Fluorescence Depolarization Study of Local Motions in Polymers at the Θ Temperature

Keiko Ono, Kazuhiko Ueda, Takashi Sasaki, Shigemitsu Murase, and Masahide Yamamoto*

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received December 7, 1994; Revised Manuscript Received October 27, 1995[⊗]

ABSTRACT: The mean relaxation times, T_m's, of four different polymers measured by the fluorescence depolarization method were compared at their Θ temperatures. These polymers, i.e., *cis*-polyisoprene (*cis*-PI), polystyrene (PS), poly(α-methylstyrene) (PαMS), and syndiotactic poly(methyl methacrylate) (*s*-PMMA), were labeled with anthracene in the middle of the main chain by living anionic polymerization. The Θ temperature is a standard point without an excluded volume effect, and the Θ temperature of these four polymers are almost the same, 34−35 °C. Therefore, the comparison of the T_m's at the Θ temperature enables us to clarify the relationship between the chain local motion and the chemical structure. The order of the reduced relaxation times, T_m/η, was T_m/η(*cis*-PI) < T_m/η(PS) < T_m/η(PαMS) < T_m/η(*s*-PMMA), and the order of activation energies, E^*, was E^*(*cis*-PI) < E^*(PS) < E^*(PαMS) < E^*(*s*-PMMA). From a molecular standpoint, the relaxation times depend on both the substituents attached to the main chain and the stereoregularity of the polymer chains. In consideration of the stereoregularity of the polymer chains, the relaxation time of atactic PαMS is estimated to be not much different from the relaxation time of atactic PMMA.

Introduction

A flexible polymer chain in a dilute solution undergoes micro-Brownian motions induced by local conformational transitions of the main or side chains.[1−6] The molecular structure of the polymer governs both the chain conformations and its molecular chain dynamics.[4] Kuhn[7] was the first to relate real chains to random-flight models. However, these random-flight models are not valid for semiflexible and stiff chains. Then, Flory[8] developed the rotational isomeric state model. Later, Yamakawa proposed a continuous model, helical wormlike chain model (HW model), and it is now widely accepted. This model can represent the static chain stiffness.[4−6] However, the relationship between molecular chain dynamics and the structure of polymer chains is not yet fully understood.

These local motions have been studied by various methods of neutron scattering,[9] NMR,[10,11] ESR,[12] dielectric relaxation,[13−15] dynamic light scattering,[16,17] and fluorescence depolarization.[18−21] Previously, we prepared polymer samples labeled with anthracene in the middle of the main chain and have monitored the relaxation times of the local motions of the chains using the fluorescence depolarization technique.[18,22−26] By this method, the orientational autocorrelation function of a polymer chain can be directly observed.

In this study, the local chain motions of four labeled polymers, i.e., *cis*-polyisoprene (*cis*-PI), polystyrene (PS), poly(α-methylstyrene) (PαMS), and syndiotactic poly(methyl methacrylate) (*s*-PMMA), are compared at their Θ temperatures (34−35 °C), and the mean relaxation times, T_m, and activation energies, E^*, are evaluated in each Θ solvent. The local motion of a polymer chain depends on the internal and external factors. The former are the polymer structure and molecular weight, and the latter are temperature and solvent (quality and viscosity). To examine the dependence of polymeric local motion on the molecular structure, the external factor should be exluded and the relaxation time must be compared under an adequate condition. As we showed previously,[26−28] the relaxation time of a polymer in the dilute solution usually depends on the segment density governed by the solvent quality. Therefore, the reduced relaxation times, T_m/η, must be compared among polymers at the Θ temperatures without the effect of the excluded volume. The Θ temperatures for the four samples, *cis*-PI, PS, PαMS, and *s*-PMMA, are in the range 34−35 °C, and the local motions can be compared in the same unperturbed state at almost the same temperature.

