excluded volume theories discussed in the section.

The parameter β does not seem to be highly affected by excluded volume. However, our result does not correspond to the value of −0.14 reported earlier[8] from the sedimentation coefficient and light-scattering data. The high sensitivity of β to experimental error in $[\eta]$ was pointed out in the previous section. Something similar also happens to the other properties[8] and, therefore, we conclude that the discrepancies in β are at least consistent within the range of error for the experimental data.

It was shown in the Revision of Theoretical Expressions section how the approximate eigenvalues lose their accuracy as $|\beta|$ increases. In our calculations for $N = 50$, this effect becomes significant for $\beta \leq -0.10$. The values of N employed in the intrinsic viscosity calculations in the two previous sections are in all interesting cases much larger than 50, and, thus, exact diagonalization results are impractical. Fortunately, the accuracy of the approximate eigenvalues increases with N, and, therefore, they should be appropriate even for the region $\beta \leq -0.10$ where our final results are located. Nevertheless, slight errors in the approximate eigenvalues may contribute somewhat to uncertainty in the final value of the very sensitive parameter β.

In conclusion, the statistical length obtained in this work is very close to that extracted from the more realistic Yamakawa–Fujii theory. This fact indicates that the results given for the wormlike chain formalism can be reproduced by the Simon model in the high molecular weight range (extension of the Simon model to shorter chains can be done by exact diagonalization of eq 9). It seems, therefore, that this simple model can be usefully applied to other dynamical properties for which the wormlike coil treatment became difficult.

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Static and Dynamic Studies on the End-to-End Intrachain Energy Transfer on a Polysarcosine Chain[1]

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ABSTRACT: Polysarcosines having a terminal β-naphthylamide group and a terminal (dimethylamino)naphthalenesulfonyl (dansyl) group were synthesized by the NCA polymerization method, and the intramolecular energy transfer from the naphthylamide group to the dansyl was studied in ethanol solution. The efficiency of the energy transfer at the photostationary state was over 0.9 for short chains having the number average degree of polymerization $\bar{n}$ smaller than 7. The efficiency decreased with an increase in the chain length, but it was still as large as 0.33 at $\bar{n} = 60$. To explain these results, two different mechanisms were considered, i.e., static and dynamic transfer. The former occurs between an energy donor and an acceptor which are closer than a critical distance r_0 at the time of excitation. The latter occurs between a donor–acceptor pair which is well separated at the time of excitation and eventually becomes closer than r_0 by the chain motion during the lifetime of the donor-excited state. The efficiencies observed for long chains were much higher than those expected for the static transfer which were evaluated from a Monte-Carlo conformational calculation. The efficiency for the dynamic transfer was separately evaluated from the fluorescence decay rate of the terminal naphthylamide group. The sum of the efficiencies observed for dynamic transfer and calculated for static transfer was in good agreement with the total efficiency observed in the photostationary state.

Recently, much attention has been focused on the use of the fluorescence probe method for the study of the conformations of a polymer chain in solution.[2] The method may not only clarify general conformational properties of polymer chains but also become a powerful approach to the study of functions of biopolymers.[3,4] There are several advantages in the fluorescence method. (1) The high sensitivity enables measurement at high dilution, which is needed for the study of intramolecular interactions. (2) Most of the fluorescence probes do not interact with each other in their ground states and hence do not disturb the conformational equilibrium of polymer chains in solution, making it possible to observe their "native" properties. (3) The fluorescence quenching or the excimer (exciplex) formation is a typical diffusion-controlled process,[5,6] and study of these phenomena on a polymer chain provides information on the chain dynamics. The last point is in contrast to the study of chemical reactions or charge-transfer interactions on a polymer chain which provides equilibrium or a static property of the chain.

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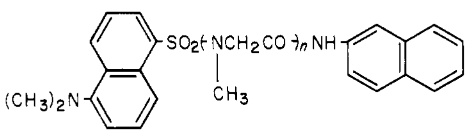
Information from the fluorescence probes is basic and easy to analyze when the probes are attached to both ends of a polymer chain of known chain length. There have been some studies along this direction. They include intramolecular excimer[7,8] or exciplex[9] formation on polymethylene and poly(ethylene glycol) chains[10] and intramolecular energy transfer on some poly(amino acid) chains.[11-16] However, there have been few cases dealing with the conformational dynamics and evaluating rate constants for diffusive motions of the terminal groups. Goshiki et al.[8] obtained the rate constants for intramolecular excimer formations in $PyCH_2OCO(CH_2)_jCOOCH_2Py$ (Py = pyrenyl group) in benzene. Frequencies of end-to-end encounters have been evaluated for intramolecular electron transfers in α-$N(CH_2)_j$-α-$N^{-\cdot}$ (α-N = α-naphthyl group)[17] and in $PI(CH_2)_jPI^{-\cdot}$ (PI = phthalimidoyl group)[18] systems by the ESR line-shape analysis. Recently, Haas et al.[19] reported the rate constants or the diffusion constants for the motions of ends of oligopeptide chains. However, most of these works have been concerned with short chains, and the rate constants for long polymer chains have been reported only for a few chains.[10,40]

In the present paper, a study of intramolecular energy transfer on a polysarcosine chain (I) is reported. The



(I)

energy of the singlet excited state of the terminal β-naphthylamide (β-N) group transfers to the (dimethylamino)naphthalenesulfonyl (dansyl = Dns) group by the Förster dipole–dipole mechanism,[5,6,11-14] and the excited Dns group emits its energy as a fluorescence at 520 nm (in ethanol). The radius of interaction sphere or the critical transfer distance r_0 for the energy transfer is as large as about 24 Å.[5,6] This is advantageous for the study of the behavior of long polymer chains.

