 2 wt% polymer. All films were dried for 24 h at 80°C under vacuum. Table I shows the appearance and T_g of the samples. Transparent blend film shows they are miscible and opaque films show phase separated.

NMR Measurements

^{13}C NMR spectra were measured using Varian XL-300 (^{13}C ; 75.5 MHz) by conventional NMR spectrometers used for liquids. We measured temperature dependence

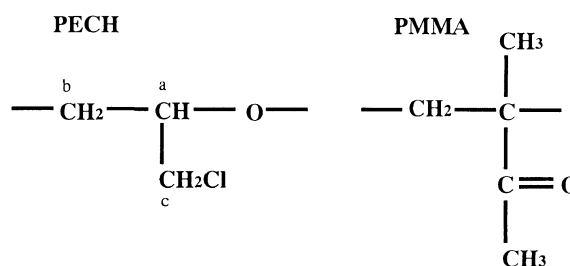


Figure 1. Structures of poly(epichlorohydrin) (PECH) and poly(methyl methacrylate) (PMMA).

Table I. T_g and appearance of blend film

Sample	Cast solvent	Appearance	$T_g/^\circ\text{C}$
Blend 1	Toluene	Transparent	14
Blend 2	THF	Opaque	-11, 38
Blend 3	THF/H ₂ O=90/10	Opaque	-20, 66

T_g (PECH) = -28.5°C ; T_g (PMMA) = 116.0°C .

of spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) for the bulk of PECH, the blend film cast from toluene, and that cast from THF solution. Temperature was increased from 40°C to 140°C . T_1 was measured by inversion recovery method and T_2 by Carr-Purcell-Meiboom-Gill method.⁶ The dimensions of samples were $50\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$. For the blend film cast from THF/H₂O, we measured only T_2 at 140°C .

We measured T_1 by solid state high resolution ^{13}C NMR spectra to observe the molecular behavior of PMMA polymer chain in bulk and blend films. Solid state high resolution ^{13}C NMR spectra were measured by high power proton decoupling (DD) and magic angle spinning (MAS). Pulse width was $5\ \mu\text{s}$. Dipole decoupling power was about 50 kHz . T_1 was measured by inversion recovery method. The magic angle sample spinning rate was about 3.5 kHz .

RESULTS AND DISCUSSION

^{13}C NMR Spectra

Figure 2 shows the ^{13}C NMR spectra of PECH in the bulk, blend film cast from toluene, and that cast from THF at 80°C . The spectra have three peaks of methine, methylene, and chloromethylene carbon peaks in PECH. The peaks in PMMA are not observed even above T_g which suggests that molecular motion of PMMA in blend films is too small for appearance of the spectra. The peaks of blends are broader than those of bulk. The peaks of transparent blend (cast from toluene) are broader than those of opaque film.

PECH peaks are broadened by blending which suggests that the molecular motion of PECH is hindered by PMMA polymer chain nearby PECH.

Temperature Dependence of Spin-Lattice Relaxation Time (T_1) in PECH

Temperature dependence of T_1 in methine carbon is shown in Figure 3. As shown in Figure 3 T_1 of methine carbon decreases, passing through a minimum and then increases with increasing temperature. But the temperature (T_{\min}) where T_1 shows a minimum value in Table II is different for the samples as shown in Figure 3. T_{\min} shifts to higher temperature by blending; T_{\min} (bulk) < T_{\min} (opaque blend film cast from THF) < T_{\min} (transparent blend film cast from toluene). The minimum T_1 shifts to higher by blending similar to T_{\min} . Methylene and chloromethylene carbon show similar behavior. T_{\min} and the minimum T_1 are shown in Table II.

