Chain Dynamics of Styrene Polymers Studied by the Fluorescence Depolarization Method

Keiko Ono, Yasuo Okada, Shunsuke Yokotsuka, Takashi Sasaki, and Masahide Yamamoto*

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

Received May 12, 1994; Revised Manuscript Received August 8, 1994[⊗]

ABSTRACT: The local motion of polystyrenes in dilute solutions was examined by the fluorescence depolarization technique. The samples, polystyrene (PS), poly(α-methylstyrene) (PαMS), and poly(*p*-methylstyrene) (P*p*MS), were labeled with the fluorescent probe anthracene in the middle of the main chain. The relaxation time of their local motion in dilute solutions was examined by fluorescence anisotropy measurement. The activation energy of the relaxation time of the polymer chain, E^*, was also evaluated by the theory of Kramers' diffusion limit. There was a close correlation between the reduced relaxation time, T_m/η, or its activation energy and the chain expansion factor; i.e., both the reduced relaxation time and the activation energy decrease as the solvent quality becomes better. The reduced relaxation time and the activation energy depended on the local segment density of the polymer chain in the solution. The local motion for each polymer was compared in a θ solvent. The relaxation time and the activation energy of PαMS were larger than those of PS. This indicated that the barrier height of the local motion for a disubstituted polymer chain is higher than that for a monosubstituted one. Furthermore, the relaxation time and the activation energy of the P*p*MS chain were larger than those of PS.

Introduction

A flexible polymer chain in a dilute solution undergoes micro-Brownian motion[1-4] of the main chain, and the relaxation time of the local motion is generally in the nano- and subnano-second regions. Such a dynamic property of a polymer chain is important in understanding macroscopic physical properties. There have been many studies on the dynamic properties of polymers reported in the literature; however, little is known about the local motion of polymer chains.

The local motion in a dilute solution has been studied by neutron scattering,[5] NMR,[6,7] ESR,[8] dielectric relaxation,[9-11] dynamic light scattering,[12,13] and fluorescence depolarization.[14-17] In our laboratory, the local motion of various polymers has been studied by the fluorescence depolarization method. In this method, a fluorescent probe is usually introduced in a specific part of a polymer to measure the relaxation time of the local motion. This method gives the orientational autocorrelation function through the measurement of the time-resolved anisotropy ratio of the labeled polymer and has the advantage that we can directly observe the orientational autocorrelation function without the assumption of any model of polymer chain dynamics.

Recently, we studied the dynamic behavior of poly(alkyl methacrylate)s[18] and polystyrenes.[19] For poly(alkyl methacrylate)s, the relaxation time of the local motion was studied in dilute solutions from the standpoint of molecular structure. The relaxation time became longer in the order of poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA), and poly(iso-propyl methacrylate) (PiPMA).[18] The dynamic chain stiffness showed a parallel relationship with the static chain stiffness, and the chain stiffness depended on both the bulkiness of the alkyl residue and the chain tacticity (racemo fraction). For the local motion of the polystyrenes, the activation energy was larger in poor solvents than in good solvents.[19] In a solvent with a viscosity higher than ca. 2 cP, the activation energy of the local motion was anomalously negative. This indicated that the relaxation time has to be measured in low-viscosity solvents. In low-viscosity solvents, the relaxation times can be compared by the reduced relaxation time, T_m/η, and in such a condition, the polymer-solvent frictional interaction can be represented by the solvent viscosity.[22]

In this study, we measured the relaxation time of a polymer chain by the fluorescence depolarization method. The sample polymers were polystyrene (PS), poly(α-methylstyrene) (PαMS), and poly(*p*-methylstyrene) (P*p*MS). First, we examined the relationship between the reduced relaxation time of each polystyrene and the local segment density in various solutions at the θ temperature. Here, we used solvents with a viscosity less than 1 cP at 20 °C except for diethyl succinate (θ solvent for P*p*MS, 2.93 cP at 20 °C), and we could evaluate the change of the local chain motion effected by the difference of chain expansion. Second, we examined the relationship between the activation energy and the local segment density for each polymer chain in various solutions. Finally, we compared the local motions of three polymers, i.e., PS, PαMS, and P*p*MS, which have almost the same tacticity and obtained information on the relation between the local motion and the chemical structure of a polymer chain.