Macromolecular chain dynamics has been studied by many workers[20,21,26,29−31] from various standpoints, e.g., labeled position[29,30] and concentration dependencies.[31] However, we know few studies in which the local chain motions were compared among various polymers. Anufrieva et al.[29] were the first to examine the relaxation time of various polymers in dilute solutions by the steady-state fluorescence depolarization method. They compared the relaxation times of PS (8.9 ns) in toluene and PMMA (8.3 ns) in methyl acetate. However, they used good solvents for polymers, not the Θ solvents. Their findings include the influence of solvent quality or the difference of chain segment density.

Monnerie et al. and Ediger et al. also prepared polymer samples labeled with anthracene in the middle of the main chain, and the local motions of polystyrene, polybutadiene, and polyisoprene were examined by the time-resolved fluorescence depolarization technique. Monnerie et al.[32,33] evaluated the model functions for best fitting to experimental data of the time-resolved anisotropy ratio and proposed the GDL model. Ediger et al.[20] measured the relaxation times of polystyrene in various highly viscous solvents (>3 cP at 20 °C) and in the Θ solvents by the time-resolved fluorescence depolarization technique.

Hitherto, the relaxation times of various polymers have not been compared at the same condition. In this study, the polymer chain dynamics is compared at the Θ temperatures. Here the fluorescence anisotropy is time-resolved.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

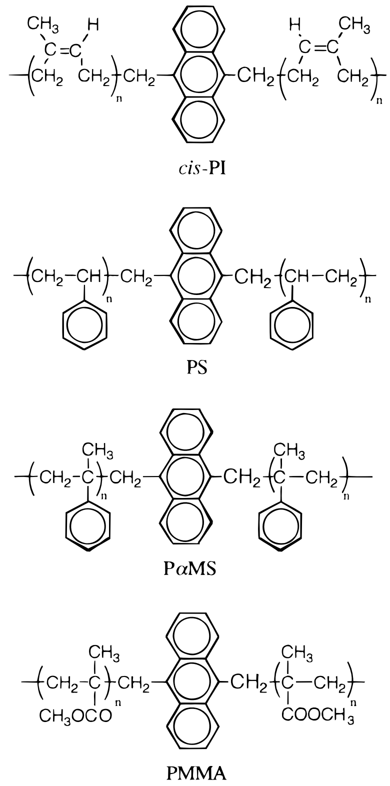

Figure 1. Polymer samples (PS, PαMS, *s*-PMMA, and *cis*-PI) labeled with anthracene.

Table 1. Molecular Weights and Racemo Fractions of Polymer Samples

	$10^{-4}M_w$	M_w/M_n	f_r
cis-PI	14.5	1.10	
PS	9.7	1.05	0.54
PαMS	21.5	1.05	0.67
s-PMMA	15.0	1.18	0.93

Experimental Section

Preparations of Polymer Samples. Four anthracene-labeled polymers, *cis*-PI, PS, PαMS, and *s*-PMMA, were prepared by living anionic polymerization, and the living ends were coupled by 9,10-bis(bromomethyl)anthracene (Figure 1). The preparative methods of these polymers are as described in refs 22, 24, and 34. We fractionated *cis*-PI, PS, and PαMS by GPC, and the fractions of the polymer labeled in the middle of the main chain were collected. As for *s*-PMMA, the anthracene group as a terminator was exhausted by the coupling reaction and was completely introduced in the middle part of the *s*-PMMA main chain.[24] Table 1 shows the characteristics of the four polymers. The molecular weights were measured by GPC. All polymer samples have molecular weights higher than ca. 100K with narrow distributions. The racemo fraction was measured by ^{13}C-NMR and ^{1}H-NMR,[35−37] and the racemo fraction of *s*-PMMA was the largest, 0.93. The microstructure of *cis*-PI measured by ^{13}C-NMR[38,39] was as follows: the *cis*-1,4 content is 76%, *trans*-1,4 content is 19%, and 1,2 content is 5%. The polymer concentrations of all the sample solutions were kept less than 0.1 wt %, and all the solutions were degassed before the measurements were taken. These solutions were prepared in quartz cells for the fluorescence anisotropy measurements.

