Macromolecules **1998,** *31,* 1197−1201

Local Chain Dynamics of Poly(oxyethylene) Studied by the Fluorescence Depolarization Method

Jun-ichi Horinaka, Shinsuke Amano, Hitoshi Funada, Shinzaburo Ito, and Masahide Yamamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Sakyo, Kyoto 606-01, Japan

Received June 23, 1997; Revised Manuscript Received December 18, 1997

ABSTRACT: The local chain dynamics of poly(oxyethylene) (POE) labeled with anthryl group in the middle of the main chain was examined by the fluorescence depolarization method. The relaxation time of the local motion was evaluated and its molecular weight dependence was shown. POE had a mean relaxation time in the order of subnanoseconds. The value of the relaxation time increased with the molecular weight in the range of MW < 4000 and reached an asymptotic value at MW of about 4000. The relaxation time and the activation energy for local motion of POE were compared with those of some styrene and methacrylate polymers and the characteristics of POE chain were discussed. POE had a much higher local chain mobility than other polymers. This high local chain mobility of POE results from the molecular structure of POE chain.

1. Introduction

The microscopic dynamics of the polymer chain essentially governs the macroscopic properties of polymers. Therefore, comprehension of the local polymer chain dynamics is an important fundamental subject in polymer science. The chain motion, which results from the local conformational transitions, has relaxation times on the order of nano- to subnanoseconds.[1,2] Many experimental methods are available for investigation of such local chain motions, e.g., NMR,[3,4] ESR,[5,6] dielectric relaxation,[7−9] dynamic light scattering,[10,11] and fluorescence depolarization.[12−18,34] The fluorescence depolarization method enables us to examine the relaxation behavior of a polymer chain directly through a fluorescent probe that is covalently bonded to the polymer chain. By using this method, we have examined the local chain dynamics of the polymers,[12−17] e.g., styrene polymers,[13] methacrylate polymers,[12,17] and poly(*cis*-1,4-isoprene) (*cis*-PIP),[16] which is labeled with an anthryl group in the middle of the main chain, in dilute solutions. The influences of molecular structure,[13,15] stereoregularity,[14] and quality of solvent[13,15−17] on the chain mobility were discussed.

As for the relationship between the molecular structure and the local chain mobility, we first studied the series of styrene polymers,[13] polystyrene (PS), poly(α-methylstyrene) (PαMS), and poly(*p*-methylstyrene) (P*p*MS). In the Θ solvents, the relaxation time and the activation energy were compared among these polymers. The chain mobility was in the order of PS > P*p*MS > PαMS. The hydrodynamic volume of the methyl group substituted at the α- or para position increases the steric hindrance for the chain rotation, thereby suppressing the local chain mobility. Moreover the methyl group at the α position makes the energy hindrance for the chain rotation higher than that at the para position. We also compared the local chain dynamics for four kinds of polymers, *cis*-PIP, PS, PαMS, and *syndiotactic*-poly(methyl methacrylate) (*s*-PMMA) in each Θ solvent.[15] The local chain mobilities estimated from the relaxation time and the activation energy were in the order *cis*-PIP > PS > PαMS > *s*-PMMA. The size of the substituents attached to the main chain was concluded to be the predominant factor in the local chain mobility. From the standpoint of molecular structure, poly(oxyethylene) (POE) is an attractive polymer; i.e., it does not have a large substituent attached to the main chain (only hydrogen) and has an ether bond in the main chain. The main chain motion is little influenced by the substituents. Therefore, study of the local chain dynamics of POE by the fluorescence depolarization method should provide fruitful information.

On the other hand, POE is a unique industrial material because of its solubility both in water and in organic solvents and has been used in biomedical applications.[19] Regarding the interest in hydrophilicity of POE, the structural properties have been extensively examined in water.[20−29] Some experimental results suggested that the conformation of POE in aqueous solution is a helix,[24,26,27] but others supported a random coil.[28,29] The conformational change of POE with the solvent has also been clarified by spectroscopic[26] and NMR[24] measurements.

