1134 *Macromolecules* **1999,** *32,* 1134−1139

Local Motion of Oligo- and Polystyrene Chain End Studied by the Fluorescence Depolarization Method

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Received September 15, 1998; Revised Manuscript Received December 4, 1998

ABSTRACT: Local motion of the oligo- and polystyrene chain end in dilute solution was examined by the fluorescence depolarization method. The molecular weight of the sample varied from 5.1×10^2 to 2.5×10^4. The relaxation time of local motion, T_m, in benzene solution increased with molecular weight and reached an asymptotic value at MW $= 2 \times 10^3$ with $T_m \cong 0.3$ ns. In ethyl acetate, which is a poorer solvent than benzene, T_m became constant at a higher molecular weight than in benzene, and the asymptotic relaxation time was longer than that in benzene. We proposed that the difference in the relaxation time and in its molecular weight dependence between the two solutions may result from the local potential for the conformational transition of the main chain bond, rather than the segment density. In comparison with the relaxation time for the polystyrene chain center, both the critical molecular weight and the asymptotic relaxation time for the chain end were about 1 order smaller than those for the chain center. This indicates that the mobility of a linear polymer chain end is sufficiently different from that of its chain center.

Introduction

Every linear polymer has two main chain ends. The chain end has a large effect on the physical and chemical properties of polymers. From the standpoint of polymer physics, it becomes more and more widely recognized that the chain end has important roles in both static and dynamic properties. Yamakawa has considered the possible effects of the chain end on the second and third virial coefficient and has shown semiquantitative agreement between theory and experiment.[1−3] There have been several ESR studies on polymer chain end mobility,[4,5,29−33] and obtained correlation times and activation energies for the chain end were compared with those for the chain center and the side chain.[29−32] Friedrich et al.[32] compared the mobility of the polystyrene chain end estimated by ESR with the results obtained by other techniques. Recently, Sakaguchi et al. have observed the molecular motion of polyethylene chain ends tethered to a surface of poly(tetrafluoroethylene) by the ESR method and assigned molecular motion modes on the basis of spectral simulations.[4,5,33] More generally, the dynamic properties of bulk polymer also depend sufficiently on the molecular weight due to the effect of the chain end.[6,7] For example, the glass transition temperature of a bulk polymer decreases as the molecular weight decreases due to larger free volume around a chain end compared with the middle segment. On the other hand, from the view of chemical reaction, the chain end is often the starting point of the succeeding reactions, e.g., polymerization with another monomer, coupling with a functional group, and tethering to a surface. In this case, information about the dynamics of the chain end is also important to control the molecular construction.

Although a study on the static or the dynamic properties with regard to the polymer chain end is no doubt important as mentioned above, it is difficult to pick up experimentally the information focused on the chain end effect. Nowadays experimental methods using spin or fluorescent probe techniques are powerful for such a purpose,[4,5,8−14] supposing that the sample labeled with a probe at a designated position can be obtained. We have examined the local chain dynamics of various polymers in dilute solution by the fluorescence depolarization method.[9−14] So far we have concentrated our attention on the center of the main chain. We have compared the local chain mobility between polymers, which differ in molecular structure[9,10,12] or stereoregularity.[14] Since the dynamic properties of polymer chains depend on the position of polymer chains, the information on the polymer chain end is indispensable. It is interesting to compare the chain mobility between the chain center and the chain end on the same linear polymer.