Experimental Section

Preparation of Samples. Anthracene-labeled PS, PαMS, and P*p*MS were used for fluorescence depolarization measurement. All were prepared by anionic polymerization initiated by *n*-butyllithium, and the living ends were deactivated by 9,10-bis(bromomethyl)anthracene (Figure 1).[19] Here, we describe only the synthesis of the anthracene-labeled P*p*MS in detail. First, the initiation of anionic polymerization was started by *n*-butyllithium in THF at −78 °C. The polymerization reaction was executed at −78 °C until all monomers were exhausted. Then a small amount of the coupling reagent 9,10-bis(bromomethyl)-anthracene dissolved in THF was added to the reaction vessel, and the solution was stirred for ca. 5 h at −78 °C. The synthesized polymer was purified by reprecipitation from benzene in methanol.

We fractionated the polymers by GPC, and the polymer fraction labeled in the middle of the main chain was collected.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

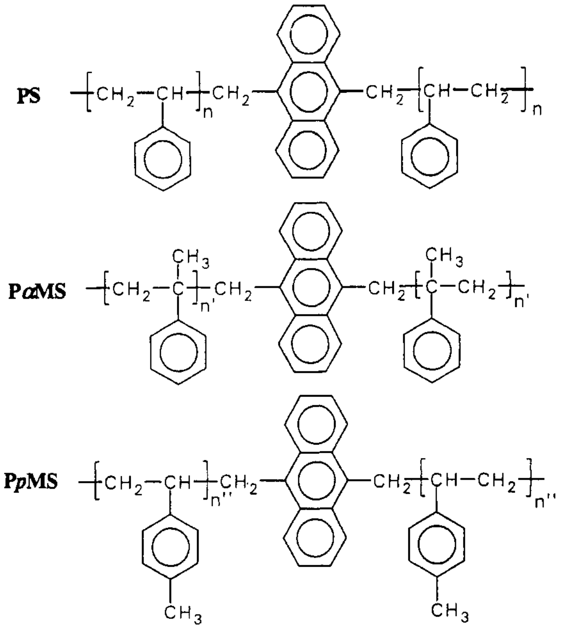


Figure 1. Samples labeled by anthracene in the middle of the polymer chain.

Table 1. Molecular Weights, Polydispersities, and Racemo Fractions of Labeled Polymers

	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	f_r
PS	9.2	9.7	1.05	0.54
PαMS	20.5	21.5	1.05	0.67
PpMS	27.5	28.5	1.03	0.69

Table 2. Solvent Viscosities at 20 °C and Activation Energies and Chain Expansions at 34.5 (PS, PαMS) and 16.4 °C (PpMS)

		E_η	$\bar{\alpha}_\eta^3$		
solvent	η (cP)	(kcal/mol)	PS	PαMS	PpMS
CH	0.979	2.9	1.00	1.00	1.23
MEK	0.402	1.7	1.11		1.01
EA	0.447	1.7	1.12		
BA	0.740	2.4	1.26		1.22
BZ	0.652	2.5	1.66	2.25	1.61
TO	0.587	2.1	1.64	2.25	1.63
EB	0.678	2.2	1.64	2.25	
DES	2.93	3.8			1.00

Table 1 shows the characterization of the three kinds of polymers. The molecular weights and tacticities were determined by GPC and ^{13}C-NMR, respectively.

Solvents. We used eight kinds of solvents for measurements, i.e., cyclohexane (CH, Nacalai Tesque, spectrophotometric grade (S)), methyl ethyl ketone (MEK, Nacalai Tesque, guaranteed reagent), ethyl acetate (EA, Nacalai Tesque, S), butyl acetate (BA, Nacalai Tesque, S), benzene (BZ, Nacalai Tesque, S), toluene (TO, Dojin, S), ethylbenzene (EB, Waken, S), and diethyl succinate (DES, Aldrich). MEK and DES were distilled before measurements, and the other solvents were used as received. Solvent viscosities and their activation energies were as reported in ref 20 (Table 2). Only DES is a high-viscosity solvent with a viscosity of ca. 3 cP, whereas the others are low-viscosity solvents with viscosities below 1 cP.

