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Segmental Motion of Polystyrene in Fluid Solution Revealed by Means of the Fluorescent Probe Method

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ABSTRACT: The molecular weight dependence of the energy-transfer process from the side-chain phenyl groups to the anthryl group at one end or the anthryl groups at both ends of a polystyrene chain has been studied in tetrahydrofuran solution by monitoring the quenching yield of the phenyl excimer fluorescence. The energy transfer was found to follow the Yokota–Tanimoto theory, and the diffusion constant of a segment having several decades of monomer units near the end group was determined to be (2.1 ± 0.2) × 10^{-6} cm^2/s. The mode of segmental motion is briefly discussed in connection with the cyclization process of polystyrene chains in fluid solution.

Introduction

The luminescent probe method gives information on fast molecular motion, kinetics of reactions, interaction among molecules and/or groups, and the microenvironments around the probes. Recently, many investigations using the luminescent probe methods have been carried out trying to monitor the dynamic motions of macromolecules in both fluid and solid solutions.[1] The segmental motion of polymer chains in fluid solution has been studied as well by this method, because its relaxation time is expected to be within the fluorescence time range. However, the number of the reports is few, and more data need to be accumulated.

The fluorescence probe techniques used to reveal segmental motion of macromolecules in dilute solution are summarized to be fluorescence polarization[2-4] and detection of excimer fluorescence.[5] Soutar et al. showed by using the fluorescence polarization technique that the motion of anthryl groups attached to the chain ends of polystyrene is 5 times as fast as that of the same groups in the chain interiors.[3] In connection with the studies of segmental motion, rate constants of intramolecular end-to-end collisions, that is, the cyclization process, have been measured by using the luminescent probe method: excimer formation between pyrenyl groups at both chain ends,[6,7] and both triplet–triplet annihilation[8,9] and photodimerization[10] between anthryl groups at both chain ends. The cyclization process itself consists of segmental motion, local motion, and/or reorientational motion of chromophores at the ends; thus it is not so easy to pick up the information on the details of the molecular motion.

The Yokota–Tanimoto theory[11] is established to be the most useful theory to describe singlet energy transfer in fluid solution;[12,13] however, it has not been effectively employed in polymer systems so far. In the present work, the Yokota–Tanimoto theory is used to analyze the energy-transfer process taking place in a polymer system and to obtain information on the segmental motion of a polymer chain from the diffusion constant calculated from the theory.

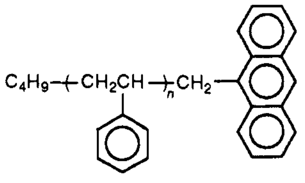
Experimental Section

Materials. Anionically polymerized polystyrenes having an anthryl group at one chain end (PSA) and anthryl groups at both chain ends (APSA) were kindly furnished by Prof. Kazuyuki Horie of the University of Tokyo and Prof. Hideharu Ushiki of the Tokyo University of Agriculture and Technology.[14,15] The characteristics of the PSA and APSA samples are summarized in Table I. The degree of polymerization, N, was determined as

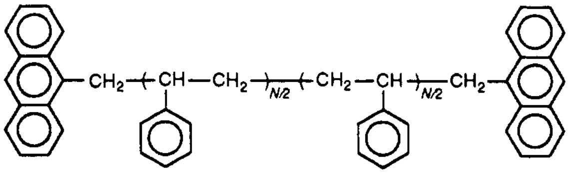
$$N = (M_n - M_{bt} - aM_{ant}/100)/M_{ph} \quad \text{for PSA}$$

$$N = (M_n - 2aM_{ant}/100)/M_{ph} \quad \text{for APSA}$$

where a is the content of terminal anthryl groups (%), M_n is the number-average molecular weight of PSA or APSA, and M_{bt}, M_{ant}, and M_{ph} are the molecular weights of the butyl end (57), the anthryl end (191), and one styrene unit (104), respectively. APSA has anthryl groups at both ends, while PSA has one anthryl end and one butyl end.



PSA



APSA

The concentrations of the phenyl groups in fluid solutions were also determined by taking the structure of the end groups into consideration. Polystyrenes with molecular weights from 2.8 × 10^3 to 9.6 × 10^4 (Tosoh) were used to determine the fluorescence intensity of polystyrene without any quenching groups.

Fluorescence measurements were carried out in tetrahydrofuran (THF) (Wako Co. Dotite Spectrosol). All sample solutions were degassed by freeze–pump–thaw cycles under high vacuum.