Waldow et al. have studied the molecular weight effect on the local motion of polyisoprene (PI) by the fluorescence depolarization method.[8] They explained the molecular weight independence of the relaxation times in a good solvent and the molecular weight dependence in a poor solvent by the segment density around the fluorescent probe. That is, the segment density in a good solvent is kept constant in the high molecular weight region due to the excluded-volume effect, while in a poor solvent the density increases with the molecular weight. Recently, we have examined the molecular weight effect on the local motion of the chain center of poly(oxyethylene) (POE)[12] and polystyrene.[13] For POE in a good solvent, the result was explained by the segment density according to Waldow et al. However, for polystyrene in both solvents, the relaxation time as well as the activation energy of the local motion increased with molecular weight below a MW of 10^4 and reached an asymptotic value. It was proposed that the relaxation time of local motion may be governed by the potential for the conformational transition of the main chain bond, rather than the segment density around the target of observation. It was also concluded that the critical molecular weight, at which the molecular weight dependence saturates, corresponds to the largest size of the local motion measured by the fluorescence depolarization method as discussed previously.[28]

10.1021/ma9814649 CCC: $18.00

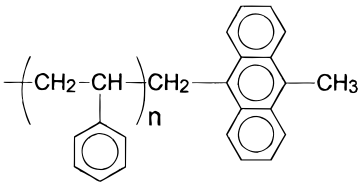

Figure 1. Molecular structure of oligo- and polystyrene labeled with anthryl group at the chain end.

Table 1. Characterization of End-Labeled Oligo- and Polystyrene Samples Used in This Study

sample	$M_n \times 10^3$	M_w/M_n	sample	$M_n \times 10^3$	M_w/M_n
DMA	0.206		eOS24	2.4	1.27
eOS5	0.51	1.03	eOS38	3.8	1.16
eOS6	0.60	1.01	eOS66	6.6	1.06
eOS12	1.18	1.11	ePS25	25.2	1.13

In the present study, we examined the local dynamics of the oligo- and polystyrene chain end in dilute solutions by the fluorescence depolarization method. Solvents are the same as in the previous study,[13] with benzene as a good solvent and ethyl acetate as a poor solvent. We examined the molecular weight effect on the local motion of the chain end of oligo- and polystyrene (PS). Moreover, we compared the relaxation times of the local motion for the chain center and for chain end. The size of the local motion which contributes to the fluorescence depolarization was estimated and compared with that of the chain center. Finally, we compared the molecular weight dependence of the local motion of the styrene chain end with that of the PS chain center.

Experimental Section

Sample Preparation. Oligo- and polystyrene samples labeled with the anthryl group at the chain end were synthesized by the living anionic polymerization in vacuo initiated by butyllithium and by termination of the living ends with 9-bromomethyl-10-methylanthracene. The polymerization was carried out in benzene that was dried over sodium in vacuo. The styrene monomer (Nacalai Tesque) was dried over fresh calcium hydride after distillation. For the polymerization of oligostyrenes, the benzene solution of butyllithium was first frozen. The styrene monomer was added to the frozen solution, and the temperature of the mixture was gradually raised to slightly above the freezing point of the solution, ca. 7 °C, with occasional stirring. The retardation of the initiation reaction leads to broadening of the molecular weight distribution. In the case of polystyrene, styrene monomer was added to the benzene solution of butyllithium at ca. 7 °C with constant stirring. Then the termination reaction was carried out at ca. 5 °C. Detailed procedures were the same as described elsewhere.[15] The product polymer was purified by reprecipitation from benzene in methanol. Then the polymer was fractionated into several parts so that each part had a narrow molecular weight distribution. The weight-average molecular weight M_w and the number-average molecular weight M_n of fractionated PS were determined by GPC. The molecular structure and the characterization of PS samples used in this study are shown in Table 1 and Figure 1, respectively. The molecular weight varies from ca. 5.1×10^2 to 2.5×10^4.

Solvents used in measurement were benzene (Dojin, spectrophotometric grade) and ethyl acetate (Nacalai Tesque, spectrosol). Both of them were used without further purification. The quality of these solvents for polystyrene was obtained by the intrinsic viscosity measurement in an earlier study.[9] Benzene ($\overline{\alpha_\eta}^3 = 1.66$) is better than ethyl acetate ($\overline{\alpha_\eta}^3 = 1.12$). In preparing the sample solution, each polymer concentration was kept less than 10^{-5} M. Each solution was put into a quartz cell and degassed.

