

STUDY OF THE MOLECULAR MOTION AND COMPATIBILITY IN AB-CROSSLINKED POLYMER BASED ON POLYURETHANE AND POLYSTYRENE-co-ACRYLIC ACID BY SOLID STATE HIGH RESOLUTION NMR*

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ABSTRACT

The ^{13}C T_1 s of $-\text{CH}_3$ side group in PPU/P(St-co-AA), AB-crosslinked polymers (i. e. ABCP) was studied by using high resolution solid state NMR. The rotation motion of $-\text{CH}_3$ side group in PPU was analyzed by means of the average spectral density functions of internal rotation. The results showed that the rotation of the $-\text{CH}_3$ side group is related closely to the compatibility between the two components. The compatibility was studied by analyzing the proton spin-lattice relaxation in rotating frame, spin-spin relaxation and spin-diffusion. The results showed that the hydrogen bonds between the components play a major role in determining the compatibility. Through spin diffusion studying, the soft phase domain size was calculated. By studying proton spin-spin relaxation, the content of each component in each phase and that of each phase in the samples can be obtained. The result shows that the content of interphase is related closely to the compatibility.

INTRODUCTION

High resolution NMR has become a powerful tool to study the structure and molecular motion of polymers in solid state^[1-5] because high resolution ^{13}C NMR spectra can be easily obtained by the combination of techniques of cross-polarization and magic angle spinning (CP/MAS) with simultaneously high power proton decoupling. Through analyzing the relaxation times, such as, ^{13}C spin-lattice relaxation time (T_1), proton spin-lattice relaxation time in rotating frame ($T_1\rho$) or proton spin-spin relaxation time (T_2),

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information about molecular motion and phase behavior or compatibility can be obtained respectively^[6-11]. While by studying the proton spin diffusion, the spin diffusion coefficient or soft phase domain size can be calculated if one of them is known^[12-13].

In this paper, the molecular motion and compatibility of ABCP based on prepolymer of polypropylene oxide urethane (PPU) and poly (styrene-co-acrylic acid) [P (St-co-AA)] were studied by using the ^{13}C T_1 values and ^1H $T_{1\rho}$ and T_2 as well as proton spin diffusion. The results of study of the internal rotation of $-\text{CH}_3$ side group in the ABCPs by using average spectral density function of internal rotation under MAS condition and the phase behavior are presented.

THEORETICAL

The dominant factor determining the relaxation is the dipole-dipole interaction between ^{13}C and ^1H for most polymers. Under this condition, the relationship between T_1 and spectral density function can be expressed as^[14]

$$\frac{1}{nT_1} = \frac{\gamma_c^2 \gamma_H^2 \hbar^2}{16r^6} [J_0(\omega_H - \omega_c) + 18J_1(\omega_c) + 9J_2(\omega_H + \omega_c)] \quad (1)$$

Under the condition of MAS, for the first order diffusive internal rotation, the average spectral density function can be expressed as^[15]

$$\overline{J_m(\omega)} = \frac{2}{5} K_m R_m(\beta_m) [BJ(\omega, D) + CJ(\omega, 4D)] \quad (2)$$

where

$$J(\omega, x) = \frac{x}{x^2 + \omega^2} \quad (3)$$

$$\overline{J_0(\omega)} = \frac{6}{5} \sin^2 2\Delta J(\omega, D) + \frac{6}{5} \sin^4 \Delta J(\omega, 4D) \quad (4-a)$$

$$\overline{J_1(\omega)} = \frac{1}{5} \sin^2 2\Delta J(\omega, D) + \frac{1}{5} \sin^4 \Delta J(\omega, 4D) \quad (4-b)$$

$$\overline{J_2(\omega)} = \frac{4}{5} \sin^2 2\Delta J(\omega, D) + \frac{4}{5} \sin^4 \Delta J(\omega, 4D) \quad (4-c)$$