Equilibrium conformations of polysarcosine chains have been studied by NMR[20-21] and by a Monte-Carlo calculation.[23] The most characteristic feature is the coexistence of cis and trans amide bonds in the main chain, which makes the chain conformations random and flexible. The high flexibility has been confirmed by a higher reactivity in an end-to-end reaction than those on other polymer chains.[24-27] The conformational dynamics of a polysarcosine chain have never been investigated.

The diffusion-controlled intrachain reaction has been theoretically investigated by Wilemski and Fixman[28] and subsequently by Doi et al.,[29] and a rate constant for the reaction has been derived. However, these theories are impractical in the present case, since they are based on exact solutions of the diffusion equation of the end-to-end motion in the absence of the reaction, and the solution can be obtained only for highly idealized chain models. Therefore, we did not try to apply these theories to the present system.

Table I
Characterization of Polymer Samples

	$\bar{n}$	Dns/N[a]	$\bar{n}$	Dns/N[a]
polymer I	5	0.92	20	0.94
	7	1.2	40	0.87
	10	1.2	60	0.95

	$\bar{n}$	N[b]		$\bar{n}$	Dns[c]
polymer II	10	1.0	polymer III	10	0.95
	35	1.0		20	0.94
	40	1.0		40	1.0

[a] The ratio of molar concentrations of dansyl and β-naphthylamide groups. [b] The fraction of polymer carrying the β-naphthylamide group. [c] The fraction of polymer carrying the dansyl group.

Experimental Section

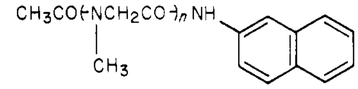
Syntheses of Low Molecular Weight Compounds. Sarcosine-β-naphthylamide. β-Naphthylamine was reacted with chloroacetyl chloride in a dioxane (2)–water (1) mixed solvent to afford β-chloroacetylnaphthylamine, which was recrystallized from methanol, mp 117 °C (lit.[30] mp 117–118 °C). The latter was dissolved in ethanol containing an excess of methylamine and kept at room temperature for 4 days. After the solvent and the amine were evaporated, aqueous $NaHCO_3$ was added, and the oil was taken up with benzene. The benzene solution was dried with sodium sulfate and evaporated. The residue was crystallized from petroleum ether and benzene to give a hygroscopic crystal: mp 58 °C; C/N ratio, calcd 5.58, found 5.57.

***N*-Dansylsarcosinedimethylamide.** Sarcosinedimethylamide[31] was mixed with an equal molar amount of dansyl chloride and a small excess of triethylamine in ether. An oil obtained after evaporating the mixture was recrystallized from benzene, mp 121 °C. Anal. Calcd: C, 58.5; H, 6.6; N, 12.0. Found: C, 58.8; H, 6.7; N, 12.1.

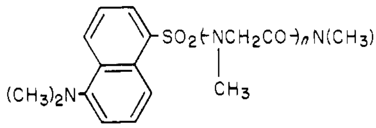
Synthesis and Characterization of Polymer Samples. Polysarcosines having energy donating and accepting chromophores (I) were synthesized by the NCA method. Sarcosine NCA was polymerized in dimethylformamide by using sarcosine-β-naphthylamide as the initiator. After the completion of the polymerization, a threefold excess of dansyl chloride was added, and the mixture was kept overnight. The polymer solution was poured into ether, and the precipitate was collected, washed with ether and acetone, and dried under vacuum. The number average degree of polymerization $\bar{n}$ was calculated from a stoichiometric ratio of the NCA and the initiator,[32]

$$\bar{n} = [\mathrm{NCA}]/[\mathrm{initiator}] + 1 \qquad (1)$$

The polymer should have a narrow Poisson-type molecular weight distribution.[33] Polysarcosine having no accepting group (II) or



(II)



(III)

no donating group (III) was synthesized in a similar manner, using an acetic anhydride/pyridine mixture instead of dansyl chloride (II) or using sarcosine dimethylamide as initiator instead of sarcosine-β-naphthylamide (III), respectively.

The amounts of chromophores incorporated into the ends of polysarcosines were measured by the absorbance at 335 nm for a dansyl group and at 293 nm for a β-naphthylamide group, the absorbance of the dansyl group at 293 nm being subtracted from the latter. The extinction coefficient for the naphthylamide group was determined with *N*-acetyl-β-naphthylamine, and that for the dansyl group was determined with *N*-dansylsarcosinedimethylamide. Ratios of the observed amount to the calculated one for each chromophore are listed in Table I. The incorporation of the two terminal groups was nearly quantitative.