Fluorescence Measurements. Fluorescence spectra and fluorescence excitation spectra were measured on a JASCO FP-550 spectrofluorometer at 25 °C. For this study, the excitation wavelength should be chosen under the conditions that (1) an anthryl group is not directly excited very much, while (2) the phenyl rings of PSA and APSA are effectively excited. Consequently, we chose 270 nm as the excitation wavelength by comparing the UV absorption spectra of polystyrene, PSA, APSA, and 9-methylanthracene as a model compound of the anthryl end. The fluorescence intensity of the phenyl monomer of polystyrene was not exactly determined because (1) its intensity is quite low and (2) almost all the excitation energy absorbed by the phenyl rings is transferred to the excimer sites. Actually, the fluorescence quantum yield of the phenyl monomer singlet of

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Table I
Characterization of PSA and APSA Samples

polymer	M_n	M_w/M_n	N^a	a^b
PS25A	2.84×10^3	1.03	24.9	100
PS42A	4.63×10^3	1.41	42.4	83.0
PS70A	7.54×10^3	1.13	70.2	95.9
PS400A	4.20×10^4	1.28	402	51.2
PS800A	8.30×10^4	1.22	796	59.2
APS135A	1.40×10^4	1.56	132	100
APS775A	8.10×10^4	1.24	775	100

[a] Degree of polymerization. [b] Percent content of terminal anthryl.

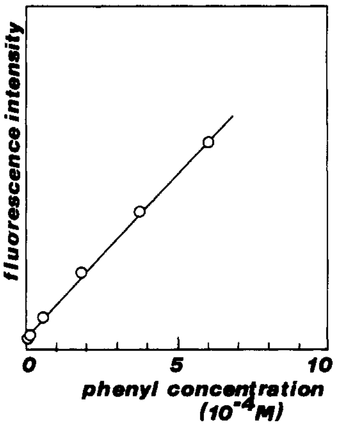

Figure 1. Concentration dependence of excimer fluorescence intensities of PS400A in THF solution.

polystyrene with $N = 20$ is 0.002,[16] while that of toluene is 0.20.[17] Five to eight different solutions with different concentrations ([phenyl] = 1×10^{-3} to 1×10^{-5} baseM) were measured to determine more precisely the fluorescence intensity of each PSA and APSA sample. Figure 1 shows the concentration dependence of the peak intensity of the excimer fluorescence, I_{peak}, of PS400A in THF as an example. It suggests that (1) intermolecular energy transfer can be neglected in this concentration range and (2) the slope gives the average value of the excimer fluorescence intensity. Thus each excimer intensity was determined from five to eight fluorescence data by using a least-squares method.

Theoretical Background

Two problems should be considered in order to theoretically examine our experimental results: (1) the kinetics of the present energy transfer and (2) the effective concentration of the donor (phenyl group) and the acceptor (anthryl group).

Kinetics of the Energy Transfer from Phenyl to Anthryl in the PSA and APSA Systems. The basic mechanism of nonradiative electronic singlet–singlet energy transfer between a pair of chromophores is usually described by using the long-range dipole–dipole mechanism of Förster.[18,19] In a system where mobility of molecules or groups is possible, the transfer of excitation energy between chromophores is influenced by the relative diffusive motion of the donor and acceptor. Accordingly, though the energy-transfer mechanism taking place in our system follows the Förster mechanism, the kinetics itself obeys either Förster kinetics (without mobility) or Yokota–Tanimoto kinetics (with diffusive motion). In general, the transient intensity of the donor fluorescence can be written in the form

$$I_D(t) = I_D(0) \exp\{-(t/\tau_0) - k_m(t)\} \qquad (1)$$

where τ_0 is the donor lifetime in the absence of acceptor and the time-dependent rate constant $k_m(t)$ describes the increase in the decay rate as a result of energy transfer to acceptor molecules or groups.