Intrinsic Viscosity Measurements. The intrinsic viscosity of the polymer solution at the θ temperature was measured by capillary viscometry. We evaluated the chain expansion parameter $\bar{\alpha}_\eta^3$, which is the ratio of the intrinsic viscosity of a sample solution to the intrinsic viscosity at the θ condition. We used cyclohexane as the θ solvent for PS and PαMS, and the θ temperature for both polymers was 34.5 °C. The θ solvent for PpMS was DES and the θ temperature was 16.4 °C.[21] Table 2 shows these values of $\bar{\alpha}_\eta^3$.

The molecular weights of the polymers, PαMS and PpMS, used for viscometry were different from those of the ones labeled with anthracene for the fluorescence depolarization measurement. The values of the intrinsic viscosity for PαMS were converted to the values for PαMS with M_w = 215K by using the relation $[\eta] = KM^a$,[20] and Table 2 shows the values for PpMS (M_w = 50K) without the correction.

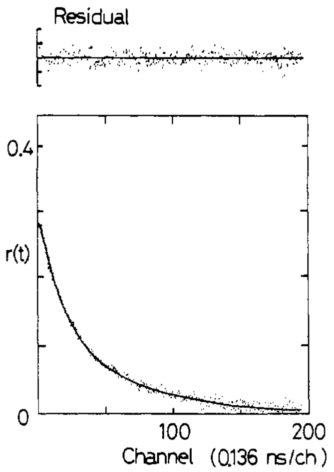


Figure 2. Decay of anisotropy ratio measured (···) and its fitting curve by the method of nonlinear least squares (—). These data are for PpMS in cyclohexane at 31.5 °C.

For the measurement of the intrinsic viscosity, we used commercial standard polymers obtained from Scientific Polymer Products, Inc., and the M_w's of the PS, PαMS, and PpMS samples were 110K, 375K, and 50K, respectively. The polydispersities (M_w/M_n) of these samples were 1.04, 1.20, and 1.05, respectively.

Fluorescence Depolarization Measurement and Analysis of Anisotropy Ratio. We measured the time-resolved fluorescence anisotropy ratio of the polymer in the same way as described previously.[22] The chromophore concentration of all polymer solutions was kept less than 10^{-5} M—i.e., the polymer concentration of all samples was kept less than 3×10^{-3} g/cm^3,—and the samples were degassed.

The measurements were performed with a single-photon-counting system which consisted of a time-to-amplitude converter (TAC, Ortec Model 457), a discriminator (Ortec Model 436), a constant fraction discriminator (Ortec Model 583), and a multichannel analyzer (Norland Ino-Tech 5300). We used the single-photon-counting system in the so-called inverse mode—that is, the start signal and the stop signal in the TAC were reversed. A PLP-01 diode laser (Hamamatsu Photonics, wavelength 411 nm) was used as a light source, and the repetition rate was 1 MHz. The detector was a microchannel plate-photomultiplier tube (MCP). The observation of emissions was through V-42 and Y-44 filters (HOYA). The fwhm of the total instrumental function was ca. 300 ps. For analysis of the anisotropy ratio $r(t)$, we first convoluted empirical eq 1 with the instrumental function, and then fitted this curve to the experimental data by the method of nonlinear least squares.[23] Figure 2 shows a fitting example of $r(t)$ with eq 1.

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

The mean relaxation time T_m is defined by eq 2, and it was calculated by eq 3. The experimental error was within ±5% for all T_ms.

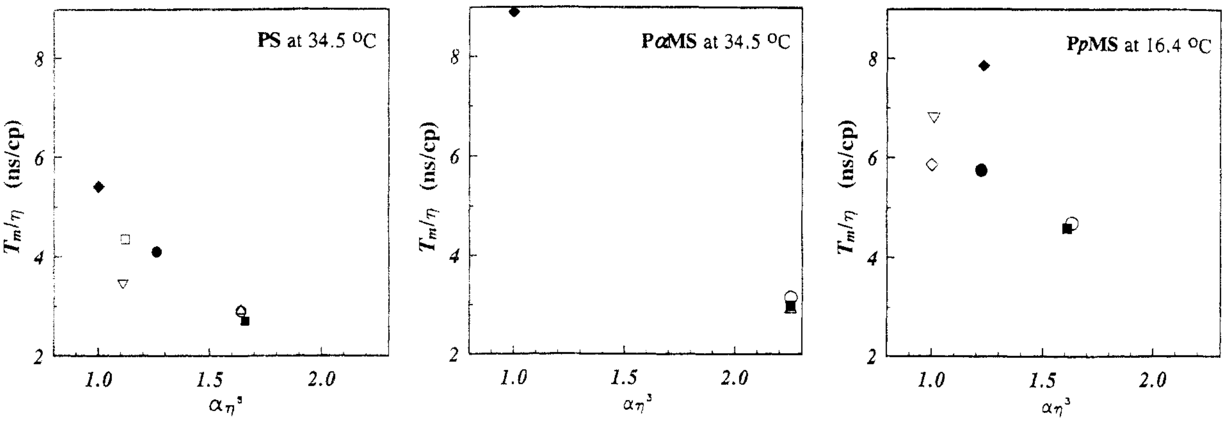
$$T_m = r_0^{-1}\int_0^\infty r(t)\,dt \qquad (2)$$

