Spin Label Study of the Factors Affecting Molecular Motion of Poly(methyl methacrylate)

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ABSTRACT: The electron spin resonance (ESR) line shape of nitroxide radical labels attached to poly(methyl methacrylate) (PMMA) chains was studied as a function of temperature. In order to clarify various factors affecting molecular motions of PMMA chains, molecular mobility of a spin-labeled PMMA chain (L-chain) in another PMMA (M-chain) matrix was estimated by the ESR method. Isotactic and atactic PMMA having narrow molecular weight distribution were used as L- and M-chains. Strong dependencies of molecular mobility on molecular weights (M_L and M_M) of the chains and tacticity of M-chains were found. For example, the transition temperature, T_{50G} at which the extrema separation width due to anisotropic hyperfine splitting drops sharply increases with increasing molecular weight of M-chains. The correlation times at the transition temperatures, calculated from the ESR spectra are compared with those in so-called relaxation map and the nitroxide rotational motion is concluded to strongly correlate with micro-Brownian motion of the PMMA chains. It was also found that the correlation times estimated by the ESR method is proportional to $M_L^{0.5}$ and M_M when $M_M < 2M_e$ and independent of M_M when $M_M > 2M_e$. Here, M_e is the molecular weight between entanglements. These experimental facts are reflected on Stokes-Einstein and reptation types of diffusions of L-chains.

KEY WORDS Electron Spin Resonance / Spin Label / Molecular Motion / Poly(methyl methacrylate) / Relaxation Map / Distribution of Correlation Time /

It has been well established that spin-label technique is very useful to characterize molecular motion in solid polymers. ESR method is a simple and effective way of determining molecular mobility on a time scale of $\sim 10^{-9}$ s. We developed spin-label technique to investigate the structure and dynamics behavior of polymer chain at a particular site in a complicate system such as polymer blends.¹

Many authors have studied molecular motion of poly(methyl methacrylate) (PMMA) by the spin-label method. Veksli *et al.*,² Bullock *et al.*,³ Shiotani *et al.*,⁴ and Tsay *et al.*⁵ have analyzed the observed spectra based on the assumption that the rotational motion relies upon the simplified expression of correlation time, τ_R proposed by Freed *et al.*⁶ for isotropic rotation in the slow-motional region and Kivelson⁷ for isotropic rotation in the motional narrowing region.

On the other hand, Shiotani *et al.*⁸ concluded the anisotropic rotation of the side chain from the detailed analysis of the ESR spectrum of the spin-labeled PMMA. Murakami *et al.*⁹ and Tsay *et al.*¹⁰ presented spectral evidence to indicate that the double-peak feature of ESR spectrum observed for the spin-labeled PMMA can be explained satisfactorily on the basis of free-volume present in the glassy state. Cameron *et al.*¹¹ also interpreted the double-peak feature of the ESR spectrum of a nitroxide spin probe as reflecting from a distribution of correlation time arising from a distribution of free-volume within a polymer matrix. On the other hand, the correlation time of the molecular motion contributing to the averaging of the magnetic parameters have been ambiguously estimated from the ESR and NMR spectra observed for solid polymers. The most convenient methods for estimating the correlation time are to apply Freed, Kivelson and so-called BPP (Bloembergen, Purcell, and Pound) equations.¹² These equations are

valid for random motion with a single correlation time. Therefore, the activation energy obtained from the temperature dependence of correlation time by use of the three equations is very small compared with the energy obtained with consideration of the distribution of correlation time in solid polymers.

We estimated the distribution from simultaneous observation of ESR and NMR spectra and concluded that the correlation time calculated from the ESR and NMR line shapes at transition temperatures, for example, T_{50G} , is absolutely true.^{13,14}

In the present paper, we first clarify various factors affecting molecular motion of PMMA chains and next relate the distribution of the chemical structure with distributions of free-volume and correlation time from the temperature dependence of ESR spectra of spin-labeled PMMA in the various matrices. Finally, we present a mechanism of molecular motion of PMMA detected by the spin-label method.