Solvent. We used cyclohexane (Nacalai Tesque, spectrophotometric grade), 1,4-dioxane (Nacalai Tesque, spectrophotometric grade), and butyl chloride (Nacalai Tesque, guaranteed reagent) as the Θ solvents for the four polymers. Each Θ solvent and Θ temperature is as follows:[40] 1,4-dioxane at 34.0 °C for *cis*-PI, cyclohexane at 34.5 °C for PS and PαMS, and butyl chloride at 35.0 °C for *s*-PMMA. In the Θ solvents, the local motions can be compared among polymers without the consideration of solvent quality except for a specific interaction such as solvation.

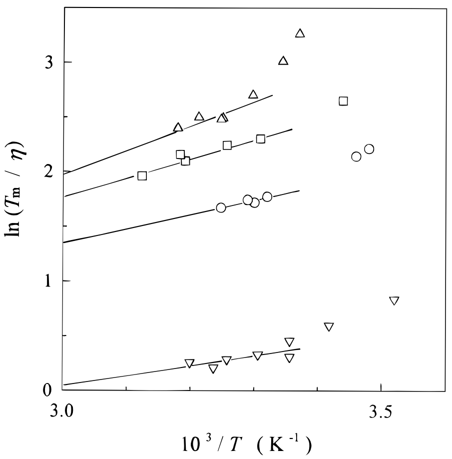

Figure 2. Arrhenius plots of $\ln(T_m/\eta)$ in various Θ solvents against $1/T$: (▽) *cis*-PI; (○) PS; (□) PαMS; (△) *s*-PMMA.

Measurements and Analysis. We measured the time-resolved fluorescence anisotropy ratio of a labeled polymer as reported previously.[25] The time-resolved measurements were done by the single-photon counting system. A diode laser (PLP-01, Hamamatsu Photonics) was used as a light source and its wavelength was 411 nm. A microchannel plate-photomultiplier tube (MCP, Hamamatsu Photonics) was used as a detector. We put the filters, V-42 and Y-44 (Hoya), in front of the MCP and collected the emission of the wavelength range, ca. 430−510 nm. In this instrumental system, the fwhm of the total instrumental function was ca. 350 ps. We convoluted eq 1 with the instrumental function to analyze the anisotropy ratio, $r(t)$, and fitted it to the experimental anisotropy data by the method of nonlinear least squares.[24]

$$r(t) = r_0\{x \exp(-t/T_1) + (1 - x) \exp(-t/T_2)\} \qquad (1)$$

The best-fit values of the parameters, r_0, x, T_1, and T_2, were obtained. Equation 1 is an empirical equation, but it fits the experimental data very well for all the samples. The mean relaxation time, T_m, is defined by eq 2 and it is calculated by eq 3.

$$T_m = r_0^{-1}\int_0^\infty r(t)\,dt \qquad (2)$$

$$T_m = xT_1 + (1 - x)T_2 \qquad (3)$$

The activation energy of the polymer chain, E^*, was evaluated by the theory of Kramers' diffusion limit,[41]

$$T_m = A\eta \exp(E^*/RT) \qquad (4)$$

where R is the gas constant, T is absolute temperature, and η is the solvent viscosity. Equation 4 is also written in eq 5.

$$T_m/\eta = A \exp(E^*/RT) \qquad (5)$$

The value of E^* can be obtained by making the plots of $\ln(T_m/\eta)$ against $1/T$.

Results and Discussion

Relaxation Times. Figure 2 shows the Arrhenius plots of $\ln(T_m/\eta)$ against $1/T$ in each Θ solvent. At temperatures higher than the Θ temperature, the relaxation times, $\ln(T_m/\eta)$, for the four polymers decreased linearly with increasing temperature. The values of T_m/η in the Θ solvents can be compared without the consideration of solvent effects (solvent viscosity and quality). The slope of these straight lines which correspond to activation energies will be discussed later.