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

We evaluated the apparent activation energy of local motion E^* by the theory of Kramers' diffusion limit[1,24] in the same way as reported previously.[22] Equation 4 was used to evaluate the apparent activation energy.

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

where R is the gas constant, T is the absolute temperature, and η is the solvent viscosity.



(a) (b) (c)

Figure 3. Plots of reduced relaxation time T_m/η vs $\bar{\alpha}_\eta^3$ for (a) PS solution, (b) PαMS solution, and (c) PpMS solution: (◆) cyclohexane; (▽) MEK; (□) ethyl acetate; (●) butyl acetate; (■) benzene; (○) toluene; (△) ethylbenzene; (◇) DES.

Solvent viscosity is represented by eq 5

$$\eta = \eta_0 \exp(E_\eta/RT) \qquad (5)$$

where E_η is the activation energy of the solvent viscosity. Furthermore, we can modify eq 4 into eq 6.

$$T_m = A\eta_0 \exp\{(E^* + E_\eta)/RT\} \qquad (6)$$

We make the plot of $\ln(T_m)$ against $1/T$, and the slope gives $(E^* + E\eta)$. Then the value of E^* can be obtained by subtracting E_η from $(E^* + E_\eta)$. The experimental error of E^* was within ±0.3 kcal mol^{-1}.

Results and Discussion

Relaxation Time. Figure 3a shows the relationship between the reduced relaxation time, T_m/η, and the chain expansion factor, $\bar{\alpha}_\eta^3$, for PS at 34.5 °C, which is the θ temperature for PS in cyclohexane. The reduced relaxation time in the θ solvent was the largest among all PS solutions, and the local motion became faster, i.e., T_m/η became shorter, as the solvent quality became good. Figure 3b shows the relationship between T_m/η and α_η^3 for PαMS at 34.5 °C, which is also the θ temperature for PαMS in cyclohexane. As Figure 3b shows, we could use only four kinds of solvents for PαMS, because PαMS does not dissolve in such solvents as ethyl acetate or butyl acetate, and we could not find other appropriate solvents. The value of T_m/η in the θ solvent was also the largest among the PαMS solutions. Figure 3c shows the relationship between T_m/η and $\bar{\alpha}_\eta^3$ for PpMS at 16.4 °C, which is the θ temperature for PpMS in DES. The value of T_m/η in the DES solvent was not the largest. This is because DES has a rather high viscosity, i.e., ca. 3 cP at 20 °C, and in such high-viscosity solvents the reduced relaxation time becomes smaller than that in low-viscosity solvents.[22] The polymer chain in a good solvent moved faster than that in a poor solvent for all the polymers examined.

The local conformational transition was considered to depend on the local segment density of the polymer chain through the excluded volume effect. As the solvent quality changes from poor to good, the polymer chain in the solution becomes more expanded, and the local segment density of the polymer chain becomes smaller.[25,26] Ediger et al.[15,16,27] calculated the local segment density about the center segment for a polyisoprene chain in a good solvent and in a θ solvent. They emphasized that the center segment investigated is different from the center of mass of the chain. They reported that the largest change in local dynamics with solvent quality occurs for a high molecular weight polymer. According to their calculation, for a polymer with M_w = 100K, the local segment density in a θ solvent is 3 times that in a good solvent. They considered that their calculated result is valid qualitatively, not quantitatively.