EXPERIMENTAL

Materials

Many kinds of isotactic PMMA were prepared by anionic polymerization of MMA monomer (Tokyo Kasei Co., Ltd.) using *tert*-butyl magnesium bromide catalyst at -78°C .¹⁵ Three kinds of spin-labeled and isotactic PMMA were also prepared by anionic copolymerization of the MMA monomer with a labeled monomer,¹⁶ 4-(methacryloyloxy)-2,2,6,6-tetramethylpiperidine using *tert*-butyl magnesium bromide catalyst at -78°C . The end part of the PMMA chain is spin-labeled by injection of label monomer after polymerization of MMA monomer. The labeled polymer is named as the end-labeled PMMA. The mid-point of the PMMA chain is also spin-labeled by injection of MMA monomer after the preparation of the end-label PMMA. The labeled polymer is named as the center-label PMMA. On the

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Table I. Names and molecular weights of PMMA used in the present study

	Name	M_n	M_w/M_n
Isotactic PMMA			
End label	LE	5.0×10^3	1.21
Center label	LC	5.7×10^3	1.27
	HC	6.8×10^4	1.26
Random label	HR	3.6×10^4	1.32
	HRB	3.0×10^4	4.20
Non label	LN	4.6×10^3	1.18
	HN	6.9×10^4	1.28
Atactic PMMA			
Non label	C03	3.0×10^3	1.07
	C1	1.1×10^4	1.11
	C5	5.3×10^4	1.07
	C60	5.9×10^5	1.04
	C130	1.3×10^6	1.06
	C4B	4.0×10^4	1.85

other hand, polymerization is begun in the coexistence of MMA and label monomer in order to obtain the sample named as the random-label PMMA, which is spin-labeled at random in the chain. The toluene solution of the PMMA sample is dropped into cyclohexane in order to remove the non-reactive MMA and label monomers. The sediment is dried under vacuum for more than 1 day at room temperature. The procedure is repeated three times. The reaction time and the content of MMA monomer are changed to obtain the sample with different molecular weight. Many kinds of atactic polymer were purchased from Aldrich Chemical Co., Ltd. and Polymer Sci. Product Inc. Table I shows the characterization and name code of the PMMA samples.

Preparation of Blends

Binary blend of spin-labeled and non spin-labeled PMMA were made by mixing in a ratio of 1:20 by weight. Films were prepared by casting ~3 wt% of benzene solution at 60°C and then dried under vacuum for more than 1 week at the same temperature.

ESR Measurements

Samples were stacked in ESR sample tubes evacuated to 10^{-5} mmHg. ESR measurements were carried out with a JEOL FE#XG spectrometer with a connected MELCOM 70/25 computer.

The signal of diphenylpicryl-hydrazyl (DPPH) was used as a g -value standard. The magnetic field sweep was calibrated with known splitting constants of Mn^{2+} .

GPC Measurements

Molecular weight and its polydispersity were characterized by gel permeation chromatography (GPC). The GPC measurements were carried out with a GMX-G1000-G2000-G4000 type apparatus (Tosoh Co., Ltd.).

RESULTS AND DISCUSSION

Factors Affecting Molecular Motions of PMMA Chains

Figure 1 shows an example of temperature dependence of ESR spectrum of spin-labeled PMMA. Although the ESR spectrum at low temperatures was a broad triplet,

Figure 1. ESR spectra of spin-labeled PMMA (LE) in the PMMA matrix of HN. The arrows indicate the outermost peaks.

Figure 2. Variation of extrema separation width ($2A_z$) with temperature: End-label (LE)/non-label (LN) (●); end-label (LE)/non-label (HN) (○); center-label (LC)/non-label (LN) (○); center-label (LC)/non-label (HN) (●).

a narrow component at higher temperatures appears. The width between the outermost peaks of the spectrum narrowed with increasing temperature because of averaging of the anisotropic hyperfine coupling due to rotational motion of the PMMA chains. The outermost splitting is a good measure of the mobility of the spin-labeled PMMA. Figure 2 shows examples of variation of extrema separation width with temperature. The outermost peaks gradually change in the lower temperature range and narrowed sharply at a characteristic

temperature. In the present paper, we call the inflection point as T_{50G} , at which the outermost splitting is 50 gauss. The estimated temperature and the correlation time at the temperature should be closely related to glass transition temperature (T_g) and time scale of micro-Brownian type molecular motion, respectively, as discussed in the following section.