Recently molecular dynamics (MD) simulations of POE have provided insight into the local conformation as well as the hydration of POE at the atomic level.[25,30] The solvent effects on the conformation and the dynamics have also been discussed from MD simulations. MD simulations were in good agreement with the experimental results. POE maintained a helical conformation in an aqueous solution, while in a benzene solution, the conformation quickly changed to a random coil.[30] Concerning dynamics, the bond vector reorientation, which had relaxation time in the picosecond order, was examined in water and in benzene.[30] Although MD simulation is useful to examine the conformational and dynamic properties at the atomic level, there are some problems; i.e., the molecular size, the potential energy function, and the duration time available for simulation are limited by the calculation capacity. Therefore the local chain dynamics of POE, which is on the order of nanoseconds, has not yet been clarified, and more detailed experimental studies are needed.

S0024-9297(97)00912-1 CCC: $15.00

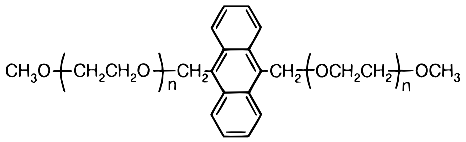

Figure 1. Molecular structure of the POE sample labeled with an anthracene group in the middle of the main chain.

Table 1. Characterization of Synthesized POE Used in This Study

	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
POE700	0.779	0.769	1.01
POE1000	1.18	1.03	1.14
POE2000	2.02	1.66	1.21
POE5000	5.30	5.01	1.06
POE10000	9.84	8.30	1.19

In the present study, we examined the local chain dynamics of POEs with various molecular weights in dilute solutions. The relaxation time of local motion was evaluated, and the molecular weight dependence was shown. The chain mobility of POE was also compared with those of other polymers mentioned above, and the characteristics of the POE chain were discussed concerning the relationship between the local chain mobility and the molecular structure.

2. Experimental Section

Sample Preparation. Anthryl group-labeled POE samples used in this study were synthesized as follows. Poly(ethylene glycol) methyl ethers (m-PEGs) with molecular weights of ca. 350, 550, 750, 2000, and 5000 were used as starting materials. m-PEGs of molecular weights of 350, 550, and 750 were purchased from Aldrich, and those of weights 2000 and 5000 were given by NOF Co., Oleo Chem. Res. Lab. Each m-PEG was allowed to react with sodium hydride in benzene at 30 °C under reflux. The resulting sodium poly(ethylene glycoxide) was coupled with 9,10-bis(bromomethyl)anthracene in dimethylformamide (DMF) at 40 °C under stirring for several days. Both benzene and DMF were distilled by each conventional method before use. The higher molecular weight polymers obtained from m-PEG 2000 and 5000 were purified by reprecipitation from benzene in hexane. The others were used without purification for the measurement. The POE sample labeled in the middle of the main chain was fractionated from an incompletely labeled product by GPC. The molecular structure and the characterization of POE samples used in this study are shown in Figure 1 and Table 1, respectively. Standard POE (Scientific Polymer Products) was used to determine the molecular weight. The molecular weight ranges from ca. 800 to 10 000.

Solvents used in measurement were DMF (Dojin, spectrophotometric grade) and cyclohexanone (Wako, guaranteed grade). DMF was used without further purification, and cyclohexanone was distilled before use. In preparing the sample solution, each polymer concentration was kept less than 10^{-5} M, so that the value of absorbance of sample solution at the wavelength of excitation was less than 0.1. The 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 second harmonic of a Ti:sapphire laser (Spectra-Physics Tsunami) was used at a wavelength of 393 nm as a light source, and a 4 MHz pulse was picked up by a pulse selector (Spectra-Physics Model 3980). 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 (MCP–PMT) (Hamamatsu Photonics R3809) through cutoff filters B370 and SC42. The signal of MCP–PMT was input to a time-to-amplitude converter (Ortec Model 457) as a start signal through a constant fraction discriminator (Ortec Model 583). The stop signal was the split fundamental laser beam detected by a photodiode. The time-resolved fluorescence intensity was analyzed by a multichannel analyzer (Norland Ino-Tech 5300). 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 alternatively to avoid data distortions due to time drift.