T_1 depends on molecular motion.⁷ The higher shifts of T_{\min} show decrease of molecular motion. So it can be said that the molecular motion of PECH is inhibited by surrounding PMMA chains, and the molecular motion of the blend film cast from THF is influenced by PMMA

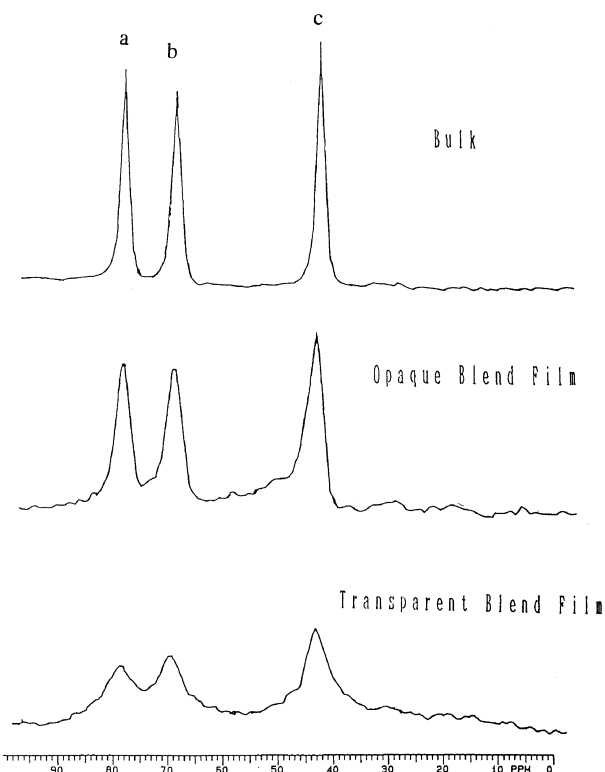


Figure 2. ^{13}C NMR spectra of PECH, peak (a) represents methine carbon, (b) methylene and (c) chloromethylene, pulse width is $25\ \mu\text{s}$ and transients are 256.

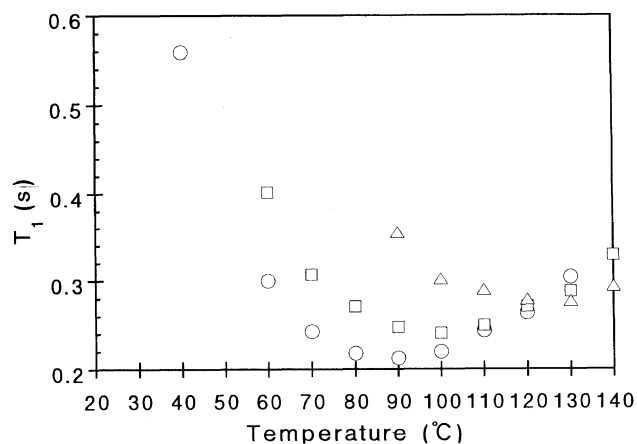


Figure 3. Temperature dependence of T_1 in PECH (methine carbon). \circ , bulk; \square , blend film cast from THF (opaque); \triangle , blend film cast from toluene (transparent).

chain. But the molecular motion of PECH in the blend film cast from THF is not much inhibited by PMMA chains compared to those cast from toluene. So it may be safely said that there is a PECH rich phase in the blend film cast from THF. The higher shifts of minimum value of T_1 show increase of distribution of correlation time on molecular motion.

Temperature Dependence of Spin-Spin Relaxation Time (T_2) in PECH

Figure 4 shows spin-spin relaxation decay of methine carbon in PECH at 140°C . We can get T_2 by fitting the spin-spin relaxation decay curve to the eq 1.

Table II. Temperature (T_{\min}) and T_1 where T_1 is minimal

	Methine		Methylene		Chloromethylene	
	$T_{\min}/^{\circ}\text{C}$	T_1 minimum/s	$T_{\min}/^{\circ}\text{C}$	T_1 minimum/s	$T_{\min}/^{\circ}\text{C}$	T_1 minimum/s
PECH (Bulk)	90	0.213	80	0.135	70	0.138
Opaque blend cast from THF	100	0.241	100	0.152	80	0.155
Transparent blend cast from toluene	130	0.277	110	0.178	90	0.200

T_{\min} is the temperature where T_1 is minimal. T_1 minimum is the minimum of T_1 .