Table 2. Relaxation Times, T_m/η, for Polymers in Various Θ Solvents at 35 °C

	T_m/η (ns cP^{-1})
cis-PI/dioxane	1.3
PS/cyclohexane	5.4
PαMS/cyclohexane	9.0
s-PMMA/butyl chloride	12.7

A further decrease of the temperature by 10−15 deg below the Θ temperature steeply increased the slope. This may be due to the microscopic aggregation of polymers subsequent to the coil−globule transition.[42,43] Chu et al.[43−46] investigated the coil−globule transition in the PS/cyclohexane system by the dynamic light scattering method. They studied the time dependence of the transition by sudden lowering of temperature (35 to 29 °C, $M_w = 8.6 \times 10^6$) and proposed a two-stage contraction process; in the first stage, fast collapse of the single chain (crumpled globule), and in the second stage, both aggregation and further collapse of the single chain (spherical globule). The steep increase of the relaxation times in this study is related to the coil−globule transition, and the steep increase is under investigation.

We monitored the relaxation times for the four polymers at 35 °C from Figure 2 and show these values in Table 2. The order of the reduced relaxation time was T_m/η (*cis*-PI) < T_m/η (PS) < T_m/η(PαMS) < T_m/η (*s*-PMMA). The reduced relaxation time, T_m/η, for *cis*-PI was 1.3 ns cP^{-1}, and the value was the smallest among these polymers. *s*-PMMA had the longest relaxation time among these polymers, and the value was 12.7 ns cP^{-1}: it was more than 10 times that for *cis*-PI. The relaxation time for PS was ca. 5.4 ns cP^{-1}: it was ca. 5 times longer than that for *cis*-PI. T_m/η for PαMS was longer than that for PS.[26] The order of the reduced relaxation times among the four polymers, *cis*-PI < PS < PαMS < *s*-PMMA, is governed mainly by the value of E^* rather than the value of A in eq 5.

We discuss the relationship between the values of the relaxation times and the polymer structure. First, *cis*-PI has a double bond in the main chain, but it does not have a large substituent besides the methyl group. Such a structure makes the *cis*-PI chain more flexible with a glass transition temperature[47] (ca. −70 °C) much lower than those of the other three polymers (PS ca. 100 °C, PαMS ca. 170 °C, *s*-PMMA ca. 105 °C). Second, the styrene polymers, PS and PαMS, have a bulky phenyl group differing from *cis*-PI, so that these relaxation times become longer. Furthermore, PαMS has a relaxation time larger than that of PS. This is because the α-methyl substitution of the main chain makes the internal potential higher and the relaxation time longer. Therefore, we conclude that the bulkiness of substituents and the substitution at the α-position induce higher steric hindrance to local motions and prolong the relaxation times. The same finding was also obtained by Anufrieva et al.[29] Finally, *s*-PMMA is a disubstituted polymer like PαMS, but the relaxation time of *s*-PMMA is longer than that of PαMS. This may be due to the difference in both stereoregularity and solvation.