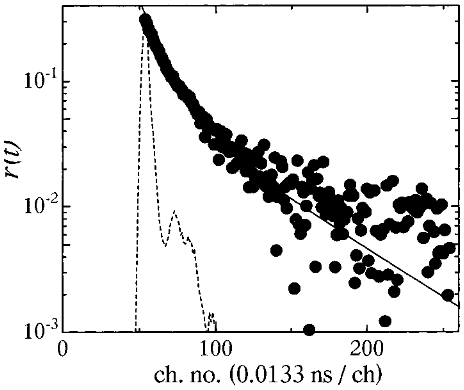

Figure 2. Example of measurement data for POE5000 in DMF at 13 °C: experimental anisotropy ratio (closed circle), fitting curve (solid line), and the instrumental function (broken line). The fitting parameters were $r_0 = 0.295$, $x = 0.203$, $T_1 = 0.749$, and $T_2 = 0.174$; see text.

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

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

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 is required and empirically concluded that the double exponential-type function, eq 2, represents the anisotropy decay quite well.[12–17] The

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

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.

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

$$= xT_1 + (1 - x)T_2 \tag{4}$$

3. Results and Discussion

Molecular Weight Effect of POE. Figure 2 shows an example of measurement data, which is for POE5000 in DMF. The instrumental function, the broken line, has a shape narrow enough to measure the anisotropy decay of the relaxation time in the order of subnanoseconds. The solid line is the fitting function for the measured anisotropy ratio represented by the closed circle.

Figure 3 shows the molecular weight dependence of the relaxation time of POE in DMF at 13 °C. The open circle in Figure 3 indicates the rotational relaxation time of the model compound, 9,10-dimethylanthracene (DMA), in DMF estimated by the steady-state measurement on the assumption that the hard sphere approximation holds. The rotational relaxation time of DMA can be treated as the limiting value of low molecular weight

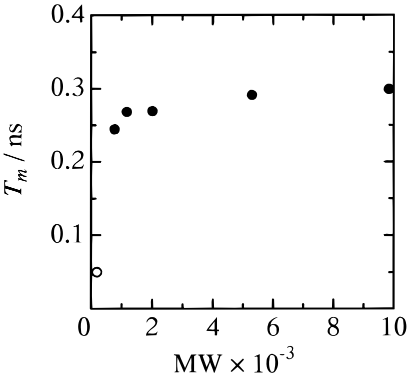

Figure 3. Molecular weight dependence of the relaxation time for POE (closed circle) and DMA (open circle) measured in DMF at 13 °C. The rotational relaxation time of DMA (ca. 50 ps) was estimated by steady-state measurement. The relaxation time reaches an asymptotic value at a MW of about 4000.

POE. Figure 3 shows that every POE used in this study has the relaxation time in the order of subnanoseconds. T_m increases with the molecular weight in the low molecular weight region and reaches an asymptotic value, $T_m = 0.3$ ns, at MW of about 4000.

Figure 3 indicates that the local motion of POE of MW < 4000 measured by the fluorescence depolarization method reflects the entire chain motion as well. The longer chain has a larger relaxation time for the entire rotation. On the other hand, the local motion in MW > 4000 is independent of the effect of the entire motion. In other words, this molecular weight, MW = 4000, corresponds to the longest length scale of the local motion of POE in DMF measured by the fluorescence depolarization method.

Bahar *et al.*[32,33] calculated the effects of chain connectivity on the local orientational motions in the flexible polyethylene chain according to the dynamic rotational isomeric state (DRIS) scheme. When the central bond of 20 bonds undergoes an isomeric transition, this rotation propagates along both sides of the mobile chain, leading to a displacement of 2 Å for each end. They concluded that such a displacement is sufficiently small to be easily accommodated by compensating motions. In other words, the cooperative length scale of one-bond orientational motion is less than 20 bonds for the flexible chain.

The segment density around the fluorescent probe also affects the local chain dynamics.[13,15−17] We examined the molecular weight effect on the local chain dynamics of *s*-PMMA of MW > 20 000 in good solvents and showed that the local motion is not influenced by the change of molecular weight.[17] It was concluded that in a good solvent, the segment density about the chain center is kept constant because of the intramolecular excluded-volume effect. A similar tendency was also observed in a self-avoiding random walk calculation for PIP chain by Waldow et al.[18] DMF is a good solvent for POE, so that the segment density around the chain center of POE is kept constant in a high molecular weight region because of the intramolecular excluded-volume effect.[17,18] Therefore, the local chain dynamics of POE in DMF is independent of the molecular weight in a high MW region, and $T_m = 0.3$ ns can be regarded as an asymptotic value.