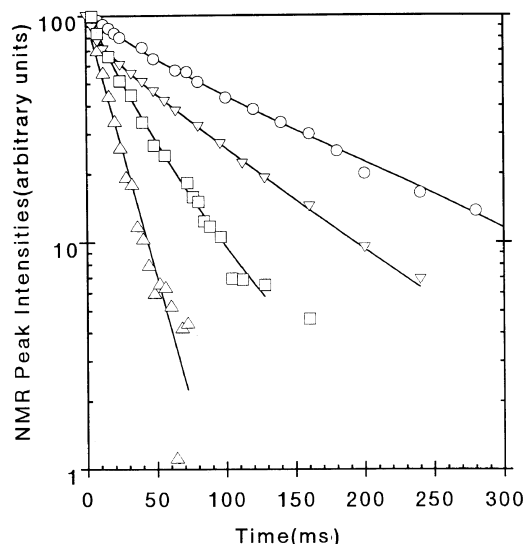


Figure 4. Spin-spin relaxation decay of methine carbon in PECH at 140°C. ○, bulk; ▽, blend film cast from THF/H₂O (opaque); □, blend film cast from THF (opaque); △, blend film cast from toluene (transparent). The lines, calculated distribution curve analysis.

$$M(t) = M(0) \exp(-t/T_2) \quad (1)$$

where $M(t)$ is signal intensity at delay time = t , $M(0)$ signal intensity, t delay time and T_2 T_2 . In Figure 4, the decay curves cannot be represented by single relaxation times described with eq 1 and indicate that there exist multiple components with different T_2 . T_2 in the opaque blend films are average values in the multiple relaxation times.

Temperature dependence of T_2 in methine carbon is shown in Figure 5. In Figure 5, T_2 in methine carbon increases with temperature. But T_2 of blend films is shorter than that of bulk. This shows that the molecular motion of PECH in blend film is inhibited by surrounding PMMA chains. T_2 of blend film cast from THF shows intermediate behavior of bulk and transparent blend film. It shows that the molecular motion of PECH in the opaque blend film is influenced by PMMA, but not so much as in the transparent blend film. These results are consistent with T_1 . But the difference of temperature where T_2 shows same value is larger than the difference of T_{\min} of T_1 , which means T_2 is more sensitive to compatibility than T_1 . Slow motion described by T_2 is more influenced by blending than the fast one described by T_1 . T_2 of methylene carbon and chloromethylene carbon show similar behavior.

Distribution Curve Analysis of T_2 and Characterization of Inhomogeneity

We observed the spin-spin relaxation of opaque blend film cast from THF/H₂O as well as the other three

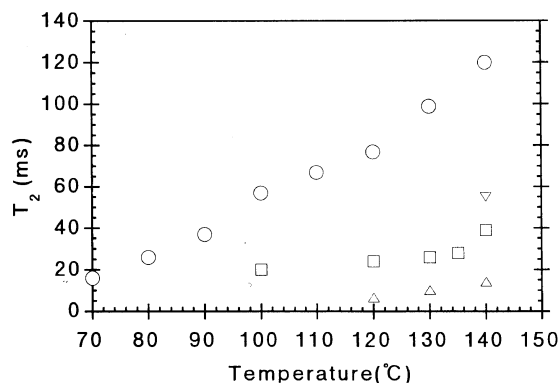


Figure 5. Temperature dependence of T_2 in PECH (methine carbon). ○, bulk; ▽, blend film cast from THF/H₂O (opaque); □, blend film cast from THF (opaque); △, blend film cast from toluene (transparent).

samples. This is because that T_2 is more sensitive to compatibility than T_1 and that T_2 is most sensitive at 140°C during our measurement.

The spin-spin relaxation decay in Figure 4 indicates multiple components with different T_2 , but not the number of components.

When the observed signal consists of several T_2 components, the relaxation decay in Figure 5 can be represented by eq 2.

$$M(t) = \sum_{i=1}^n A_i \exp(-t/T_{2i}) \quad (2)$$

where t is delay time, $M(t)$ signal intensity at delay time t , n number of components, A_i intensity of i -th component, T_{2i} T_2 of i -th component.