Förster Kinetics. If the mobility of the donor and acceptor can be neglected, the energy-transfer process follows Förster kinetics and the transfer rate $k_m(t)$ is given by

$$k_m(t) = 2\gamma(t/\tau_0)^{1/2} \qquad (2)$$

where

$$\gamma = C_A/C_0 \qquad (3)$$

C_A is the acceptor concentration and C_0 is a critical acceptor concentration which is defined as

$$C_0 = 3000/(2\pi^{1.5}N_A R_0^{\,3}) \qquad (4)$$

where N_A is Avogadro's number and R_0 is the critical transfer distance at which energy transfer and deactivation of the donor by fluorescence or internal quenching are of equal probability. The units of C_0 are M (mol/L). R_0 can be obtained from the calculation of the overlap integral of the emission spectrum of the donor with the absorption spectrum of the acceptor. In regard to the PSA and APSA systems, we used $R_0 = 1.54$ nm and $C_0 = 0.123$ M according to the reference value (donor: polystyrene; acceptor: 9-methylanthracene).[20]

Yokota–Tanimoto Kinetics. On the other hand, if the diffusion of the donor or acceptor has an effect on the energy transfer, it should be taken into consideration. The mobility of the segment near the end groups of polystyrene in our system is not assumed to be so high that Stern–Volmer kinetics[21] is valid. Thus we try to apply Yokota and Tanimoto's kinetics[11] to our experimental data. Their equation, which was solved by using the Padé approximation, is given as

$$k_m(t) = 2B\gamma(t/\tau_0)^{1/2} \qquad (5)$$

where

$$B = \{(1 + 10.87X + 15.50X^2)/(1 + 8.743X)\}^{3/4} \qquad (6)$$

with

$$X = D\alpha^{-1/3}t^{2/3} \qquad (7)$$

and

$$\alpha = R_0^{\,6}/\tau_0 \qquad (8)$$

D is the diffusion constant. Notice that eq 5 reduces to Förster kinetics (eq 2) when $B = 1$, which is the case when molecular diffusion is negligible ($D \cong 0$).

Assessment. For the purpose of examining which kinetics is more appropriate to reproduce our experimental results, we used the Durbin–Watson factor (DW)[22,23] to assess the validity of the fitting. DW is calculated from

$$\text{DW} = \sum_{i=2}^{7}(R_i - R_{i-1})^2 \Big/ \sum_{i=1}^{7} R_i^{\,2} \qquad (9)$$

where the weighted residual $R_i = (Y_i - F_i)/Y_i^{1/2}$, Y_i and F_i are the values of the experimental data and trial calculation value corresponding to sample number i (in the same order as Table II), and 7 is the number of experimental samples. For the best fit, the value of DW approaches 2.0.

Estimation of the Local Concentration of Phenyl and Anthryl Groups in the PSA and APSA Systems. As described above, the electronic energy transfer from the polystyrene excimer to the terminal anthryl group follows the Förster mechanism whether the mobility of donors and acceptors is important (Yokota–Tanimoto kinetics) or not (Förster kinetics). This means that the distance between the donor and the acceptor is the main variable affecting the quenching yield of the phenyl excimer fluorescence. Since the main objective of the present paper is to judge which kinetics is more valid to describe this energy-transfer process, we would like to employ simplified parameters concerning the behavior of the polymer chain such as the end-to-end distance.[24]

When each phenyl group is numbered in turn from the end which the anthryl group is attached to, the distance between the ith phenyl group (excimer) and the anthryl, r_i, is assumed to be expressed by

$$r_i = \alpha_s(\langle r_0 \rangle^2)^{1/2} \tag{10}$$

with

$$\langle r_0 \rangle^2 = 10.6 \times (2i)b^2 \tag{11}$$

where α_s, $\langle r_0 \rangle^2$, and b are the expansion coefficient, the mean-square end-to-end length, and the bond length (0.154 nm), respectively. Equation 11 was obtained for atactic polystyrene at 30 °C by Krigbaum et al.[27] Each value of α_s was obtained from

$$\alpha_s = M_w^{\,0.0844} \exp(-0.556) \tag{12}$$

which was calculated using the data for polystyrene in THF by Schulz and Baumann.[28]

Since each phenyl ring is assumed to have the same probability to absorb a photon and to form an excimer, basically the effective concentration C_A of an N-mer (N = degree of polymerization) is expressed in the form

$$\frac{p}{N}\sum_{i=1}^{N}\left\{\frac{4}{3}\pi r_i^{\,3}\right\}^{-1}$$

where p is the number of anthryl groups per polymer chain (PSA: $p = 1$; APSA: $p = 2$). Thus C_A is given using a unit of M (mol/L) as eq 13.