For the first order three equal site jump

$$\overline{J_0(\omega)} = \frac{6}{5} (\sin^2 2\Delta + \sin^4 \Delta) J(\omega, \tau_i) \quad (5-a)$$

$$\overline{J_1(\omega)} = \frac{1}{5} (\sin^2 2\Delta + \sin^4 \Delta) J(\omega, \tau_i) \quad (5-b)$$

$$\overline{J_2(\omega)} = \frac{4}{5} (\sin^2 2\Delta + \sin^4 \Delta) J(\omega, \tau_i) \quad (5-c)$$

where Δ is the angle between the C-H vector and the rotation axis. By

fitting the ^{13}C T_1 to equation (1), (4), (5), the correlation time of $-\text{CH}_3$ rotation can be obtained.

The proton spin-lattice relaxation time in rotating frame and proton spin-spin relaxation time are very sensitive to the inhomogeneity in system. If the polymer system is homogeneous in corresponding scale, the multiple exponential behavior can be observed in the decay curves of proton magnetization in rotating frame and transverse. That is, the decay obeys the following formula

$$M = \sum_{i=1}^n M_{0i} \exp(-t/T_{1pi}) \quad (6)$$

for proton spin-lattice relaxation time in rotating frame. Where n equal 1 or 2 depending on the compatibility. For the proton spin-spin relaxation, the decay obeys the following formula

$$M = \sum_{i=1}^m M_{0i} \exp[-0.5(t/T_{2i})^2] + \sum_{j=1}^n M_{0j} \exp(-t/T_{2j}) \quad (7)$$

The first term corresponds to Gaussian decay and the second Lorentzian decay. $n=2, m=1$ or $n=1, m=2$ depending on the compatibility. That is, the decay curves can be decomposed into three components, two Gaussian components and one Lorentzian component or one Gaussian component and two Lorentzian components.

For proton spin diffusion experiment, the proton diffusion obeys diffusion equation^[12]

$$\frac{d}{dt} M(x, y, z, t) = D \cdot \Delta M(x, y, z, t) \quad (8)$$

Where D is the diffusion coefficient and $M(x, y, z, t)$ is the local magnetization density at position (x, y, z) at t time. When the time of diffusion is very short, the recovery factor $R(t)$ can be expressed as^[12]

$$\begin{aligned} R(t) &= 1 - \frac{M_1(t) - M_1(t \rightarrow \infty)}{M_1(t=0) - M_1(t \rightarrow \infty)} \\ &= \frac{2n}{\sqrt{\pi}} \left(\frac{Dt}{\bar{b}^2} \right)^{1/2} \quad t \ll \bar{b}^2/D \end{aligned} \quad (9)$$

where n is the number of space dimension and $\bar{b}^2$ the average square of the domain size of soft phase, $M_1(t)$ is the magnetization of the soft phase at t time. If diffusion coefficient (D) is known, $\bar{b}^2$ can be calculated by data fitting.

EXPERIMENTAL

Measurement

The ^{13}C $T_{1\rho}$ and ^1H $T_{1\rho}$ were measured on BRUKER MSL-400 spectrometer at 293K. The sample spinning rate is 3.7kHz. The field strength of decoupling and locking is 49kHz. The 90° pulse width for ^{13}C and ^1H are $4.8\mu\text{s}$ and $5.5\mu\text{s}$, respectively. The contact time is 1.5ms. The resonance frequencies of ^1H and ^{13}C are 400.13MHz and 100.6MHz, respectively. The pulse sequences used in this paper are showed in Figure 1 with waiting delay $D_0 = 5\text{s}$. The pulse sequence (a) was used to measure ^{13}C T_1 , the pulse sequence (b) used to measure ^1H $T_{1\rho}$, the pulse sequence (c) was used to measure ^1H T_2 indirectly^[16]. In pulse sequence (c), there is a variable delay time τ , during which the transverse relaxation of proton occur. As a result, the magnetization of ^{13}C produced by cross-polarization is proportional to the magnetization of proton remaining at the end of relaxation time. So, the transverse relaxation behavior of proton is observed by ^{13}C signal. In pulse sequence (d) used to measure proton spin diffusion, a solid echo block is added to avoid effects of the inhomogeneity of magnetic field and dead time of receiver.