In a good solvent, the polymer chain interacts with solvent molecules more strongly than with the segments of a polymer chain itself—i.e., it is free-draining. The local motion of the conformational transition of a polymer chain has a smaller resistance, and the relaxation time becomes shorter in a good solvent than in a poor solvent. The conformational transition of a polymer chain strongly depended on the segment density for all the polymers examined.

Activation Energy. Figure 4a shows plots of $\ln(T_m/\eta)$ vs $1/T$ for each PS solution. In a cyclohexane solution[28] a line has an inflection point at ca. 20 °C, which is ca. 10 °C below the θ temperature. This seems to be due to the microscopic aggregation of PS. Parts b and c of Figure 4 show plots of $\ln(T_m/\eta)$ vs $1/T$ for PαMS and PpMS solutions, respectively. For PαMS in a cyclohexane solution, the inflection point was also observed as in the case of PS. Table 3 summarizes the activation energy.

For PS and PαMS solutions, the value of E^* was largest in a θ solvent above the θ temperature and became smaller with improvement of the solvent quality. These findings can be explained by the fact that the segment density becomes higher as the solvent quality becomes poorer. For example, the value of E^* in the PS/CH solution was 2.6 kcal mol^{-1} and it decreased to ca. 1.3 kcal mol^{-1} in good solvents. In the case of PpMS solutions, E^* in the θ solvent DES was small, and E^* in CH, which is a better solvent than DES, was larger, 2.8 kcal mol^{-1}. This is because DES has a rather high viscosity, 3 cP, and the activation energy of the solvent viscosity E_η is larger than that of the effective viscosity; then the value of E^* in high-viscosity solvents becomes smaller than the true activation energy.[22]

Parts a–c of Figure 5 show the relationship between E^* and $\bar{\alpha}_\eta^3$ for PS at 34.5 °C, PαMS at 34.5 °C, and PpMS at 16.4 °C, respectively. The value of the intrinsic viscosity changes most steeply near the θ temperature.[29] The temperature dependence of the intrinsic viscosity increases as the solvent quality becomes poor, but in a good solvent, there is less change in the expansion of the polymer chain with the change of temperature.[30,31] This explains why the activation energy becomes smaller with the improvement of the solvent quality. That is, in a θ solvent and in poor solvents, the temperature dependence of the segment density becomes larger, so that the change of relaxation time with the change of temperature becomes

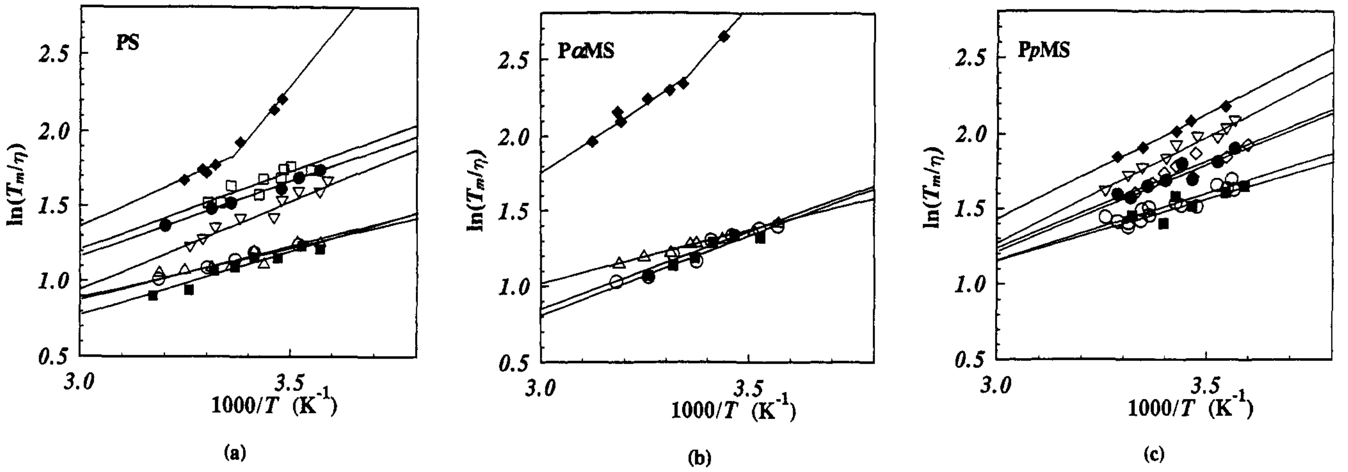


Figure 4. Plots of $\ln(T_m/\eta)$ vs $1/T$ for (a) PS solution, (b) PαMS solution, and (c) PpMS solution. Symbols are the same as in Figure 3.