The difference in racemo fraction between *s*-PMMA ($f_r = 0.93$) and PαMS ($f_r = 0.67$) makes the relaxation time of *s*-PMMA longer. Generally, in the same kind of polymer, the polymer chain with syndiotactic regularity has a greater static stiffness than that with isotactic regularity.[48] Fujii et al.[49] evaluated the static chain stiffness, λ^{-1}, for various polymers. They especially examined the differences in λ^{-1} between the isotactic and syndiotactic types of the same kind of polymers. For example, the values of λ^{-1} are λ^{-1}(*i*-PS) = 26.4 Å, λ^{-1}(*s*-PS) = 37.5 Å; λ^{-1}(*i*-PαMS) = 17.8 Å, λ^{-1}(*s*-PαMS) = 76.5 Å; and λ^{-1}(*i*-PMMA) = 32.7 Å, λ^{-1}(*s*-PMMA) = 65.6 Å. The static chain stiffness strongly depends on the stereoregularity and may have a relationship parallel to the local chain dynamics. Then, the local chain dynamics is affected by the stereoregularity;[48,49] the structure of a polymer with a higher racemo fraction may prolong the relaxation time. The ester group is polar, and greater solvation of the ester group makes the side group bulkier; thus the reduced relaxation time becomes longer. It is not clear whether stereoregularity or solvation is the dominant factor at this stage, but both may be operating.

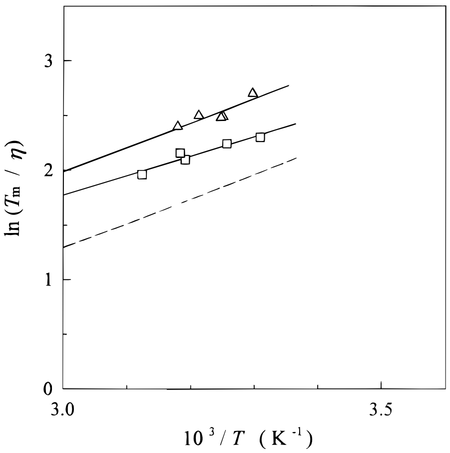

Figure 3. Arrhenius plots of ln(T_m/η) against 1/T for PαMS in cyclohexane (□; solid line) and *s*-PMMA in butyl chloride (△; solid line) and the predicted relaxation time of *i*-PMMA (broken line).

We compared the T_m/η of *a*-PMMA with that of *a*-PαMS with the same stereoregularity: $f_r = 0.5−0.8$. The experimental difficulty is that we cannot prepare polymers having the same stereoregularity with a uniform molecular weight distribution. Previously,[28] we found[50] that T_m/η for *i*-PMMA is 0.5−0.6 times that for *s*-PMMA in the Θ solvent, where the molecular weights are in the range 2.1×10^4 to 2.5×10^4. We used this relationship to evaluate T_m/η of *i*-PMMA with $M_n > 10^5$ in which relaxation times are independent of molecular weights.[27] Then, the relaxation times of *a*-PMMA cover the range between the solid line (△) and the broken line in Figure 3. The T_m/η of *a*-PαMS represented by a solid line with the square symbol is in the region for *a*-PMMA ($f_r = 0.5−0.8$), and we may conclude that T_m/η(*a*-PαMS) is similar to T_m/η(*a*-PMMA).

Activation Energy. The temperature dependence of the relaxation times represents the activation energy of a local chain motion, not the temperature effect on the coil dimension, because the latter effect is negligibly small[51] compared to the former one; the change of coil dimension is only ca. 0.2% °C^{-1}.

The activation energies for the four polymers, E^*, were estimated from the straight lines in Figure 2. Table 3 shows these values of E^*. Apparently, the order of the value of E^* was E^*(*cis*-PI) < E^*(PS) < E^*(PαMS) < E^*(*s*-PMMA). E^* for *cis*-PI was the lowest value, 1.6 kcal mol^{-1}. The *cis*-PI chain has rigid double bonds, but its single bonds are mostly freely-rotating ones; thus the activation energy for *cis*-PI is very small. PS has a bulky phenyl group which makes E^* higher than that of *cis*-PI. The value of E^* of PS was 2.6 kcal mol^{-1}, and that of PαMS was ca. 3 kcal mol^{-1}. The energy