Data processing

The data of magnetization and varying delay were transferred to IBM-PC microcomputer. Then, the ^{13}C T_1 and ^1H $T_{1\rho}$ were calculated by the data fitting by using program written in TURBO PASCAL language. By fitting the ^{13}C T_1 to corresponding model on VAX-11-785 computer, the correlation time of $-\text{CH}_3$ side group can be obtained. For the rotation of $-\text{CH}_3$, the relationship between

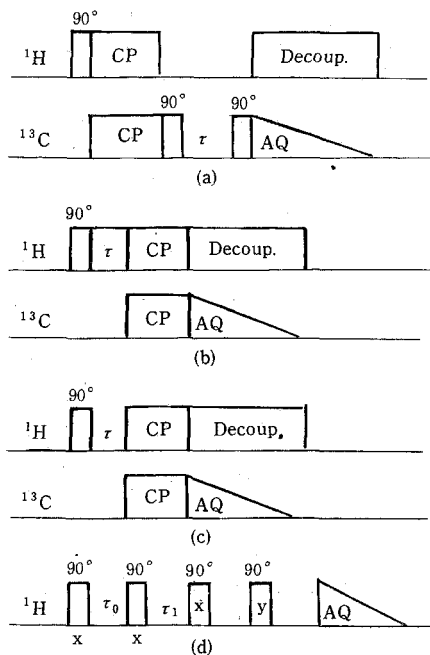


Fig. 1 The pulse sequences used to measure (a) ^{13}C T_1 ; (b) ^1H $T_{1\rho}$; (c) ^1H T_2 indirectly; (d) Proton Spin-Diffusion (Modified Goldman-Shen Sequence).

the activation energy and correlation time (or diffusion coefficient) can be expressed by^[17]

$$D = \frac{1}{6\tau} = 1.7 \times 10^{13} \exp(-E_a/RT) \quad (10)$$

The activation energy of the rotation of $-\text{CH}_3$ can be obtained by substituting the correlation time into equation (10). The $^1\text{H } T_2$ s were calculated by data fitting by using program written in QUICK BASIC language. By the data fitting, the $^1\text{H } T_2$ values and content of each composition can be calculated. In the processing of spin diffusion data, at first, the decay curve was analyzed by using the same program as that used in fitting $^1\text{H } T_2$, then the recovery curve was fitted by using program written in TURBO PASCAL language.

RESULTS AND DISCUSSION

The rotation of $-\text{CH}_3$ side group

The $^{13}\text{C } T_1$ s and motion parameters of $-\text{CH}_3$ side group of PPU in the ABCPs are listed in Table 1. The longer the T_1 , the slower the $-\text{CH}_3$ rotates as the correlation time of the rotation of $-\text{CH}_3$ side group is on slow side of $T_{1\text{min}}$. As the content of acrylic acid increases, the compatibility becomes better at first and then worse (see later) and the $^{13}\text{C } T_1$ of side $-\text{CH}_3$ becomes longer at first and then shorter because the intercomponent and intracomponent hydrogenbonds are dominant alternatively^[18]. These results mean that the rotational motion of $-\text{CH}_3$ side group is slower when the content of acrylic acid is lower and faster when the content of acrylic acid is higher. From the results of data fitting, see Table 1, it can be seen that more PS is incorporated into PPU phase as the compatibility becomes better. So the rotation of $-\text{CH}_3$ side group of PPU is restricted. Otherwise, the side $-\text{CH}_3$ rotates more freely. The activation energy of rotation of $-\text{CH}_3$ side group is nearly unchanged because the volume of $-\text{CH}_3$ group is too small. The relationship between the correlation time of $-\text{CH}_3$ side group and the content of acrylic acid is showed in Figure