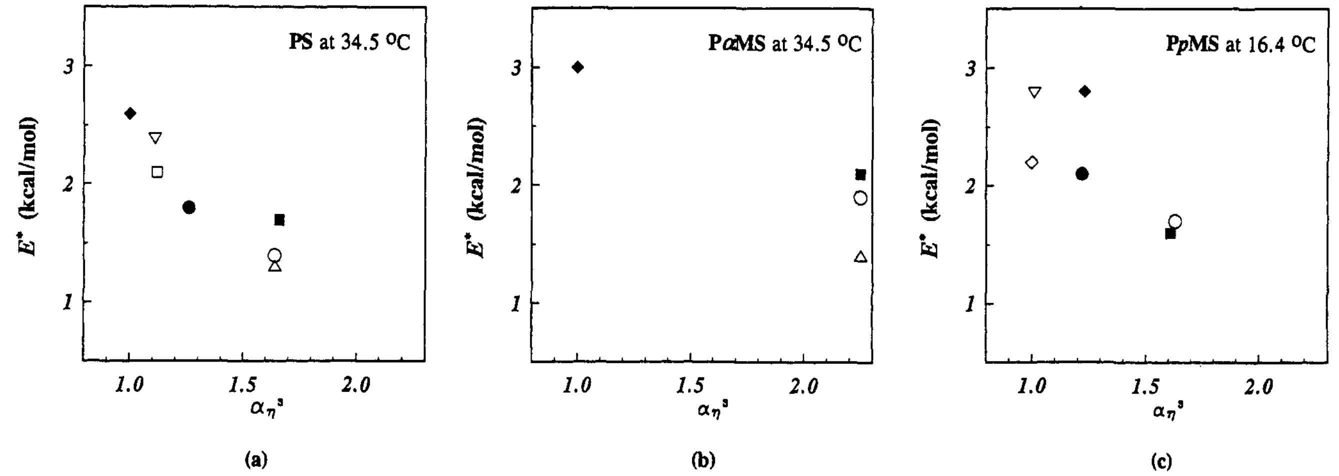


Figure 5. Plots of the activation energy E^* vs $\bar{\alpha}_\eta^3$ for (a) PS solution, (b) PαMS solution, and (c) PpMS solution. Symbols are the same as in Figure 3.

Table 3. Activation Energies E^* (kcal mol^{-1}) for PS, PαMS, and PpMS Solutions

solvent	PS	PαMS	PpMS
CH	2.6	3.0	2.8
MEK	2.4		2.8
EA	2.1		
BA	1.8		2.1
BZ	1.7	2.1	1.6
TO	1.4	1.9	1.7
EB	1.3	1.4	
DES			2.2

larger, and E^* also becomes larger. Therefore the relaxation time and the activation energy also depend on the segment density of the polymer chain.

Waldow et al.[16] reported the activation energies for PS solutions measured by the method of fluorescence depolarization. They used anthracene-labeled PS with M_w = 68K as a polymer sample. For example, the activation energy for cyclohexane solution was 5 ± 0.5 kcal mol^{-1} and that for MEK solution was 1.9 ± 0.5 kcal mol^{-1}. The value of E^* for cyclohexane solution they reported is 2 times higher than the value we obtained. This discrepancy is probably due to the difference of the temperature range used; i.e., they used a lower temperature for measurement than we did. On the other hand, the value of E^* for the MEK solution we obtained was similar to the value they reported. The activation energies for other solutions reported by Waldow et al. cannot be compared with those we obtained, because they used solvents with viscosities above 3 cP at 20 °C. Waldow et al. evaluated E^* in high-viscosity solvents by using E_η as the contribution of the temperature dependence of the solvent friction. In high-viscosity solvents the hydrodynamic friction between the polymer chain and the solvent molecules cannot be represented by the solvent viscosity. In other words, the *effective* solvent viscosity which governs the polymer local motion is smaller than the solvent viscosity η itself, and the temperature dependence of the effective solvent viscosity is also smaller than that of η. When the effective solvent viscosity is overestimated by using η, the obtained reduced relaxation time becomes smaller than the true value of T_m/η. The temperature dependence of the effective viscosity in a high-viscosity solvent is also smaller than the temperature dependence of the solvent viscosity η, i.e., E_η.[22] Therefore we used solvents with a viscosity below 1 cP except for DES (Table 2).