Table 3. Activation Energies, E^*, for Polymers in Θ Solvents

	E^* (kcal mol^{-1})
cis-PI/dioxane	1.5
PS/cyclohexane	2.6
PαMS/cyclohexane	3.0
s-PMMA/butyl chloride	5.0

barrier of a conformational transition is strongly affected by the number and size of the substituted groups attached to the main chain: The same tendency was observed for the relaxation time. The PαMS chain is a disubstituted polymer, and the two substituted groups make the energy barrier of the conformational transition higher than that of the monosubstituted polymer,[49] such as PS. The activation energy of *s*-PMMA was largest among the four polymers. The *s*-PMMA chain has a disubstituted group attached to the main chain as in PαMS, and the substituents of PMMA, i.e., the methoxycarbonyl groups, make the hydrodynamic volume larger compared to the phenyl group in PS, and this makes the steric hindrance for the conformational transition higher.

The activation energy for the conformational transition of a polymer chain has been studied experimentally by many workers,[3,13,20,22] but theoretically by only a few.[52−54] For example, Bahar et al.[52] calculated the relaxation process for the polyethylene chain, and they concluded that the activation energy is 3.25 kcal mol^{-1}. Helfand et al.[2,53] simulated the relaxation behavior by the Brownian dynamics study and calculated the barrier height. The value was 3.3 kcal mol^{-1}. These two values for polyethylene are larger than that obtained in our experiments. The activation energies for other kinds of polymers have not been calculated previously.

Comparison of the Results under Various Conditions. The relaxation time of a polymer in a dilute solution usually depends on the segment density governed by the solvent quality. Therefore, the reduced relaxation time, T_m/η, must be compared among polymers at the Θ temperatures without the effect of the excluded volume and it is essential to show the values of T_m/η at the Θ temperatures and E^* in the Θ solvents.

We examined the relaxation times of PS,[26] *s*-PMMA,[27] and *cis*-PI[34] in various solvents. For PS in cyclohexane, the value of T_m/η was 5.4 ns cP^{-1} (34.5 °C, Θ), and the value in a good solvent, toluene, was 2.88 ns cP^{-1} (34.5 °C). The value in a good solvent was half that in the Θ solvent. For *s*-PMMA[27] in butyl chloride, the T_m/η was 12.7 ns cP^{-1} (35 °C, Θ) and the value in toluene was 4.6 ns cP^{-1} (35 °C), being one-third of that in the Θ solvent. The relaxation time in good solvents is smaller than that in the Θ solvents, and therefore, we cannot compare the relaxation times of polymer chains without the adoption of a Θ temperature. Around the Θ temperature, E^* of PS in cyclohexane (Θ solvent) was 2.6 kcal mol^{-1} and that of PS in a good solvent (toluene) was 1.4 kcal mol^{-1}. The same tendency as the relaxation time, that the value in good solvents is smaller than that in the Θ solvents, was observed.

Ediger et al.[20,55] also investigated the local chain motions in dilute solutions by the fluorescence depolarization method. For PS ($M_n = 68$K) in cyclohexane,[20] they obtained a relaxation time of 7.2 ns cP^{-1} (34.5 °C), which is similar to our value of 5.4 ns cP^{-1}, and the activation energy of 5 kcal mol^{-1}, which is ca. 2 times larger than our value of 2.6 kcal mol^{-1}. The relaxation time for *cis*-PI ($M_n = 104$K, *cis*-content = 54%) in a good solvent, toluene,[55] is 0.8 ns cP^{-1} (34 °C) and the activation energy is 1.8 kcal mol^{-1}, respectively. Their values for PS and *cis*-PI as a whole are similar to our values considering the difference in the experimental conditions such as instruments, samples, and methods of analysis.

Conclusion

We measured the relaxation times for four different polymers, i.e., *cis*-PI, PS, PαMS, and *s*-PMMA, in Θ solvents by the fluorescence depolarization technique. We evaluated the local chain dynamics without the effect of the segment density.