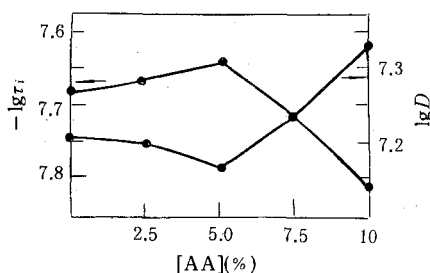


Fig. 2 The relationship between the correlation time of the rotation of the $-\text{CH}_3$ side group in PPU and the content of acrylic acid

2. It is clear that the change trends of the rotation of side $-\text{CH}_3$ and compatibility as the change of the content of acrylic acid are consistent to each other. These results show that the copolymerization of acrylic acid with PS has strong effect both on the rotation of $-\text{CH}_3$ side group and the compatibility even though the content of acrylic acid is low. It can be concluded from the above discussion that the relative strength of intercomponent or intracomponent hydrogen bond is very important in determining the molecular motion and compatibility. When the intercomponent hydrogen bond is stronger than the intracomponent hydrogen bond, the compatibility becomes better and when the intracomponent hydrogen bond is stronger than the intercomponent hydrogen bond, the compatibility becomes worse.

Table 1 The T_1 values and motion parameters of side $-\text{CH}_3$ of PPU in ABCPs, PPU/P(St-co-AA)

Composition (PPU : PS : AA)	T_1 (S)	Eq · Three-Site Jump		Diffusion rotation	
		$\tau_1 \times 10^8$ (S)	E_a (KJ · mol ⁻¹)	$D_i \times 10^{-7}$ (S ⁻¹)	E_a (KJ · mol ⁻¹)
50 : 50 : 0	0.407	2.07	35.5	1.62	33.8
50 : 47.5 : 2.5	0.415	2.11	35.5	1.59	33.8
50 : 45 : 5	0.449	2.28	35.7	1.46	34.0
50 : 42.5 : 7.5	0.381	1.94	35.3	1.73	33.6
50 : 40 : 10	0.309	1.56	34.8	2.14	33.1

The compatibility

The fitting results of magnetization decay in ^1H $T_{1\rho}$ experiment by using equation (6) are listed in Table 2. It can be seen that the contents of PPU in hard phase and PS in soft phase increase at first and then decrease as the contents of acrylic acid ([AA]) increase but that PS in hard phase and PPU

Table 2 The ^1H $T_{1\rho}$ values and relative content of each composition in each phase in ABCPs, PPU/P(St-co-AA) samples

ABCP (PPU : PS : AA)	PPU				P(St-co-AA)			
	Hard phase		Soft phase		Hard phase		Soft phase	
	$T_{1\rho}$ (ms)	$W(\%)$	$T_{1\rho}$ (ms)	$W(\%)$	$T_{1\rho}$ (ms)	$W(\%)$	$T_{1\rho}$ (ms)	$W(\%)$
50 : 50 : 0	3.09	41.0	0.367	59.0	4.70	65.8	1.35	34.2
50 : 47.5 : 2.5	2.67	63.2	0.427	36.8	3.61	49.3	1.46	50.7
50 : 45 : 5	Single exponential $T_{1\rho} = 1.59$				Single exponential $T_{1\rho} = 2.45$			
50 : 42.5 : 7.5	2.19	72.3	0.415	27.7	3.09	51.4	1.52	48.6
50 : 40 : 10	3.68	45.2	0.366	64.8	4.10	66.9	1.23	33.1

in soft phase decrease at first and then increase. When the content of acrylic acid is 5%, the decay exhibits single exponential characteristic, that means the sample is homogeneous in $^1\text{H } T_{1\rho}$ scale. These results imply that the compatibility becomes better when the [AA] increases further from 0% to 5% but the compatibility becomes worse when the [AA] increases further from 5% to 10%. This result is consistent with the result of dynamic mechanical analysis^[18]. The decay curve of magnetization in $^1\text{H } T_{1\rho}$ experiment and the fitting curve are showed in Figures 3, 4.