$$C_A = \frac{3000p}{4\pi N_A N}\sum_{i=1}^{N} r_i^{-3} \tag{13}$$

As a matter of course, eqs 10–13 are on a first approximation and not correct under the condition that i is small. There are two ways to deal with this short-chain problem: (1) to substitute experimental values of PS25A for distance (r_i) or local concentration (C_A) of the short chain having up to 25 monomer units and (2) to calculate r_i or C_A on the basis of a statistical treatment such as the rotational isomeric state formalism. Since the latter simulation method has given successful results to interpret fluorescence data,[29,30] it would be desirable in our future work; however, here we try to estimate the values of the concentration when i is small as follows by using C_A of PS25A: first, we calculate γ (Förster kinetics) or a set of γ and D (Yokota–Tanimoto kinetics) to reproduce the experimental value (Φ_D) of PS25A; second, since the quantity obtained by substituting $N = 25$ into eq 13 must be equal to C_A of PS25A, we substitute the value of $C_0\gamma$ of PS25A (see eq 3) into the summation value of eq 13 from $i = 1$ to $i = 25$. Here the value of $C_0\gamma$ of PS25A is defined as C_{25A}; next, we calculate each C_A of the other PSA and APSA samples by using C_{25A}. Thus each concentration, C_A, of PSA or APSA N-mer sample is derived from eq 13 to be

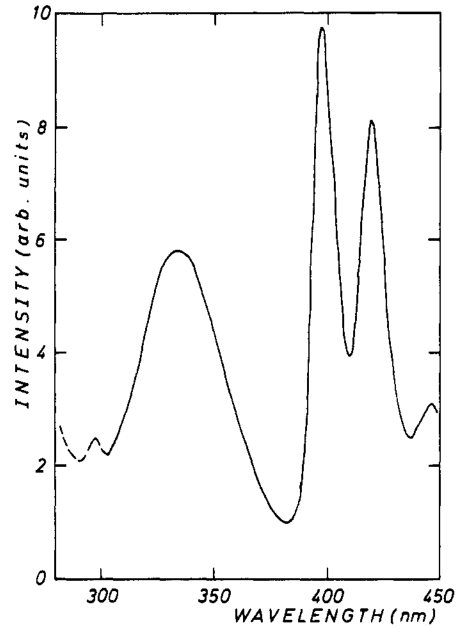

Figure 2. Fluorescence spectrum of PS800A in THF (excitation wavelength 270 nm). The emission whose peak is around 330 nm and that between 400 and 450 nm are assigned to the fluorescence of the phenyl excimer and the terminal anthryl, respectively.

$$C_A = \frac{25}{N}pC_{25A} + \frac{3000p}{4\pi N_A N}\sum_{i=26}^{N} r_i^{-3} \tag{14}$$

Its units are M (mol/L). Each r_i is calculated from eqs 10–12.

Results and Discussion

Figure 2 shows the fluorescence spectra of PS800A in THF solution. The peak near 330 nm is assigned to the excimer emission of the phenyl groups, and the emission band between 400 and 450 nm is assigned to the fluorescence of the anthryl group at the end of the polystyrene. The intensities of the excimer fluorescence of lower molecular weight PSA and APSA samples were found to be weaker than those of polystyrene with nearly same molecular weight. This proves that energy transfer takes place from the phenyl excimer to the anthryl group at the end of the PSA or APSA.

The fluorescence quenching yield of the polystyrene excimer by the terminal anthryl groups is determined by monitoring the peak intensity of the excimer fluorescence, I_{peak}. Taking into account the content of the terminal anthryl group (a; see Table I), the real fluorescence intensity of the excimer of a PSA or APSA sample, $I_{excimer}$, is calculated to be

$$I_{excimer} = 100\,(I_{peak} - I_{PS\,peak}(1 - a/100))/a \tag{15}$$

where $I_{PS\,peak}$ is the peak intensity of the excimer fluorescence of polystyrene with nearly same molecular weight as the PSA or APSA sample and displays the excimer fluorescence intensity without being quenched by the terminal anthryl group. Here the quenching yield, Φ_D, is defined as $I_{excimer}/I_{PS\,peak}$, while the quantum efficiency of the energy transfer from the phenyl excimer to the anthryl group is expressed as $1 - \Phi_D$. The experimental results are summarized in Table II. In the case of PS25A, 40% of the energy absorbed by phenyl groups is found to be transferred to the terminal anthryl group, while the excimer fluorescence of PS800A is not

Table II
Quenching Yield of Excimer Fluoresence by Terminal Anthryl Groups (Φ_D) and Comparison of Calculated Values of Φ_D with Experimental Values

polymer	Φ_D	calcd values using Förster kinetics	calcd values using Yokota–Tanimoto kinetics
PS25A	0.60	0.55	0.60
PS42A	0.68	0.68	0.68
PS70A	0.74	0.78	0.76
PS400A	0.94	0.96	0.94
PS800A	1.0	0.98	0.97
APS135A	0.75	0.77	0.74
APS775A	0.95	0.95	0.94
DW		1.10	1.72

quenched very much. With respect to Table II, it should be pointed out that Φ_D of APS-N-A, that is, N-mer, is almost identical with that of PS-(N/2)-A. This fact demonstrates the exactness of our experiment.