The order of the reduced relaxation times is T_m/η(*cis*-PI) < T_m/η(PS) < T_m/η(PαMS) < T_m/η(*s*-PMMA). This order of T_m/η mainly depends on the barrier height of the polymeric local motion. The order of the activation energies is E^*(*cis*-PI) < E^*(PS) < E^*(PαMS) < E^*(*s*-PMMA). The relaxation time and the height of the energy barrier depend on whether the polymer is either monosubstituted or disubstituted and also depend on the bulkiness of the substituents. However, the stereoregularity is an important factor comparing the relaxation times among various polymers.

Acknowledgment. Thanks are due to Dr. Hirokazu Hasegawa, Kyoto University, for helpful suggestions for the polymerization of anthracene-labeled *cis*-PI. We are indebted to Shunsuke Yokotsuka for the preparation of the anthracene-labeled PαMS. In addition this work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, Photochemical Reactions (No. 06239107) from the Ministry of Education, Science, and Culture of Japan.

References and Notes

(1) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(2) Helfand, E.; Wasserman, Z. R.; Weber, T. A. *Macromolecules* **1980**, *13*, 526.
(3) Stockmayer, W. H. *Pure Appl. Chem.* **1976**, *15*, 539.
(4) Yamakawa, H. *Macromolecules* **1977**, *10*, 692.
(5) Yashizaki, T.; Fujii, M.; Yamakawa, H. *J. Chem. Phys.* **1985**, *82*, 1003.
(6) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(7) Kuhn, W. *Kolloid-Z.* **1934**, *68*, 2; **1936**, *76*, 258; **1939**, *87*, 3.
(8) Flory, P. J. *Principle of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(9) Higgins, J. S.; Maconnachie, A. In *Methods of Experimental Physics*; Skold, K., Price, D. L., Eds.; Academic Press: New York, 1987; Vol. 23, Part C, p 287.
(10) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(11) Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47.
(12) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers*; Clarendon Press: Oxford, U.K., 1981; Chapter 9.
(13) Mashimo, S. *Macromolecules* **1976**, *9*, 91.
(14) Mashimo, S.; Winsor, P. R., IV; Cole, H.; Matsuo, K.; Stockmayer, W. H. *Macromolecules* **1986**, *19*, 682.
(15) Adachi, K. *Macromolecules* **1990**, *23*, 1816.
(16) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic: New York, 1991.
(17) Pecora, R., Ed. *Dynamic Light Scattering*, Plenum: New York, 1985.
(18) Sasaki, T.; Yamamoto, M. *Macromolecules* **1989**, *22*, 4009.
(19) Ediger, M. D. *Annu. Rev. Phys. Chem.* **1991**, *42*, 225.
(20) Waldow, D. A.; Ediger, M. D.; Yamaguchi, Y.; Matsushita, Y.; Noda, I. *Macromolecules* **1991**, *24*, 3147.
(21) Valeur, B.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 11.
(22) Yokotsuka, S.; Okada, Y.; Tojo, Y.; Sasaki, T.; Yamamoto, M. *Polym. J.* **1991**, *23*, 95.
(23) Sasaki, T.; Arisawa, H.; Yamamoto, M. *Polym. J.* **1991**, *23*, 103.

(24) Sasaki, T.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 610.

(25) Ono, K.; Okada, Y.; Yokotsuka, S.; Ito, S.; Yamamoto, M. *Polym. J.* **1993**, *26*, 199.

(26) Ono, K.; Okada, Y.; Yokotsuka, S.; Sasaki, T.; Yamamoto, M. *Macromolecules* **1994**, *27*, 6482.

(27) Horinaka, J.; Ono, K.; Yamamoto, M. *Polym. J.* **1995**, *27*, 429.

(28) Ono, K.; Sasaki, T.; Yamamoto, M.; Yamasaki, Y.; Ute, K.; Hatada, K. *Macromolecules* **1995**, *28*, 5012.

(29) Anufrieva, E. V.; Gotlib, Y. Y. *Adv. Polym. Sci.* **1981**, *40*, 1.