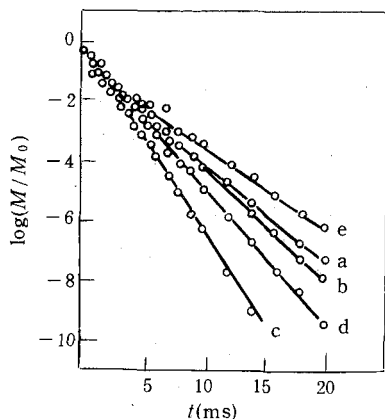


Fig. 3 The semi-log plot of the decay of the magnetization of PPU in the ABCPs in $^1\text{H } T_{1\rho}$ experiment and the fitting curve.

PPU/PS/AA, 50/50/0.0, a; 50/47.5/2.5, b; 50/45.0/5.0, c; 50/42.5/7.5, d; 50/40/10, e.

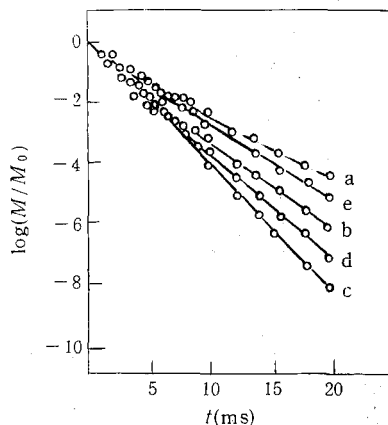


Fig. 4 The semi-log plot of the decay of the magnetization of PS in the ABCPs in $^1\text{H } T_{1\rho}$ experiment and the fitting curve.

The notes are the same as in Fig. 3.

The relationships between the ^{13}C magnetization and delay time τ and the fitting curve are showed in Figures 5 and 6. The fitting results are listed in Tables 3 and 4. Comparing to $^1\text{H } T_{1\rho}$, $^1\text{H } T_2$ is sensitive to smaller domain size, so the decay curve can be decomposed into more components. For each component in each sample, the decay curves can be composed of three components, i. e. two Gaussian components corresponding to hard phase and interphase and one Lorentzian component corresponding to soft phase. From the fitting results it can be seen that the distribution of each component in each phase has changed as the [AA] increases. As the compatibility becomes better, the content of PPU in hard phase and interphase and PS in interphase are increased, but the content of PPU in soft phase and PS in soft and hard phase are decreased. The results are consistent with those of the $^1\text{H } T_{1\rho}$ experiment and dynamic mechanical analysis. The content of each

phase in sample can be calculated from the results in Tables 3 and 4, listed in Table 5. It is clear that the content of interphase is closely related to the compatibility. The better the compatibility, the more the content of interphase. That means that the content of interphase plays a major role in determining the compatibility.

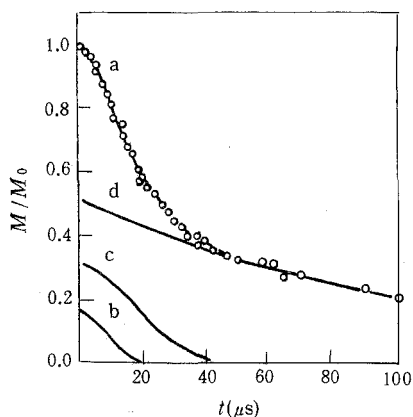


Fig. 5 The decay curve of the magnetization (integrated intensity) of PPU in PPU/PS/AA, 50/50/0.0, ABCP and the fitting curve.
a) Experimental curve; b, c) Guassian decay;
d) Lorentzian decay.