Dependencies of Molecular Mobility of PMMA Chains (L-Chains) on Matrix Molecular Weight M_M and Tacticity. The narrowing curves of the outermost splitting shifted to higher temperatures with increasing molecular weight M_M of matrix polymer as shown in Figure 2. The remarkable difference of the molecular mobility between the segments located at the end and center of a chain can not be detected. In order to confirm the molecular weight dependence, we observed molecular motion of PMMA chains in binary blends of end-labeled PMMA (L-chains) and atactic PMMA having narrow molecular weight distribution. Figure 3 shows variation of the narrowing curve with molecular weight M_M of the atactic PMMA (M-chains). The curves shift to higher temperatures with increasing the value of M_M . For instance, the transition temperature, T_{50G} increases with increasing molecular weight of the matrix polymer. The T_{50G} are plotted against the reciprocal molecular weight

Figure 3. Variation of extrema separation width ($2A_z$) with temperature: Dependence of the variation on molecular weight M_M of atactic PMMA. C03 (■); C1 (▣); C5 (▤); C60 (▥); C130 (□).

Figure 4. Plots of T_{50G} of isotactic PMMA (●) and atactic PMMA (○) samples as a function of M_M^{-1} .

(M_M^{-1}) as shown in Figure 4. The linear relationship is similar with that of T_g temperature against the reciprocal molecular weight (M_n^{-1}) given by Fox and Flory.¹⁷

$$T_g = T_{g,\infty} - K/M_n \quad (1)$$

where $T_{g,\infty}$ is T_g of the polymer with a infinite molecular weight and K is a polymer-specific constant. When the correlation time at T_{50G} , estimated from ESR data satisfy the WLF equation as discussed in detail in the following section, the difference, ΔT between T_{50G} and T_g should be constant and the eq 1 is converted to

$$T_{50G} = T_{g,\infty} + \Delta T - k/M_n \quad (2)$$

Ute *et al.*¹⁸ recently fractionated highly isotactic and highly syndiotactic PMMA into the individual homologues from the 13 mer to 50 mer by means of supercritical fluid chromatography and fitted plot of T_g vs. M_n^{-1} by a linear relationship, eq 1. They found that the K value, 9.4×10^4 for highly uniform syndiotactic PMMA is smaller than that for atactic PMMA obtained by other workers and suggested that the T_g s of the non-uniform PMMAs are lower than those uniform PMMAs. The K value, $(6.9-11) \times 10^4$ estimated from the linear relationship of T_{50G} vs. M_M^{-1} as shown in Figure 4 agrees with that for that obtained by Ute *et al.* rather than that for non-uniform and atactic PMMAs. These facts suggest that the transition temperature, T_{50G} should be related to the temperature, T_g and the characteristic molecular motion of L-chains in matrix polymer with a narrow distribution of molecular weight is detected. It was also found that T_{50G} for the matrix polymer of the isotactic PMMA was more than 25°C lower and the K value, 5.6×10^4 was smaller than for those for the atactic PMMA. These facts suggests that the configuration effect and structural uniformity are very important factors for the molecular motion.

Dependence of Molecular Mobility of L-Chains on Its Molecular Weight M_L . Figure 5 shows variation of the extrema separation width vs. temperature curve of the polymer (L-chains) with molecular weight M_L . We can estimate molecular mobility of L-chains in binary blends of spin-labeled PMMA with different molecular weight M_L and non-labeled PMMA with molecular weight of 7×10^4 . The narrowing curves shift to higher tempera-

Figure 5. Variation of extrema separation width ($2A_z$) with temperature: Dependence of the variation on molecular weight M_L . Label monomer/non-label (HN) (◆); center label (LC)/non-label (HN) (●); center label (HC)/non-label (HN) (▲).

tures with increasing values of M_L . This experimental fact suggests that molecular mobility decreases with increasing molecular weight.

Dependence of Molecular Mobility on Distribution of Molecular Weight. Figure 6 shows variations of the extrema separation width vs. temperature curve with polydispersity of molecular weight, M_w/M_n of the matrix polymer. The outermost splitting observed at a temperature is reflected on the average of correlation time and then, for the sake of convenience we use another shape factor, ΔT_w of the extrema separation width vs. temperature curve, i.e., the difference between the temperatures, T_{60G} and T_{40G} at which the splittings are 60 and 40 Gauss, respectively. The shape factor, ΔT_w as shown in Figure 6 should be a good measure of the magnitude of a distribution of correlation time according to temperature-time superposition principle. The value of ΔT_w seems to increase with increasing the polydispersity. Figure 7 shows the dependence of the shape factor on the polydispersity, M_w/M_n , obtained from the Figures 2, 3, and 6. It was found that the distribution of correlation time increased with increasing distribution of molecular weight.

Figure 6. Variation of extrema separation width ($2A_z$) with temperature: Dependence of the variation on polydispersity of molecular weight M_w/M_n .