But it is difficult to determine the number and T_2 of the components in opaque blend films.

So we got the distribution curves of T_2 from curve fitting by eq 2. T_{2i} values are predetermined and spread over the time range and fixed in eq 2. We can get the best fitted A_i by non-linear least squares method. In this method, minimization of squared errors is made by varying the intensities of components (A_i) only. In the case of bulk, the estimated A_i values show zero except the T_2 range from 105 ms to 190 ms even though predetermined T_{2i} values are spread over the time range wider. So we determined the range of T_{2i} values in bulk from 105 ms to 190 ms. The squared errors decrease as n increases until 12. We determined the number of components (n) to 12. For blend films, we determined the range of T_{2i} values and n like the case of bulk.

The results of the distribution curve analysis of Figure 4 are shown in Figure 6. In Figure 6, the bulk and blend film cast from toluene show sharp distributions. This indicates that bulk and transparent blend film are

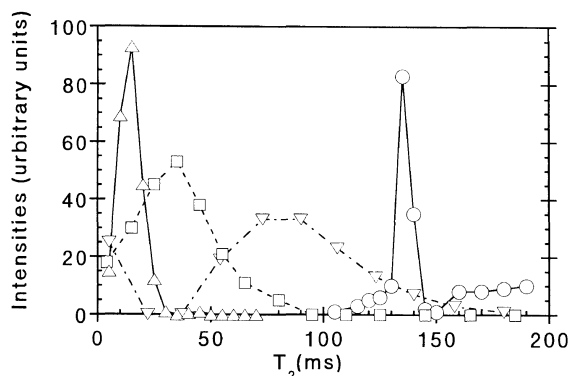


Figure 6. Distribution curves of T_2 in PECH (methine carbon). markings: calculated intensities (A_i), \circ , bulk; ∇ , blend film cast from THF/ H_2O (opaque); \square , blend film cast from THF (opaque); \triangle , blend film cast from toluene (transparent). The lines, distribution lines guessed from A_i .

homogeneous.

But in the case of the opaque blend film cast from THF, the components are distributed over a wide range of T_2 ; from 5 ms to 100 ms. In the distribution curve, the T_2 range from 5 ms to 20 ms is equal to that of the transparent blend film. So the opaque blend film cast from THF contains the PECH chains where the molecular motion described by T_2 is equal to that of the transparent blend film. In the distribution curve, T_2 range from 20 ms to 100 ms indicates the existence of the PECH polymer chains as intermediate molecular mobilities between transparent blend film and bulk. There are no intensities in the range from 120 ms to 150 ms. The range from 120 ms to 150 ms is equal to that of bulk. This shows there is no PECH polymer chains having equal molecular motion to bulk.

The wide range distribution of T_2 indicates the existence of polymer chains having different mobilities, and the mobilities of molecular chains have wide distribution. That the distribution curve is wide and continuous suggests a gradient in molecular motions of PECH described by T_2 .

From these results, we consider the existence of gradient in local concentration of PECH and PMMA in the opaque blend film cast from THF. It is considered that the existence of PECH polymer chains in the local concentration with PMMA is equal to that of the transparent blend film, which has the component distribution over T_2 range from 5 ms to 20 ms. From the components distributed over the T_2 range from 20 ms to 100 ms, it is suggested that the blend film has the PECH chains where the local concentration of PECH is higher than in transparent blend.

In the case of the opaque blend film cast from THF/ H_2O solution, the main part of the distribution curve is the range between 35 ms and 150 ms of T_2 . It is wider than that of the film cast from THF solution. So there may exist PECH polymer chains with intermediate molecular mobilities between the blend film cast from THF solution and bulk. Thus the local concentration of PECH rich polymer chains is higher in this film cast from THF solution, and the distribution of local concentration is wider. Therefore, PECH and PMMA are much separated by water in the cast solution.