(30) Kasparyan-Tardiveau, N.; Valeur, B.; Monnerie, L.; Mita, I. *Polymer* **1983**, *24*, 205.

(31) Veissier, V.; Viovy, J.-L.; Monnerie, L. *Polymer* **1989**, *30*, 1262.

(32) Viovy, J.-L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.

(33) Viovy, J.-L.; Monnerie, L.; Merola, F. *Macromolecules* **1985**, *18*, 1130.

(34) Ono, K.; Ueda, K.; Yamamoto, M. *Polym. J.* **1994**, *26*, 1345.

(35) Sato, H.; Tanaka, Y. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 181.

(36) Inoue, Y.; Nishioka, A.; Chujo, R. *Makromol. Chem.* **1972**, *156*, 207.

(37) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17*, 977.

(38) Sato, H.; Ono, A.; Tanaka, Y. *Polymer* **1977**, *18*, 580.

(39) Duch, M. W.; Grant, D. M. *Macromolecules* **1970**, *3*, 165.

(40) (a) Abe, M.; Fujita, H. *J. Phys. Chem.* **1965**, *69*, 3263. (b) Noda, I.; Mizutani, K.; Kao, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 787. (c) Kirste, R. G.; Schultz, G. V. *Z. Phys. Chem.* **1961**, *27*, 310. (d) Poddubnyi, Ya. I.; Ehrenburg, E. G. *J. Polym. Sci.* **1962**, *57*, 545.

(41) Kramers, H. A. *Physica* **1940**, *7*, 284.

(42) de Gennes, P.-G. *J. Phys. Lett.* **1985**, *46*, L-639.

(43) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.

(44) Park, I. H.; Wang, Q.-W.; Chu, B. *Macromolecules* **1987**, *20*, 1965.

(45) Yu, J.; Wang, Z.; Chu, B. *Macromolecules* **1992**, *25*, 1618.

(46) Grosberg, A. Y.; Kuznetsov, D. V. *Macromolecules* **1993**, *26*, 4249.

(47) *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons, Inc.: New York, 1975; Chapter III, p 2.

(48) Yoshizaki, T.; Yamakawa, H. *J. Chem. Phys.* **1984**, *81*, 982.

(49) Fujii, M.; Nagasawa, K.; Shimada, J.; Yamakawa, H. *Macromolecules* **1983**, *16*, 1613.

(50) We previously[28] reported the Arrhenius plots of T_m/η for *s*- and *i*-PMMAs in θ solvents, butyl chloride and acetonitrile. The molecular weight, M_n, of *s*-PMMA was 2.1×10^4, and that of *i*-PMMA was 2.5×10^4; both were lower than that of *s*-PMMA examined in this study (15.7×10^4). The racemo fraction of *s*-PMMA was 0.93, and the value was the same as that in this paper. f_r of *i*-PMMA was <0.01. The reduced relaxation time, T_m/η, at 35 °C was, in butyl chloride, 5.5 ns cP^{-1} for *s*-PMMA and 3.4 ns cP^{-1} for *i*-PMMA and, in acetonitrile, 5.2 ns cP^{-1} for *s*-PMMA and 2.6 ns cP^{-1} for *i*-PMMA. T_m/η for *i*-PMMA was 0.5−0.6 times that for *s*-PMMA in the θ solvent.

(51) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley & Sons, Inc.: New York, 1969.

(52) Bahar, I.; Erman, B. *Macromolecules* **1987**, *20*, 2310.

(53) Helfand, E.; Wasserman, Z. R.; Weber, T. A.; Skolnick, J.; Runnels, J. H. *J. Chem. Phys.* **1981**, *75*, 4441.

(54) Yamakawa, H.; Yoshizaki, T.; Fujii, M. *J. Chem. Phys.* **1986**, *84*, 4693.

(55) Adolf, D. B.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1992**, *25*, 867.

MA946434U