Figure 7. Plots of ΔT_w as a function of polydispersity of molecular weight, M_w/M_n .

A Mechanism of Molecular Motion of PMMA Detected by the Spin-Label Method

Molecular Motion in a Lower Temperature Range. As mentioned in the previous section, the inflection point, T_{50G} in the extrema separation width vs. temperature curve is a transition temperature detected at an ESR frequency range.

What molecular relaxation mechanism reflects the transition phenomena? In order to answer the question, we should first apply well-known WLF equation,¹⁹

$$\log_{10}(\tau/\tau_g) = -17.44(T - T_g)/(51.6 + T - T_g) \quad (3)$$

The representative correlation time, τ_{ESR} at the temperature, T_{50G} can be calculated from the Freed's equation,

$$\tau_{ESR} = 1.10 \times 10^{-9} (1 - 2A_z/2A_0)^{-1.01} \quad (4)$$

for "moderate jump diffusion" model, where $2A_z$ (50.0 Gauss) and $2A_0$ (68.0 Gauss) are extrema separation width at a certain temperature and that the rigid state, respectively. Then, the τ_{ESR} and $\tau_g = 100 \text{ s}^{20}$ are substituted into the eq 3 and $\Delta T = T_{50G} - T_g$ is calculated to be 74°C. As well-known, T_g for atactic PMMA is 105°C. Therefore, the calculated value of T_{50G} , 179°C agrees with the experimental value, 177°C for the matrix of atactic PMMA with high molecular weight as shown in Figure 4. The estimated time, τ_{ESR} is converted to correlation frequency ($f = 1/2\pi\tau$) and plotted in Figure 8 together with correlation frequency for PMMA as measured for dielectric relaxation, dynamic mechanical and nuclear magnetic resonance spectroscopy.²¹

The calculated value, f_{ESR} agrees with that of micro-Brownian type molecular motion (α -mechanism). The value of f_{ESR} is one order of magnitude larger than that of the ester group motion (β -mechanism). Velski *et al.*¹ and Tsay *et al.*⁴ also compared ESR data with the results obtained by the other techniques. However, they discussed the relaxation mechanism without consideration of the distribution of correlation times which is a very important factor affecting the relaxation phenomena of polymer substance.

From these discussions, it is concluded that the narrowing behavior of extrema separation width around T_{50G} should be reflected on the WLF type, for instance,

Figure 8. A relaxation map of poly(methyl metacrylate): Plot arranged by Wada (○); correlation frequency at T_{50G} , calculated from ESR data (●); correlation frequency in higher temperature range, calculated by using Kivelson's equation from ESR data (▲) The dotted part in the figure (a) is magnified by 2 times (b).

large-scale main chain segmental motion.

Consequently, T_g and the correlation times at temperatures can be estimated from the experimental value of T_{50G} by using the eq 3 on the assumption of validity of WLF type behavior for the other PMMA samples. The marks (○) in Figure 9 shows the calculated values of correlation times at 177°C vs. molecular weight of M-chains of atactic PMMA, whereas the marks (●) in Figure 9 shows the calculated times at 148°C vs. molecular weight of L-chains of isotactic PMMA by using the eq 3. (In the present study, we used only the isotactic PMMA with low value of M_L to estimate the effect of molecular weight of L-chains because we could not obtain the spin-labeled and atactic PMMA with high value of M_L .)

Current theories^{22,23} predict that the center of mass diffusion of a polymer chain of molecular weight L in an entangled polymer matrix of molecular weight M_M may occur by three different process: reptation, constraint release, or Stokes-Einstein diffusion. The diffusion coefficient in unentangled matrices ($M_M < 2M_e$) is $D_{SE} \sim M_L^{-0.5} M_M^{-1}$, whereas that in entangled matrices is independent of M_M and proportional to the inverse of M_L^2 .

Here, M_e is the molecular weight between entanglements. Time constant of the diffusion should correspond to correlation time estimated by the spin-label method. At large values of the molecular weight of the matrix, the correlation times, τ are independent of M_M as shown in Figure 9. This behavior is consistent with diffusion of the L-chain by reptation in a "fixed" environment of constraints. On the other hand, the correlation times seem to be proportional to M_M and $M_L^{0.5}$ in the range of low molecular weight, M_L and M_M as shown in Figure 9. These facts suggest that the molecular motion of PMMA with low molecular weight ($M_L, M_M < 2M_e \sim 4 \times 10^4$) observed at T_{50G} by the ESR method is attributed to Stokes-Einstein diffusion. Molecular mobility of long chains in entangled matrices and L dependence should be studied in future.