Hence, we considered that POE5000 and -10000 have a large enough molecular weight to examine the local chain dynamics of the chain center. In the next section we discuss the result for POE5000 as a representative one in the comparison with other polymers.

Table 2. Characterization of Polymers Used in This Study

polymer	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	ref
POE	0.530	0.501	1.06	
PS	9.7	9.2	1.05	13
PαMS	21.5	20.5	1.05	13
P*p*MS	28.5	27.5	1.03	13
PEMA	17.7	15.7	1.12	15
PMMA	15.0	12.8	1.18	15
cis-PIP	14.5	13.1	1.10	16

Table 3. Mean Relaxation Time of POE in Comparison with Other Polymers[a]

polymer	T_m, ns	polymer	T_m, ns
POE	0.55	P*p*MS	13
PS	8.5	PEMA	13
PαMS	10	PMMA	17

[a] Measured in cyclohexanone, 13 °C.

Comparison with Other Polymers. We compared the relaxation time for POE5000 with those for PS, PαMS, P*p*MS, *s*-PMMA, and poly(ethyl methacrylate) (PEMA) in cyclohexanone,[15] which is a good solvent for these polymers. Characterization of the polymers used for comparison is shown in Table 2. Each polymer has a molecular weight of ca. 10^5 or above. The difference in the molecular weight between POE and the others is not serious, because every polymer had a sufficiently high molecular weight for the study of the respective local motion.[12,17]

Table 3 shows the relaxation time for each polymer in cyclohexanone at 13 °C. The value of T_m for POE is about of 1 order of magnitude smaller than those for other polymers; i.e., POE has a much higher local chain mobility than other polymers. This noticeable difference arises from the characteristic molecular structure of POE. POE does not have a large substituent attached to the main chain carbon (only hydrogen) compared with other polymers. Therefore, the local motion of POE is not suppressed by the steric hindrance between substituents and POE main chain shows high dynamic flexibility. A tendency existed where the larger the substituent the more suppressed the chain mobility in the series of styrene polymers was.[13] Moreover, in the case of POE, the ether bond in the main chain contributes to the flexibility.[36]

Now let us mention the perturbation of the fluorescent probe to the chain dynamics. Since the anthryl group in the middle of the main chain is relatively larger than the ethoxy unit, the fluorescent probe may perturb the local motion toward decreasing the chain mobility, compared with the unlabeled chain, but every sample has the same structure in the vicinity of the fluorescent probe. Hence, we can say that the difference of the relaxation time comes from the molecular structure of the polymer itself. Consequently the fluorescent probe does not perturb our conclusion that POE has high chain mobility because of its molecular structure.

Activation Energy. Next, we evaluated the activation energy for local motion by the theory of Kramers' diffusion limit from the temperature dependence of relaxation time.[1] According to the theory, the velocity coefficient, k, of a particle with a frictional coefficient, ζ, passing over an energy barrier of the height E is represented as

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

where R is the gas constant and T is 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

$$T_m/\eta = A \exp(E^*/RT) \qquad (6)$$

Figure 4 shows a T_m/η vs $1/T$ plot for POE5000 in DMF. The viscosity at each temperature was estimated from the reported value in the literature.[31] The activation energy, E^*, was evaluated to be 1.1 kcal/mol from the slope of the plot. We compared this value with those for PS, *s*-PMMA, and *cis*-PIP in good solvents.[15,16] The characterization of *cis*-PIP is shown in Table 2.

Table 4 shows the value of the activation energy for each polymer. The value of E^* for POE is smaller than half of that for *s*-PMMA and slightly smaller than that for *cis*-PIP. This indicates that the local motion of POE has a lower energy barrier than those for other polymers. POE does not have a large side group, and the steric hindrance for local motion is not serious. That is, the high dynamic flexibility was also supported by the comparison of the activation energy from the standpoint of the relationship between the local chain mobility and the molecular structure.