First let us consider which kinetics, Förster or Yokota–Tanimoto, is more appropriate to reproduce the energy-transfer process in our PSA and APSA systems. In Yokota–Tanimoto kinetics, the introduction of the diffusion coefficient as an adjustable parameter improves the agreement between theory and experiments; thus it is quite natural that the Yokota–Tanimoto theory gives a better fitting. Thus what we actually examine is how much better our experimental results are fitted to Yokota–Tanimoto kinetics. In other words, if no great difference is perceptible between the fitting results using the two kinetics, our data would be too rough to be dealt with the Yokota–Tanimoto theory.

Before the examination, three assumptions are presented: (I) The process of energy transfer from the phenyl monomer to anthryl is neglected due to its small contribution, (II) singlet energy migration among the phenyl rings is not considered explicitly because energy migration appears to equally contribute to both the increase (influx to the quenching area) and the decrease (escape from the quenching area) of energy-transfer efficiency, and (III) the diffusion constant D is assumed to be constant among all the PSA and APSA samples.

The assumption that there is no molecular weight dependence of the diffusion constant (assumption III) requires some discussion; the other assumptions appear to be reasonable and actually they do not influence our results very much. Since the diffusional motion observed by fluorescence quenching, which follows the Förster mechanism depending on the distance between the donors and acceptors, is that of only the terminal chain segment including the terminal anthryl, the question of assumption III is whether the mobility of the end-chain segment consisting of several to at most a couple of decades of styrene units depends on the whole molecular size or not; although it is possible that styrene units far from the chain end can three-dimensionally approach the terminal anthryl (such a case is involved in our treatment), the probability is so small that it can be neglected as a first approximation. We assumed that the mobility of the terminal segment taking place within the phenyl excimer lifetime is somewhat local and their molecular weight dependence is not observed intensively; however, it should be reexamined in future work analyzing transient fluorescence data. In any case, we employ assumption III in the present paper. The fluorescence yield of the excimer is expressed by integration of eq 1; that is

$$\Phi_D = \frac{\int_0^\infty I_D(0)\exp\{-(t/\tau_0) - k_m(t)\}\,dt}{\int_0^\infty I_D(0)\exp\{-(t/\tau_0)\}\,dt} = \tau_0\int_0^\infty \exp\{-(t/\tau_0) - k_m(t)\}\,dt \quad (16)$$

The value of τ_0 for polystyrene excimer (20 ns)[16] is substituted into eq 16.

First, we calculated γ (Förster kinetics) of a set of γ and D values (Yokota–Tanimoto kinetics) to reproduce the experimental value (Φ_D) of PS25A. Although the experimental value of Φ_D is 0.60 ± 0.02, the calculation was carried out in the range of Φ_D between 0.55 and 0.65. Second, the C_A values of the PSA and APSA samples were evaluated from γ for PS25A (Förster kinetics) or γ for PS25A and D (Yokota–Tanimoto kinetics) which give a calculated value of Φ_D between 0.55 and 0.65 (eq 16) using eq 14. Next, the Φ_D values of PSA and APSA were calculated from eq 16 by the evaluated C_A. Finally, the Durbin–Watson factors (eq 9) for seven samples are compared for the assessment.

The calculated values of Φ_D which give the best Durbin–Watson factor on the assumption of both Förster kinetics and Yokota–Tanimoto kinetics are summarized in Table II. The calculated results suggest that the Yokota–Tanimoto theory offers by far the better relationship to explain the energy transfer taking place in our systems. Since there are only two parameters (D and γ for PS25A) in our systems, the value of 1.7 for the Durbin–Watson factor appears to be good enough to determine the kinetics.