Molecular Motion in a Higher Temperature Range. The transition phenomena around T_{50G} discussed previously

Figure 9. Dependencies of molecular mobility (τ) of PMMA chains on molecular weight (M). Correlation times, τ_{ESR} of L-chains in the matrix of HN at 148°C as a function of its molecular weight (●) and correlation times, τ_{ESR} of L-chains (LE) at 177°C as a function of the molecular weight of the matrix (○).

reflect the averaging of the anisotropic interaction between electron and nuclear spins and then, the correlation frequency should be calculated from the anisotropic hyperfine width due to the interaction. We can estimate molecular mobility also from the narrowing of line width of ESR spectrum after the averaging of the anisotropic spin interaction.

What molecular relaxation mechanism reflects the temperature dependence of the line widths of the spin-labeled PMMA?

First, the correlation times are calculated by using Kivelson's equation.

$$\tau = 15\pi\sqrt{3} W_0 \{ (h_0/h_1)^{0.5} - (h_0/h_{-1})^{0.5} \} / (8b\Delta\gamma H) \quad (5)$$

Here, h_1 , h_0 and h_{-1} are respective peak heights of three components. W_0 is the line width of central component, H is the static magnetic field applied, b and $\Delta\gamma$ in the equation are the quantities for the anisotropic of g - and A -tensors. The estimated correlation times for the matrix of atactic PMMA with high molecular weight (the sample of C60) are converted to correlation frequencies and plotted in the so-called relaxation map²⁰ (Figure 8). The calculated values agree with those of the ester group motion (β -mechanism) rather than those of α -mechanism. This fact suggests that the motional narrowing of line width is reflected on the ester group relaxation.

However, the slope estimated from the spin-label method seems to be smaller than that obtained by the other techniques. This disagreement is responsible for the distribution of the correlation time for the molecular motion. Kivelson's expression is valid for random motion with a single correlation time. Figure 10 shows examples of plots of logarithmic correlation times against the reciprocal temperatures. The activation energies estimated from the slope decrease with increasing polydispersity of molecular weight, M_w/M_n as shown in Table II. The potential barrier for molecular rotation of the ester side group should be strongly affected by the surrounding environments, *i.e.*, inter molecular interaction, segmental density, steric hindrance, and *etc.* However, it can be considered that the polydispersity of molecular weight of PMMA with the same value of M_n does not affect the surrounding environments. Therefore,

Figure 10. Examples of temperature dependencies of correlation time of spin-labeled PMMA: LE/C60 (●); LE/HN (○); HRB (△).

Table II. Activation energies estimated from temperature dependencies of correlation time (Figure 10)

Sample	M_w/M_n	$E_a/\text{kcal mol}^{-1}$
LE/C60	1.04	13.4
LE/HN	1.28	9.2
HRB	4.20	7.3

M_w/M_n dependence of the activation energy as shown in Figure 10 is caused mainly by the distribution of molecular weight which bring about the structural distribution, and the distribution of correlation times.

In general, the activation energy estimated by the magnetic resonance method should be both functions of the magnitude of the distribution and the potential barrier of molecular motion. The anisotropic rotation of the side group from the spectrum simulation of the spin-labeled PMMA was studied by Shiotani *et al.*⁶ For the sake of brevity, the anisotropic rotational correlation times, $\tau_{\parallel}$ and $\tau_{\perp}$ and the degree of anisotropic rotational reorientation, $N = \tau_{\parallel}/\tau_{\perp}$ are calculated by using Freed's equation.²⁴ Here, $\tau_{\parallel}$ and $\tau_{\perp}$ are rotational correlation times about major and minor axes of the axially symmetric rotor. The average correlation times, $\sqrt{\tau_{\parallel}\tau_{\perp}}$ have similar value to that based on the isotropic rotational model (eq 5). It is well-known that the major axis is parallel to the direction of the N–O axis (approximately perpendicular to the main chain axis). The values of N , which is calculated to be 2–3 in the higher temperature range, increase with increasing temperature. For instance, the rotational motion around the major axis can be a slow rotation of the ester side group in comparison with the rotation around other axes. The motional narrowing of ESR spectrum can be observed when the time constant corresponding to the ESR line width is comparable to that of the slow motion. These facts support the molecular motion of the spin-labeled

PMMA in the higher temperature range is attributed to the rotation of the ester side group.

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