Mashimo reported[9] the activation energies measured by the method of dielectric relaxation for poly(*p*-chlorostyrene) in ethylbenzene and toluene. These values were 2.9 and 2.8 kcal mol^{-1} and higher than the value we obtained for PpMS in toluene, 1.7 kcal mol^{-1}. Gronski et al.[32,33] reported the activation energy measured by ^{13}C-NMR for PS in toluene. They used a model based on local jumps with two correlation times ρ and θ, in which ρ is the correlation time characterizing the conformational jumps. They derived the activation energy from a plot of ρ against $1/T$, and the value was 2.5 kcal mol^{-1}. This value is also higher than the value we obtained, 1.4 kcal mol^{-1}. We consider that the values of E^* depend on the time range used for each technique;[32] i.e., the difference among the values of E^* depends on the difference in the motional modes obtained by these methods.

Comparison of Local Motions between PS, PαMS, and P*p*MS. Next, we discuss the effect of the molecular structure on the local motion of a polymer chain. As described in a previous section, the local motion of a polymer chain is affected by the segment density. Therefore, if we compare the local dynamics among different polymers, we must compare the relaxation times in the unperturbed condition, in which there is no excluded volume effect. We compared the T_m for PS with that for PαMS in a θ solvent, cyclohexane. The value of T_m for PαMS was longer than that for PS in the range of measurement (Figure 4a,b). The value of E^* for PαMS was also higher than that for PS (Table 3). The longer relaxation time and higher activation energy for PαMS may be due to the fact that PαMS has a methyl group substituted at the α-position in the main chain. Disubstitution of a polymer chain makes the barrier height of the local motion higher than that for monosubstitution.[34]

The value of T_m for PS and that for P*p*MS cannot be compared directly in each θ solvent because the θ solvent DES for P*p*MS has a high viscosity. Therefore, we compared the relaxation times in MEK, which is a poor solvent near the θ solvent for both PS and P*p*MS. In MEK, the relaxation time of the local motion is slightly shorter than those in other solvents with a similar segment density. This is because the relaxation time for a polymer chain depends on not only the segment density but also the solvent characteristic, i.e., solvation between a polymer chain and solvent molecules. However, it does not matter for the relative comparison of the relaxation times in MEK between PS and P*p*MS, because the strength of solvation is similar for the two polymers. The T_m for P*p*MS was larger than that for PS, and E^* for P*p*MS was also larger than that for PS. Since the methyl group at the para position makes the hydrodynamic volume larger, the relaxation time becomes long, and the activation energy is high.

Lauprêtre et al.[35,36] reported the dynamics of monosubstituted polystyrene in 10% (w/w) solutions studied by ^{13}C-NMR. The spin-lattice relaxation time T_1 of PS and P*p*MS in $CDCl_3$ solutions at 30 °C studied with 25 MHz ^{13}C-NMR was 0.046 s for $-CH_2-$ of P*p*MS, 0.049 s for $-CH_2-$ of PS, 0.078 s for $-CH-$ of P*p*MS, and 0.089 s for $-CH-$ of PS. The mean relaxation time T_m was proportional to the inverse of T_1, and the relaxation time of the P*p*MS main chain was longer than that of the PS main chain. The longer relaxation time for P*p*MS may be caused by the fact that the P*p*MS chain has the largest hydrodynamic volume owing to methyl group substitution at the para position.[37]

We cannot accurately compare the local chain dynamics between PαMS and P*p*MS in a proper poor solvent near the θ solvent. PαMS cannot be dissolved in the many solvents in which P*p*MS can be dissolved, and the solvents which dissolve both PαMS and P*p*MS have a high viscosity. However, E^* for PαMS in a θ solvent was larger than that for P*p*MS in MEK near the θ solvent as Figure 5 shows, and we conclude that a methyl group at the α-position makes the energy hindrance for chain rotation higher than that at the para position: $E^*(\mathrm{P\alpha MS}) > E^*(\mathrm{P}p\mathrm{MS})$.