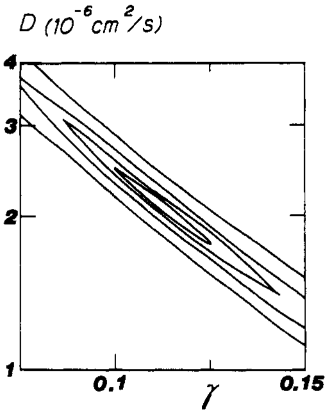

Figure 3. Comparison of calculated values based on the Yokota–Tanimoto theory using a set of diffusion constant (D) and γ ($=C_A/C_0$; see eq 3) of PS25A with experimental values. Contour lines show sets of D and γ of PS25A which give the same Durbin–Watson (DW) factor. Lines are DW = 1.7, 1.6, 1.4, and 1.0 from the inside.

Figure 3 shows the relationship between a set of D and γ for PS25A and the Durbin–Watson factor calculated from this set of D and γ. The diffusion constant D giving better values of the Durbin–Watson factor than 1.7 is found to be around (2.1 ± 0.2) × 10^{-6} cm^2/s. We determine this value to be the diffusion constant mainly due to the segmental motion of the polystyrene main chain near the chain end. Both the terminal anthryl group and the excimer formed somewhere near the chain end move in fluid solution by means of the segmental motion of the polystyrene chain, and this mobility is considered to have an effect on the energy transfer from the phenyl to the anthryl group.

As described in the Introduction, the dynamic process of cyclization has been investigated intensively and extensively.[6-10,31,32] Our result is concerned with the motion of at most several decades of monomer units near the chain end; thus they could be referred to the end-to-end collision of oligomers and polymers with rather low molecular weight. Let us examine the appropriateness of the obtained diffusion constant by comparison with cyclization data.

Basically, there are two factors to be considered as regards the cyclization process: the end-to-end distance and the diffusional motion for both ends of the polymer chain to encounter. Modes of molecular motion influencing the cyclization process would depend on the lifetime of the probe molecule. In fact, experiments using different probe molecules show different chain length dependences of rate constants for intramolecular end-to-end collision, k_{intra}. In the case of the cyclization of a polystyrene chain in a good solvent at room temperature, the chain dependence is described by $k_{\mathrm{intra}} \cong N^{-n}$ with $n = 1.5$ (N = degree of polymerization) monitoring excimer formation of pyrenyl groups at both chain ends,[6,7,32] while $k_{\mathrm{intra}} \cong N^{-n}$ with $n = 1.0$ monitors triplet–triplet annihilation between anthryl groups at both chain ends.[8] This difference of the chain length dependence results from the difference in probe lifetimes: a pyrene singlet, 250 ns; an anthracene triplet, 1 ms. Since we employ fluorescence probes, our data should be compared with the cyclization data obtained by monitoring the pyrene excimer.

In general, the distance a molecule or a group is able to diffuse within a time τ_{M} is described by eq 17 on the

$$L^2 = 6D\tau_{\mathrm{M}} \tag{17}$$

assumption of a three-dimensional random walk process. L is the root-mean-square displacement and D is the diffusion constant. We calculate values of D from the k_{intra} obtained by cyclization experiments monitoring pyrene excimer formation. L can be substituted by the averaged end-to-end distance of an N-mer, r_N, evaluated from eq 10, and τ_{M} can be substituted by the singlet lifetime of a pyrenyl group, which is expressed as eq 18 using the fluorescence lifetime of a pyrenyl group without excimer formation, τ_{F}, and k_{intra}

$$1/\tau_{\mathrm{M}} = 1/\tau_{\mathrm{F}} + k_{\mathrm{intra}} \tag{18}$$

The calculated values of D from the cyclization of a polystyrene chain in toluene at 22 °C[32] are 1.0×10^{-6} (100-mer), 1.1×10^{-6} (150-mer), and 1.4×10^{-6} (200-mer) cm^2/s. These values are not only of the same order but relatively close to our value. On the other hand, although the mode of the translational motion of the whole molecule is different from that of the segmental motion, a self-diffusion constant of low molecular weight polystyrene in dilute toluene solution has been measured to be 1.5×10^{-6} (M_{w} = 10 700) to 2.9×10^{-6} (M_{w} = 3100) cm^2/s by means of dynamic light scattering method.[34] Nearly the same values of the constant have also been obtained by using the pulsed field gradient NMR method.[35] Thus it could be concluded that (i) the mode of the cyclization process of polymers with rather low molecular weight is quite similar to that of the motion of the units near the end group detected by monitoring the energy transfer and (ii) the diffusion constant of 2×10^{-6} cm^2/s appears to be reasonable for the segmental motion of at most several decades of monomer units near the chain end.

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