Anisotropy Decay Measurement. The measurement of time-resolved anisotropy decay was carried out by the single photon counting system. The apparatus was the same as that used in the previous study.[12,13] The second harmonic of Ti:sapphire laser was used as a light source. The excitation light was vertically polarized, and the parallel and perpendicular fluorescence components to the plane of the excitation light were measured by a microchannel plate−photomultiplier tube. The time-resolved fluorescence intensity was analyzed by a multichannel analyzer. The fwhm of the total instrumental function was ca. 60 ps. The parallel component, $I_{VV}(t)$, and the perpendicular component, $I_{VH}(t)$, were measured alternately to avoid data distortions due to time drift. Anisotropy decay measurements were carried out in the temperature range from 10 to 30 °C.

Data Analysis. The fluorescence anisotropy ratio, $r(t)$, is defined as

$$r(t) = (I_{VV}(t) - GI_{VH}(t))/(I_{VV}(t) + 2GI_{VH}(t)) \qquad (1)$$

where G is the compensating factor. We estimated G to be unity in this study. The local motion which contributes to the rotational relaxation of the fluorescence probe consists of various motional modes; i.e., $r(t)$ can be represented by a polynomial sum of exponential-type decay functions. We examined how many exponential terms are required and empirically concluded that the double-exponential-type function, eq 2, represents the anisotropy decay quite well.[9−14]

$$r(t) = r_0[x \exp(-t/T_1) + (1 - x) \exp(-t/T_2)] \qquad (2)$$

Concerning the local polymer chain motion, many theoretical orientational autocorrelation functions based on different models have been proposed.[34,35] It was revealed that for the local motion of PMMA the discrete models including the Hall−Helfand (H−H) model show a good agreement with the experimental results, especially in a high-viscosity solvent.[35,36] In the H−H model, it is assumed that two processes of the conformational transitions contribute to the local chain motion, i.e., an isolated mode and a cooperative mode.[34] However, in the recent studies of local chain dynamics, conformational transitions are not necessarily responsible for the decay of the orientational correlation functions.[37−39] Moro considers both conformational transition and “coupled librations” to be important in the polymer dynamics.[37] “Libration” is a small-amplitude motion which occurs within a given torsional potential well. In Moro's theory, librational motions contribute substantially to the rotor correlation function. MD computer simulations performed by Ediger and co-workers also show that librational motions are responsible for the vector reorientation.[38,39] To our knowledge, there is no specific model that successfully describes such a local motion. Hence, we choose empirical analysis for fluorescence anisotropy decay data instead of adopting any specific models.

The function in which eq 2 was convoluted with the instrumental function was fitted to eq 1. For discussion about the chain mobility, we used the mean relaxation time, T_m, which is defined as eq 3 and can be calculated by eq 4 with best-fit parameters T_1, T_2, and x.

$$T_m = r_0^{-1} \int_0^\infty r(t)\, dt \qquad (3)$$

$$= xT_1 + (1 - x)T_2 \qquad (4)$$

Results and Discussion

Relaxation Time. Figure 2 shows the temperature dependence of the relaxation time for oligo- and polystyrene in benzene. The logarithm of the relaxation time reduced by the solvent viscosity, $\ln(T_m/\eta)$, was plotted against $1/T$ according to the theory of Kramers’ diffusion limit. We see from Figure 2 that the values of $\ln(T_m/\eta)$ for eOS5 and eOS6 are sufficiently lower than those for

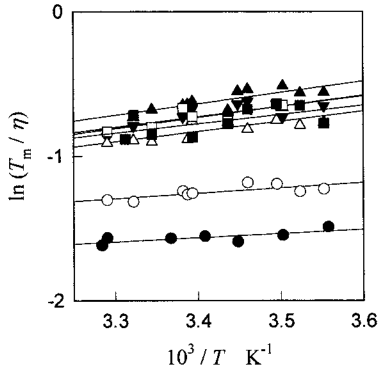

Figure 2. Arrhenius plot of T_m/η according to the theory of Kramers' diffusion limit. T_m was measured in benzene: (●) eOS5, (○) eOS6, (■) eOS12, (□) eOS24, (▲) eOS38, (△) eOS66, (▼) ePS25. Solvent viscosity at each temperature was estimated from the reported value in the literature.