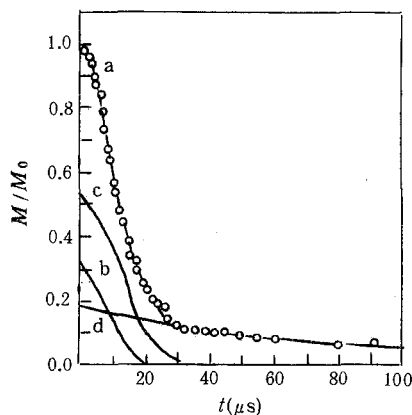


Fig. 6 The decay curve of the magnetization (integrated intensity) of PS in PPU/PS/AA, 50/50/0.0, ABCP and the fitting curve.
The notes are the same as in Fig. 5.

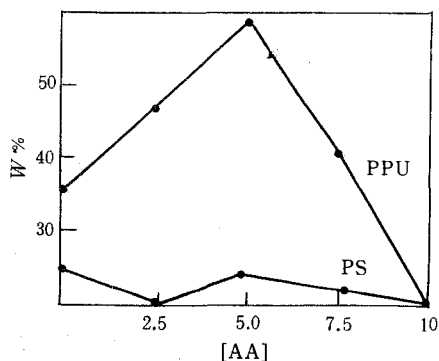


Fig. 7 The relationship between the content of PS in soft phase and PPU in hard phase and the content of acrylic acid ([AA])

This result is easy to be understood from the view of diffusion because the T_g of PPU is lower than that of PS. Comparing to PS, PPU is easier to diffuse into interphase and hard phase.

The content of PPU in hard phase and that of PS in soft phase can also be calculated from the fitting results in Tables 3 and 4, see Figure 7. The results show that the relative content of PS in soft phase remains almost constant and the content of PPU in hard phase increases as the compatibility becomes better. This implies that the change of the compatibility results from the incorporation of PPU into interphase and hard

Table 3 The ^1H T_2 values and content of PPU
in each phase in ABCP, PPU/P(St-co-AA)

ABCP (PPU : PS : AA)	Hard phase		Interphase		Soft phase	
	$T_2(\mu\text{S})$	$W(\%)$	$T_2(\mu\text{S})$	$W(\%)$	$T_2(\mu\text{S})$	$W(\%)$
50 : 50 : 0	8.10	16.9	16.4	31.7	113	51.4
50 : 47.5 : 2.5	7.38	18.1	15.6	37.6	79.7	44.3
50 : 45 : 5	7.12	19.7	15.4	46.1	68.6	34.2
50 : 42.5 : 7.5	7.03	14.8	16.1	34.8	92.6	50.4
50 : 40 : 10	7.70	11.4	12.9	25.0	102	63.6

Table 4 The ^1H T_2 values and content of P(St-co-AA)
in each phase in ABCP, PPU/P(St-co-AA)

ABCP (PPU : PS : AA)	Hard phase		Interphase		Soft phase	
	$T_2(\mu\text{S})$	$W(\%)$	$T_2(\mu\text{S})$	$W(\%)$	$T_2(\mu\text{S})$	$W(\%)$
50 : 50 : 0	7.58	30.8	11.1	52.0	79.9	17.2
50 : 47.5 : 2.5	6.22	20.6	14.3	68.0	85.7	11.4
50 : 45 : 5	5.87	13.7	15.6	75.3	80.1	11.0
50 : 42.5 : 7.5	6.03	21.6	12.3	63.8	71.5	14.6
50 : 40 : 10	6.95	44.5	12.4	38.7	74.2	16.8

Table 5 The content of each phase in ABCP, PPU/P(St-co-AA). ($W\%$)

ABCP (PPU : PS : AA)	Hard phase	Interphase	Soft phase
50 : 50 : 0	23.9	41.8	34.3
50 : 47.5 : 2.5	19.3	52.8	27.9
50/45/5	16.7	60.7	22.6
50 : 42.5 : 7.5	18.2	49.3	32.5
50/40/10	28.0	31.8	40.2

In spin diffusion experiment, for simplicity, the data are processed according to Cheung's route^[12]. The relationships between the recovery factor and diffusion time are showed in Figures 8 and 9. It can be seen that the relationships between recovery factor and the square root of diffusion time are linear when the diffusion time is short ($t \ll \bar{b}^2/D$). The values of $D/\bar{b}^2$ calculated from the initial slope of the recovery curves are listed in Table 6. Assuming the copolymerization of acrylic acid with PS do not affect the spin diffusion coefficient, the domain sizes of soft phase can be calculated (see Table 6) from equation (9) because the spin diffusion coefficients of