The results of the distribution curve analysis from

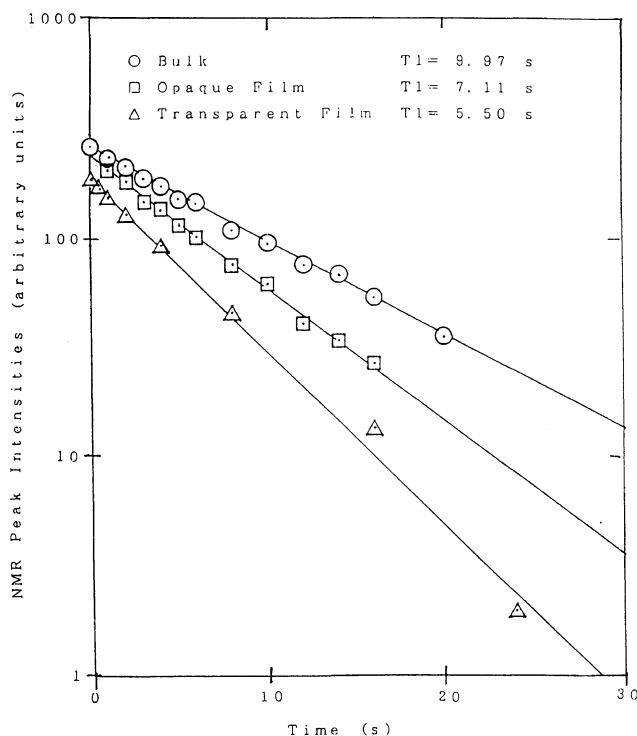


Figure 7. Spin-lattice relaxation decay of methoxy carbon in PMMA. \circ , bulk; \square , blend film cast from THF (opaque); \triangle , blend film cast from toluene (transparent). The lines are calculated by single-exponential decay.

spin-spin relaxation of methylene carbon and of chloromethylene carbon in PECH indicate the similar behavior with those of methine carbon.

In the case of the opaque blend film cast from THF/ H_2O , the distribution curve of methine carbon has a small component in the range of about 5 ms. The component is separated from another component distributed over the range between 35 ms and 150 ms. So there may be a separated phase in this film. But there are no such components in the distribution curves of methylene carbon and chloromethylene carbon. So it is considered that only the molecular motion of methine carbon is much decreased in this phase.

Spin-Lattice Relaxation of PMMA at Room Temperature

Spin-lattice relaxation of methoxy carbon in PMMA is shown in Figure 7, where we got spin-lattice relaxation time (T_1). T_1 of transparent blend film is shorter than that of PMMA bulk. T_1 of the opaque blend film cast from THF is intermediate that of transparent blend film and PMMA bulk. We consider that the molecular motion of PMMA polymer chains in the blend films increases by surrounding PECH polymer chains. The increase of molecular mobility of PMMA chains depends on the compatibility of PMMA and PECH. This agrees with the result of PECH. But we cannot discuss molecular motion of PMMA chains with only the present experimental results. We need temperature dependence of T_1 etc. for discussion about molecular motions of PMMA.

CONCLUSIONS

- (1) From the line shape and temperature dependence

of T_1 and of T_2 , molecular motion of PECH chains in blend film PECH/PMMA are inhibited by surrounding PMMA chains and the decrease in molecular motion depends on the compatibility.

(2) The slow motion described by T_2 is more influenced by blending than the fast one described by T_1 .

(3) Analysis of the distribution of T_2 is useful for investigating the inhomogeneity of the blend film.

(4) The transparent blend film cast from toluene solution and PECH bulk have the sharp distribution of molecular motion in PECH, and are homogeneous in molecular motion.

(5) In opaque blend film cast from THF solution, there are PECH polymer chains with different mobilities, and wide and continuous distribution.

(6) The width of distribution range of T_2 depends on the cast solutions and wide distribution in the opaque blend films may indicate a gradient in local concentration of PECH. The distribution of local concentration becomes wider by water in cast solution.

(7) T_1 of methoxy carbon in PMMA shows change of molecular motion of PMMA chains by blending with PECH, and this agrees with the result of PECH.

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