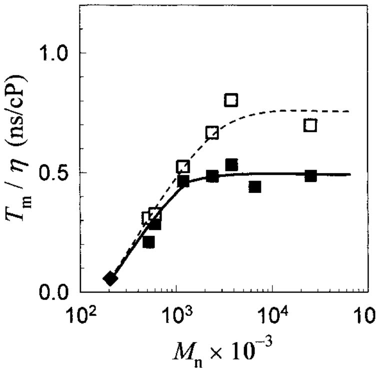

Figure 3. Molecular weight dependence of the relaxation time T_m/η at 20 °C in benzene (■) and in ethyl acetate (□). (◆) represents the rotational relaxation time for DMA, the probe molecule. The relaxation time was reduced by the solvent viscosity.

the other samples. It is also clearly observed that the value and its temperature dependence for the higher molecular weight samples are the same within the experimental error. These facts indicate that the relaxation time increases with molecular weight and reaches an asymptotic value in the oligomer region.

Figure 3 shows the relationship between T_m/η and MW at 20 °C. T_m/η at 20 °C was evaluated from the least-squares fitting for the plot in Figure 2. In Figure 3, we also show the relaxation times in ethyl acetate; they were evaluated in the same way as those for benzene solution. The filled diamond in Figure 3 indicates the reduced rotational relaxation time of the model compound, 9,10-dimethylanthracene (DMA), in benzene at 20 °C estimated by the steady state. The relaxation time of DMA can be treated as the limiting value of low molecular weight oligostyrene. The solvent viscosities at 20 °C are 0.65 cP for benzene and 0.45 cP for ethyl acetate.[18] The influence of the solvent viscosity on the local motion is discussed in the following subsection of the activation energy. T_m/η in benzene increases with molecular weight and reaches an asymptotic value at about MW = 2×10^3, with the asymptotic value of $T_m \cong 0.3$ ns. The local motion of oligo- and polystyrene chain end in benzene had a relaxation time on the order of subnanoseconds that saturates in the oligomer region. This indicates that the local motion of the oligostyrene chain end in benzene measured by the fluorescence depolarization method reflects the entire end-to-end rotational motion to some extent in MW < 2×10^3, while the local motion is independent of the overall motion in MW > 2×10^3. In other words, the local motion of the oligostyrene chain end in benzene consists of 20 monomers or less. The relaxation time for ethyl acetate solution similarly increases with molecular weight and reaches an asymptotic value at MW $\cong 4 \times 10^3$. The asymptotic T_m/η in ethyl acetate is larger than that in benzene. We also see from Figure 3 that the critical molecular weight, M_c, at which the relaxation time reaches its asymptotic value, is somewhat larger in ethyl acetate than in benzene.

As mentioned in the Introduction, concerning the local motion of PI and POE, the molecular weight dependence was explained by the concept of segment density.[8,12] That is, the relaxation time in a good solvent with a molecular weight in the high molecular weight region was constant because the segment density is kept constant in the high molecular weight region due to the excluded-volume effect. To the contrary, for the polystyrene chain center, the relaxation time became constant irrespective of the change of molecular weight even in a poor solvent.[13] Thus, we proposed the local potential for the conformational transition of the main chain bond as the cause instead of the concept of the segment.