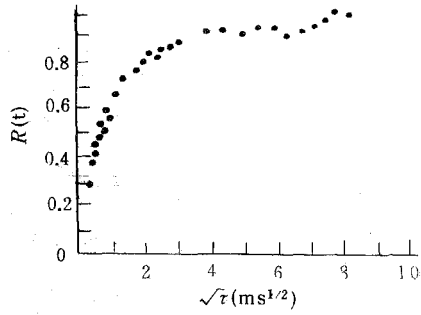


Fig. 8 The recovery curve of the hard phase in PPU/PS/AA, 50/50/0.0, ABCP.

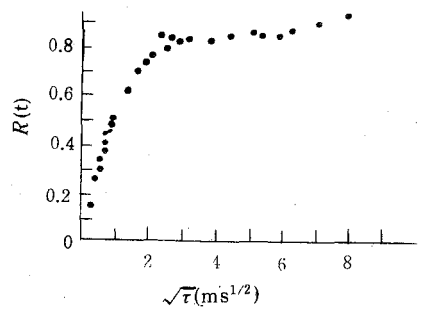


Fig. 9 The recovery curve of the hard phase in PPU/PS/AA, 50/47.5/2.5, ABCP.

polymers range from $10^{-12} \sim 10^{-11} \text{cm}^2/\text{s}$. The results show that the domain sizes of soft phase become larger at first and smaller as the content of acrylic acid increases further, which is consistent with the results of dynamic mechanical analysis, $^1\text{H } T_{1\rho}$ and $^1\text{H } T_2$ experiments. For block and graft copolymers, the systems have regular layer structure when the contents of two components are equal^[19-20]. Considering the similarity of structure between the ABCP and block and graft copolymers, the soft phase may have layer structure, which corresponds to one-dimensional diffusion. So the layer thickness of soft phase in the ABCPs range from 0.7—3nm.

Table 6 The calculated domain size of soft phase in ABCP, PPU/P(St-co-AA)

ABCP (PPU : PS : AA)	$(D/\bar{b}^2)^{1/2}(\text{ms}^{-1/2})$			$\bar{b}^{2**}(\text{nm})$		
	1-D*	2-D	3-D	1-D	2-D	3-D
50 : 50 : 0	0.389	0.195	0.130	0.81~2.57	1.62~5.13	2.43~7.69
50 : 47.5 : 2.5	0.464	0.232	0.155	0.68~2.16	1.36~4.31	2.04~6.45
50 : 45 : 5	0.470	0.235	0.157	0.67~2.13	1.34~4.26	2.01~6.37
50 : 42.5 : 7.5	0.368	0.184	0.123	0.86~2.72	1.72~5.43	2.57~8.13
50 : 40 : 10	0.351	0.176	0.117	0.90~2.85	1.80~5.68	2.70~8.55

* D; Dimensional
* * $D=10^{-12} \sim 10^{-11} \text{cm}^2/\text{s}$

CONCLUSION

The rotation of side $-\text{CH}_3$ of PPU in the ABCPs is closely related to the compatibility. The samples are inhomogeneous or homogeneous in $^1\text{H } T_{1\rho}$ scale depending on the content of acrylic acid, but in $^1\text{H } T_2$ scale, the samples are inhomogeneous. By measuring the $^1\text{H } T_2$ indirectly, not only the

content of each phase in the samples but also the composition of each phase can be obtained. The interphase plays a major role in determining the compatibility. The domain sizes of soft phase are estimated by spin diffusion experiment. The calculated domain sizes range from 0.7—3nm.

Keywords:

Spin-lattice relaxation; AB-crosslinked polymer; Molecular motion; Compatibility, Spin-diffusion

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