Concerning the evaluation of the activation energy for local motion, some other approaches have been proposed.[16,37−43] 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. Grote and Hynes[44] removed the assumption of white noise and considered that the transition rate of solute depends on the friction of solvent at a frequency comparable to that of the solute at the barrier. When the frequency at the barrier is quite high, effective friction is much 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. Fleming *et al.*[42,43] found that their photochemical isomerization rate data shows a power law dependence on the solvent viscosity with a power of less than unity. Bagchi and Oxtoby[45] calculated the multiplicative factor x, which is the ratio of the observed rate constant to the transition state rate constant, starting with the generalized Langevin equation proposed by Grote and Hynes, assuming time-dependent friction, and showed that a plot of x against zero shear viscosity can be fitted very well to the power law form proposed by Fleming et al. Ediger et al. showed that in the study of the local chain dynamics of PIP in dilute solution the power law form also holds, i.e., $\tau_c \propto \eta^{0.75}$ at constant temperature in the fluorescence depolarization study,[38] while in the NMR study[39] $\tau_c \propto \eta^{0.41\pm0.02}$. Accordingly we reevaluated the activation energy assuming that the power law dependence holds for our POE data, namely

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

We estimated α to be 0.69 at 13 °C from the gradient of the logarithm plot of T_m vs η. Although only two solvents were used in this study, the value of α for POE is appropriate compared with that for PIP by Ediger et al. Then we reevaluated the activation energy to be 1.9 kcal/mol with $\alpha = 0.69$. On the other hand, the power law dependence of the local dynamics on solvent viscosity results from the breakdown of the white noise assumption, and the value of α should change with the chain mobility and solvent viscosity. That is, α becomes small as the chain mobility and/or the solvent viscosity becomes high. DMA and cyclohexanone have viscosities of 1.0 cP and 2.6 cP at 13 °C, respectively. Hence α for POE in DMF should be larger than 0.69 and so the activation energy should be less than 1.9 kcal/mol. Ono *et al.*[16] examined whether Kramers' theory is valid for local motion of PIP in low viscosity (<2 cP) solvents studied by the fluorescence depolarization method and obtained a power of unity instead of 0.75 by Ediger et al. Consequently as long as we compare the chain mobility in low viscosity solvents below 1 cP, the evaluation of activation energy with Kramers' theory is appropriate.

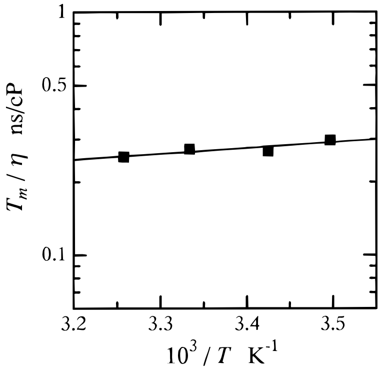

Figure 4. T_m/η vs $1/T$ plot according to the theory of Kramers'diffusion limit. T_m was measured in DMF. The viscosity at each temperature was estimated from the reported value in the literature. The slope corresponds to the activation energy for the local motion.

Table 4. Activation Energy of POE Local Motion in Comparison with Other Polymers[a]

polymer	E_a, kcal/mol	polymer	E_a, kcal/mol
POE	1.1	PS	1.3−1.7
cis-PIP	1.2−1.3	PMMA	2.4−2.7

[a] Measured in good solvents.

4. Conclusion

We synthesized anthryl group-labeled POE in the middle of the main chain by coupling of sodium poly(ethylene glycoxide) with 9,10-bis(bromomethyl)anthracene. We obtained five POEs, which vary in molecular weight, and examined the local chain dynamics in dilute solutions by the fluorescence depolarization method. The molecular weight effect on the relaxation time is below MW = 4000 and reaches an asymptotic value at MW of about 4000. This molecular weight corresponds to the largest scale of the local motion measured by the fluorescence depolarization method. Next, we compared the relaxation time for POE5000 with those for PS, PαMS, P*p*MS, *s*-PMMA, and PEMA in cyclohexanone. POE has a subnanosecond relaxation time, which is shorter than one-tenth of those for other polymers. This high local chain mobility results from the molecular structure of the POE chain. We also compared the activation energy for local motion of POE with those for other polymers including *cis*-PIP. POE has the lowest activation energy among the polymers compared. We concluded that POE is dynamically flexible because of the characteristic molecular structure. That is, POE does not have a large substituent attached to the main chain and has an ether bond in the main chain.

Acknowledgment. We would like to thank NOF Co., Oleo Chem. Res. Lab., for supplying m-PEGs of higher molecular weight. 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 from the Japan Society for the Promotion of Science for Young Scientists.