Abe et al. have studied the excluded-volume effects on the mean-square radius of gyration $\langle S^2 \rangle$ and on the intrinsic viscosity $[\eta]$ for oligo- and polystyrenes in dilute solutions.[1,16,17] They showed that the data of both $\langle S^2 \rangle$ and $[\eta]$ in toluene, a good solvent, at 15 °C are in good agreement with those in cyclohexane at Θ for the weight-average degree of polymerization $x_w < 20$. This agreement implies that the dimensions and conformations of the polystyrene chain may be considered the same under the two solvent conditions and may be in the unperturbed state. In this way, oligostyrene in MW < 2×10^3 is free from the intramolecular excluded-volume effect, and so the concept of segment density is not applicable. We can see from Figure 3 that the relaxation time for the oligostyrene chain end in each solvent reaches its asymptotic value in such a low molecular weight region. Moreover, the value of T_m/η for ethyl acetate solution is larger than that for the benzene solution over the whole measured molecular weight range. These facts obviously indicate that the local motion of the oligo- and polystyrene chain end is independent of the segment density but that there is something local that causes the difference between the two solvents. According to the case of the PS chain center, we proposed that the local potential energy for conformational transition of the main chain bond affects the local motion of the PS chain end. Although our scheme seems to be inconsistent with Abe's results that the dimensions and conformations are the same under the two solvent conditions in $x_w < 20$, the effect of the potential energy on the dynamic properties is different from that on the static one. That is, the dynamic property is influenced by both the value of energy potential minimum and the energy barrier height, while the static property is influenced by the former. Moreover, the unperturbed chain dimension is not independent of solvent and temperature. In our case, it is possible that the chain dimension is slightly different between the two solvents. To our knowledge the relationship between the local potential energy and solvent effect for C−C bond rotation so far has not been understood, and this is a future problem to be solved.

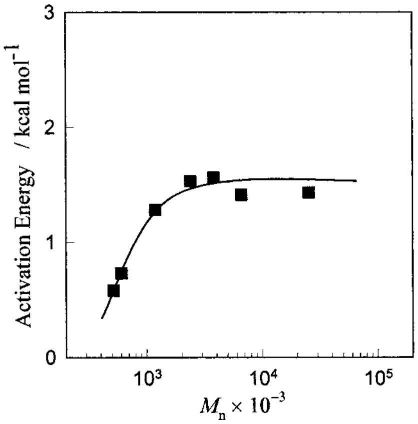

Figure 4. Molecular weight dependence of the activation energy for benzene solution evaluated from the temperature dependence of the relaxation time according to the theory of Kramers' diffusion limit.

Here we comment on the components of eq 2. Although both T_1 and T_2 increase with molecular weight, the increase of T_1 was larger than that of T_2, and its fraction x did not change in one direction with molecular weight. Then the average relaxation time T_m was determined by the longer component T_1 with x. As stated in data analysis, T_1 and T_2 merely represent the various motional modes and are not identified with any specific mode. We mean for example that it is not appropriate to consider that T_1 is identified with the entire rotation and T_2 represents the local motion. We suppose that the distribution of the relaxation time extends to a longer region with molecular weight, and the representative components become longer. That is, T_1 includes the contribution of the entire rotation to some extent below M_c, while both T_1 and T_2 represent the local motional modes above M_c.

Activation Energy. We evaluated the activation energy of the local motion of the oligo- and polystyrene chain end in benzene from the slope of the plot in Figure 2 according to the theory of Kramers' diffusion limit as follows. The velocity coefficient, k, of a particle with a frictional coefficient, ζ, passing over an energy barrier of the height E is represented as

$$k \propto \zeta^{-1} \exp(-E/RT) \tag{5}$$

where R is the gas constant and T is the absolute temperature. The fact that T_m is proportional to the reciprocal of k and the solvent viscosity, η, is proportional to ζ, according to Stokes' law, leads to

$$T_m/\eta = A \exp(E^*/RT) \tag{6}$$

Thus, the activation energies were estimated from the slope of the plot in Figure 2. The solvent viscosity was estimated from the value reported in the literature.[18]

Figure 4 shows the relationship between the molecular weight and the estimated activation energy in benzene solution. The activation energy as well as the relaxation time tends to increase with molecular weight and to become constant near MW = 2×10^3 with $E^* =$ ca. 1.5 kcal/mol. The fact that the activation energy is constant in MW > 2×10^3 implies that the mode of the measured local motion is the same, i.e., independent of the molecular weight in this region. That is, the local motion of the oligo- and polystyrene chain end consists of 20 monomers or less as stated in the discussion for relaxation time.