Conclusion

We examined the local motion for PS, PαMS, and P*p*MS in a dilute solution by the fluorescence depolarization method. The fluorescent probe anthracene was labeled specifically in the middle of the main chain. For all three samples, the relaxation time of each polymer decreased with the expansion of the chain coil in a good solvent. The activation energy also decreased with the chain expansion. The conformational transition of the main chain strongly depended on the segment density.

We also compared the local motion between PS and PαMS and between PS and P*p*MS. A methyl group substituted at the α-position increased the steric hindrance for the chain rotation, thereby increasing the relaxation time and the barrier height, and the hydrodynamic volume of a methyl group substituted at the para position increased the relaxation time and the activation energy.

Acknowledgment. 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, 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.; Gobush, W.; Chikahisa, Y.; Carpenter, D. K. *Faraday Discuss. Chem. Soc.* **1970**, *49*, 182.
(4) Yoshizaki, T.; Fujii, M.; Yamakawa, H. *J. Chem. Phys.* **1985**, *82*, 1003.
(5) Higgins, J. S.; Maconnachie, A. *Methods of Experimental Physics*; Skold, K., Price, D. L., Eds.; Academic Press: New York, 1987; Vol. 23, Part C, p 287.
(6) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(7) Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47.
(8) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers*; Clarendon Press: Oxford, 1981; Chapter 9.
(9) Mashimo, S. *Macromolecules* **1976**, *9*, 91.
(10) Mashimo, S.; Winsor, P., IV; Cole, R. H.; Matsuo, K.; Stockmayer, W. H. *Macromolecules* **1986**, *19*, 682.
(11) Adachi, K. *Macromolecules* **1990**, *23*, 1816.
(12) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.
(13) Pecora, R., Ed. *Dynamic Light Scattering*; Plenum Press: New York, 1985.
(14) Sasaki, T.; Yamamoto, M. *Macromolecules* **1989**, *22*, 4009.
(15) Ediger, M. D. *Annu. Rev. Phys. Chem.* **1991**, *42*, 225.
(16) Waldow, D. A.; Ediger, M. D.; Yamaguchi, Y.; Matsushita, Y.; Noda, I. *Macromolecules* **1991**, *24*, 3147.
(17) Valeur, B.; Monnerie, L. *J. Polym. Sci., Polym. Phys Ed.* **1976**, *14*, 11.
(18) Sasaki, T.; Arisawa, H.; Yamamoto, M. *Polym. J.* **1991**, *23*, 103.
(19) Yokotsuka, S.; Okada, Y.; Tojo, Y.; Sasaki, T.; Yamamoto, M. *Polym. J.* **1991**, *23*, 95.
(20) *Kagaku Binran Kiso Hen*, 3rd ed.; The Chemical Society of Japan, Ed.; Maruzen: Tokyo, 1984; Vol. 2, Chapter 6.
(21) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.
(22) Ono, K.; Okada, Y.; Yokotsuka, S.; Ito, S.; Yamamoto, M. *Polym. J.* **1994**, *26*, 199.
(23) Sasaki, T.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 610.
(24) Kramers, H. A. *Physica* **1940**, *7*, 284.
(25) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(26) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.
(27) Waldow, D. A.; Johnson, B. S.; Hyde, P. D.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1989**, *22*, 1345.
(28) Bullock, A. T.; Cameron, G. G.; Smith, R. M. *J. Chem. Soc., Faraday Trans. 2* **1974**, *2*, 1202.
(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(30) (a) Fox, T. G., Jr.; Flory, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 1909. (b) *Ibid.* **1951**, *73*, 1915.
(31) Fox, T. G., Jr.; Flory, P. J. *J. Phys. Colloid Chem.* **1949**, *53*, 197.
(32) Friedrich, C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *Macromolecules* **1981**, *14*, 1119.
(33) Gronski, W.; Schafer, T.; Peter, R. *Polym. Bull.* **1979**, *1*, 319.
(34) Fujii, M.; Nagasaka, K.; Shimada, J.; Yamakawa, H. *Macromolecules* **1983**, *16*, 1613.
(35) Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2143.
(36) Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2127.
(37) Yoshizaki, T.; Yamakawa, H. *J. Chem. Phys.* **1984**, *81*, 982.