References and Notes

(1) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(2) Yamakawa, H. *Macromolecules* **1977**, *10*, 692.
(3) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(4) Lauprêtre, F.; Noël, C.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2127.
(5) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers*; Clarendon Press: Oxford, England, 1981.
(6) Bullock, A. T.; Cameron, G. G.; Smith, P. M. *J. Phys. Chem.* **1973**, *77*, 1635.
(7) Mashimo, S. *Macromolecules* **1976**, *9*, 91.
(8) Mashimo, S.; Winsor, P.; Cole, R. H.; Matsuo, K.; Stockmayer, W. H. *Macromolecules* **1986**, *19*, 682.
(9) Adachi, K. *Macromolecules* **1990**, *23*, 1816.
(10) Yoshizaki, T.; Yamakawa, H. *J. Chem. Phys.* **1993**, *99*, 9145.
(11) Takaeda, Y.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1994**, *27*, 4248.
(12) Sasaki, T.; Yamamoto, M. *Macromolecules* **1989**, *22*, 4009.
(13) Ono, K.; Okada, Y.; Yokotsuka, S.; Ito, S.; Yamamoto, M. *Macromolecules* **1994**, *27*, 6482.
(14) Ono, K.; Sasaki, T.; Yamamoto, M.; Yamasaki, Y.; Ute, K.; Hatada, K. *Macromolecules* **1995**, *28*, 5012.
(15) Ono, K.; Ueda, K.; Sasaki, T.; Murase, S.; Yamamoto, M. *Macromolecules* **1996**, *29*, 1584.
(16) Ono, K.; Ueda, K.; Yamamoto, M. *Polym. J.* **1994**, *26*, 1345.
(17) Horinaka, J.; Ono, K.; Yamamoto, M. *Polym. J.* **1995**, *27*, 429.
(18) Waldow, D. A.; Johnson, B. S.; Hyde, P. D.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1989**, *22*, 1345.
(19) *Poly(Ethylene Glycol) Chemistry*; Harris, J. M., Ed.; Plenum: New York, 1992.
(20) Bailey, F. E., Jr.; Callard, R. W. *J. Appl. Polym. Sci.* **1959**, *1*, 373.
(21) Bailey, F. E., Jr.; Koleske, J. V. *Poly(ethylene oxide)*; Academic Press: New York, 1976.
(22) Nakayama, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1683.
(23) Saeki, S.; Kuwahara, N.; Nakata, M. Kaneko, M. *Polymer* **1976**, *17*, 685.
(24) Tasaki, K.; Abe, A. *Polym. J.* **1985**, *17*, 641.
(25) Tasaki, K. *J. Am. Chem. Soc.* **1996**, *118*, 8459.
(26) Matsuura, H.; Fukuhara, K. *J. Mol. Struct.* **1985**, *126*, 251.
(27) Matsuura, H.; Fukuhara, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 763.
(28) Koenig, J. L.; Angood, A. C. *J. Polym. Sci.* **1970**, *8*, 1787.
(29) Maxfield, J.; Shepherd, I. W. *Polymer* **1975**, *16*, 505.
(30) Tasaki, K. *Macromolecules* **1996**, *29*, 8922.
(31) Advances in Chemistry Series 29; *Physical Properties of Chemical Compounds III*; American Chemistry Society: Washington, DC, 1961.
(32) Bahar, I.; Erman, B.; Monnerie, L. *Macromolecules* **1990**, *23*, 1174.
(33) Bahar, I.; Erman, B.; Monnerie, L. *Adv. Polym. Sci.* **1994**, *116*, 147.
(34) Gény, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 131; 147.
(35) Viovy, J. L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.
(36) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley and Sons: New York, 1969.
(37) Adolf, D. B.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1992**, *25*, 867.
(38) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(39) Ono, K.; Okada, Y.; Yokotsuka, S.; Ito, S.; Yamamoto, M. *Polym. J.* **1994**, *26*, 199.
(40) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553.
(41) Velsko, S. P.; Waldeck, D. H., Fleming, G. R. *J. Chem. Phys.* **1983**, *78*, 249.
(42) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, *73*, 2715.
(43) Bagchi, B.; Oxtoby, D. W.; *J. Chem. Phys.* **1983**, *78*, 2735.

MA970912U