We have discussed the solvent viscosity dependence of the relaxation time previously, i.e., whether the Kramers' theory can be applied to the measured local motion or not. In Kramers' theory the correlation time of the motion of the solvent particles is thought to be much shorter than that of the solute (polymer chain) so that the assumption of white noise holds and the local chain dynamics linearly depends on the zero-frequency shear viscosity of the solvent. When the frequency of the solute at the barrier is quite high, effective friction is smaller than the zero-frequency shear viscosity of the solvent. That is, in such a case the effect of solvent viscosity is overestimated by Kramers' theory, and the activation energy is underestimated. Through some theoretical and experimental studies several groups have proposed a power law dependence on the solvent viscosity with a power, α, of less than unity,[19-24] namely

$$T_m \propto \eta^{\alpha} \exp(E^*/RT) \tag{7}$$

The power law dependence of the local dynamics on solvent viscosity results from the breakdown of the white noise assumption, so that α becomes small as the chain mobility becomes high. However, the fact that the value of α should change with the chain mobility and solvent quality makes the estimation of α quite complicated. So far, we concluded that as long as we examine the local motion of the polymer chain center, like polystyrene,[9,10,13] poly(methyl methacrylate),[11,14] and POE,[12] in low-viscosity solvents below 1 cP, the evaluation of activation energy with Kramers' theory is appropriate. In the case of POE,[12] we estimated the activation energy from the temperature dependence of the relaxation time of around 0.3 ns in a solvent with a viscosity of ca. 1 cP. In this study, the relaxation time for oligo- and polystyrene is ca. 0.3 ns, and the solvent viscosity of benzene is 0.45 cP. That is, it is reasonable to assume that the local motion of the oligo- and polystyrene chain end in benzene meets the requirement of Kramers' theory that the correlation time of the motion of the solvent particles is much shorter than that of the solute (polymer chain).

Comparison with Chain Center. Next, we will compare the local motion of the oligo- and polystyrene chain end in benzene with that of the polystyrene chain center. Figure 5 shows the relationship between the relaxation time as well as the activation energy and the molecular weight both for the chain end and for the chain center. The values for polystyrene chain center in benzene were quoted from our previous study.[13] From Figure 5, we clearly see that the asymptotic relaxation time for the chain end is markedly shorter than that for the chain center. That is, the chain mobility of the chain end is much larger than that of the chain center. We believe that this result simply reflects the difference of the position along the main chain. At the chain end, the main chain extends in one direction from the fluorescent probe, anthryl group, as shown in Figure 1, whereas at the chain center, the main chain extends in both directions of the probe. For the main chain motion, the neighboring bonds need to delocalize the distortion caused by a certain conformational transition.[25,26] Therefore, for the chain center, the rotational relaxation of a fluorescent probe will be more efficiently suppressed.

The difference in the chain mobility between the chain end and the chain center also appears at the critical

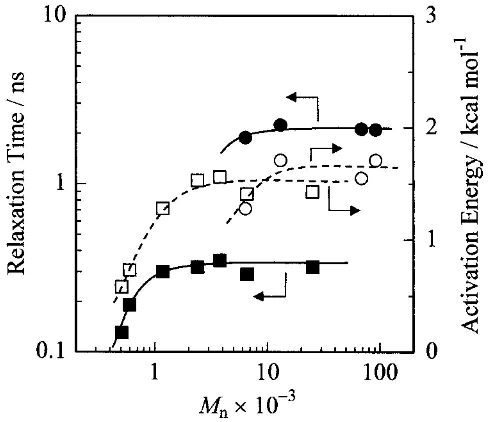

Figure 5. Comparison of the molecular weight dependence of the relaxation time and of the activation energy between the oligo- and polystyrene chain end and chain center in benzene. Filled symbols represent the relaxation time and unfilled symbols represent the activation energy. (■) and (□) are for the chain end, while (●) and (○) are for the chain center.

molecular weight, at which the relaxation time or the activation energy reaches its asymptotic value. Figure 5 shows that the critical molecular weight for the chain end (MW $\cong 2 \times 10^3$) is much smaller than that for the chain center (MW $\cong 10^4$). At the chain end, the rotational relaxation of the fluorescent probe can be realized by the small-scale local motion of an attached main chain due to the high chain mobility. In other words, the chain end is sufficiently flexible, and the contribution of the entire rotation that corresponds to the critical molecular weight becomes negligible for the rotational relaxation of the probe.

Here, we turn our attention to the activation energy. In Figure 5, we see that the asymptotic value of the activation energy for the chain end ($E^* \cong 1.5$ kcal/mol) is smaller than that for the chain center ($E^* \cong 1.7$ kcal/mol). The low activation energy for the chain end results in the high chain mobility to some extent. However, the difference in the activation energy between the chain end and the chain center is not so marked as compared to the difference in the relaxation time and in the critical molecular weight. Indeed the asymptotic relaxation time and the critical molecular weight nearly differ by 1 order between the chain end and the chain center. We assumed that the activation energy is mainly determined by the size of the side group attached to the main chain.

The trend that the polystyrene chain end has a higher mobility than other chain positions was also observed by ESR.[29,31,32] For example, at room temperature, the correlation time (relaxation time) for the end-labeled polystyrene was about 2.2×10^{-10} s, whereas the correlation time for the ring-labeled one was 5.5×10^{-10} s.[31] They also differ in activation energies, that is, 2.9 and 4.5 kcal/mol for end-labeled and ring-labeled polystyrene, respectively.

Zhu et al. estimated the internal energy barrier for polystyrene C−D vector orientation to be ca. 3.3 kcal/mol by ^{2}H NMR T_1 measurement.[40] For the estimation of the activation energy, they used the power law dependence, which was stated above, with $\alpha = 0.76$. Their activation energy is higher than our one for polystyrene chain center estimated with $\alpha = 1$. The difference of α and the activation energy may result from the presence of the chromophore in the optical measurement. By using the fluorescence depolarization method, Waldow et al. estimated α and the activation energy for polystyrene chain center to be ca. 0.90 and ca. 2.6 kcal/mol, respectively.[41]

Conclusion

We have examined the local motion of the oligo- and polystyrene chain end in dilute solutions by the fluorescence depolarization method. Solvents used were benzene as a good solvent and ethyl acetate as a poor solvent. In each solvent, the relaxation time increases with molecular weight and reaches its asymptotic value in the oligomer region. The critical molecular weight and the asymptotic relaxation time for benzene solution were smaller than those for the ethyl acetate solution. We suggested that these differences come from the energy potential for conformational transition or libration about the main chain bond, rather than the segment density, because the segment density has nothing to do with the chain mobility in the oligomer region. The local motion of the oligo- and polystyrene chain end was compared with that of the polystyrene chain center. The chain mobility for the chain end is much higher than that for the chain center, so that the relaxation time for the chain end is shorter by about 1 order. This indicates that the mobility of a linear polymer chain end is much different from that of its chain center.

Acknowledgment. We thank Mr. Tsuyoshi Sasaki for the preparation and the synthetic technique of the anthryl group-labeled PS. This work was supported by a Grant-in-Aid (No. 09450359) from the Ministry of Education, Science, Sports and Culture of Japan and was partly supported by a Research Fellowship of Japan Society for the Promotion of Science for Young Scientists.

References and Notes

(1) Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions*; Springer-Verlag: Berlin, 1997.
(2) Yamakawa, H. *Macromolecules* **1992**, *25*, 1912.
(3) Yamakawa, H.; Abe, F.; Einaga, Y. *Macromolecules* **1994**, *27*, 3272.
(4) Sakaguchi, M.; Shimada, S.; Yamamoto, K.; Sakai, M. *Macromolecules* **1997**, *30*, 3620.
(5) Sakaguchi, M.; Shimada, S.; Yamamoto, K.; Sakai, M. *Macromolecules* **1997**, *30*, 8521.
(6) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(7) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley and Sons: New York, 1980.
(8) Waldow, D. A.; Johnson, B. S.; Hyde, P. D.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1989**, *22*, 1345.
(9) Ono, K.; Okada, Y.; Yokotsuka, S.; Sasaki, T.; Ito, S.; Yamamoto, M. *Macromolecules* **1994**, *27*, 6482.
(10) Ono, K.; Ueda, K.; Sasaki, T.; Murase, S.; Yamamoto, M. *Macromolecules* **1996**, *29*, 1584.
(11) Horinaka, J.; Ono, K.; Yamamoto, M. *Polym. J.* **1995**, *27*, 429.
(12) Horinaka, J.; Amano. S.; Funada, H.; Ito, S.; Yamamoto, M. *Macromolecules* **1998**, *31*, 1197.
(13) Horinaka, J.; Aoki, H.; Ito, S.; Yamamoto, M. *Polym. J.*, in press.
(14) Ono, K.; Sasaki, T.; Yamamoto, M.; Yamasaki, Y.; Ute, K.; Hatada, K. *Macromolecules* **1995**, *28*, 5012.
(15) Sasaki, T.; Yamamoto, M.; Nishijima, Y. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 345.
(16) Abe, F.; Einaga, Y.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1884.
(17) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1891.
(18) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry II, Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970.

(19) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, *73*, 2715.
(20) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553.
(21) Velsko, S. P.; Waldeck, D. H.; Fleming, G. R. *J. Chem. Phys.* **1983**, *78*, 249.
(22) Bagchi, B.; Oxtoby, D. W. *J. Chem. Phys.* **1983**, *78*, 2735.
(23) Adolf, D. B.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1992**, *25*, 867.
(24) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(25) Fuson, M. M.; Ediger, M. D. *Macromolecules* **1997**, *30*, 5704.
(26) Fuson, M. M.; Hanser, K. H.; Ediger, M. D. *Macromolecules* **1997**, *30*, 5714.
(27) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(28) Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2127.
(29) Bullock, A. T.; Cameron, G. G.; Reddy, N. K. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 727.
(30) Yang, H. W. H.; Chien, J. C. W. *J. Polym. Sci., Polym. Symp.* **1978**, *63*, 263.
(31) Yang, H. W. H.; Chien, J. C. W. *Macromolecules* **1978**, *11*, 759.
(32) Friedrich, C.; Lauprêtre, F.; Noël, C.; Monnerie, L. *Macromolecules* **1981**, *14*, 1119.
(33) Shimada, S.; Suzuki, A.; Sakaguchi, M.; Hori, Y. *Macromolecules* **1996**, *29*, 973.
(34) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(35) Viovy, J. L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.
(36) Sasaki, T.; Yamamoto, M.; Nishijima, Y. *Macromolecules* **1988**, *21*, 610.
(37) Moro, G. *J. Chem. Phys.* **1992**, *97*, 5749.
(38) Moe, M.; Ediger, M. D. *Macromolecules* **1995**, *28*, 2329.
(39) Moe, M.; Ediger, M. D. *Macromolecules* **1996**, *29*, 5484.
(40) Zhu, W.; Ediger, M. D. *Macromolecules* **1997**, *30*, 1205.
(41) Waldow, D. A.; Ediger, M. D.; Yamaguchi, Y.; Matsushita, Y.; Noda, I. *Macromolecules* **1991**, *24*, 3147.

MA9814649