Other Reagents. Commercial *N*-acetyl-β-naphthylamine was used after recrystallization from benzene. Spectrograde ethanol was redistilled from Magnesium metal immediately before use.

Measurements. UV and visible spectra were recorded on a Shimadzu UV-210 instrument. Fluorescence spectra were obtained by Hitachi MPF-2A and MPF-4 instruments. All fluorescence and excitation spectra were corrected by using Rhodamine B as the reference substance. Single-photon counting measurements were carried out on an Ortec 9200 nanosecond fluorescence spectrometer system. All measurements were carried out in an air-saturated ethanol solution at room temperature. The

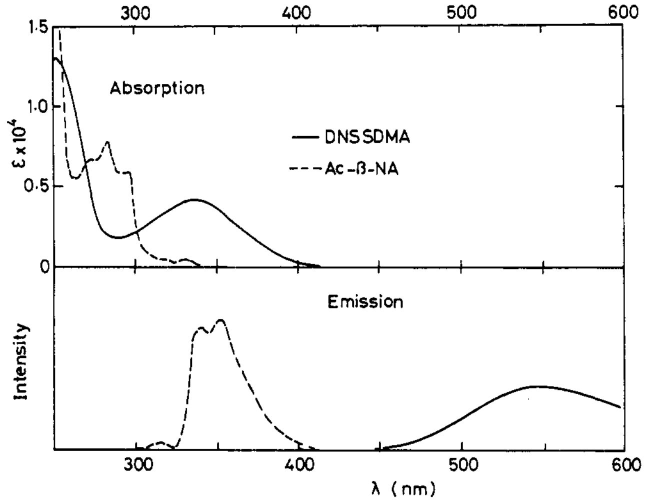


Figure 1. Absorption and emission spectra of *N*-dansylsarcosinedimethylamide (—) and *N*-acetyl-β-naphthylamine (- - -) in ethanol solution.

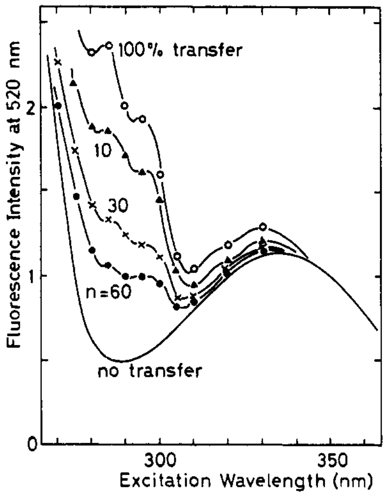


Figure 2. Fluorescence excitation spectra of polymer in ethanol solution. Numbers indicate the degree of polymerization $\bar{n}$. "No transfer" denotes the spectrum of polymer III and "100% transfer" is the absorption spectrum of polymer I normalized in a manner so that the intensity at 350 nm is the same as that in the excitation spectra.

concentration of each chromophore was adjusted to 2 × 10^{-6} M for the measurement of stationary spectra and to 10^{-5} M for the single-photon measurement.

Results and Discussion

Intramolecular End-to-End Energy Transfer. Figure 1 shows absorption and fluorescence spectra of model compounds for the two terminal groups, i.e., *N*-acetyl-β-naphthylamine and *N*-dansylsarcosinedimethylamide. The fluorescence band of the former overlaps the absorption band of the latter, indicating excitation energy can transfer from the former to the latter.[5,6] The excitation energy of a dansyl group is emitted as fluorescence at 520 nm with a high quantum yield. Figure 2 shows fluorescence excitation spectra of the bifunctional polysarcosines (I) monitored at the fluorescence band of the dansyl group (520 ± 20 nm). The spectrum indicated as "no transfer" is that of the polymer III, in which no chain-length dependence was seen with $\bar{n}$ = 10, 20, and 40. With the introduction of a β-naphthylamide group into the second end of the polysarcosine chain, a characteristic band corresponding to the absorption band of the β-naphthylamide group appeared in the excitation spectra around 290 nm, indicating the energy transfer. The

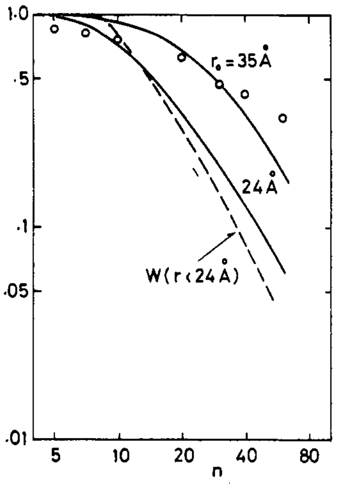


Figure 3. Log–log plot of the efficiency of energy transfer as a function of the degree of polymerization: (○) observed points in a photostationary state; (- - -) static-transfer efficiency calculated by eq 5; (—) static-transfer efficiency calculated by eq 10.

transfer efficiency, i.e., the fraction of donor-excited energy which transferred to the dansyl group, can be calculated as,[11-13]

$$T = \frac{h - h_0}{h_{100} - h_0} \qquad (2)$$

where h, h_0, and h_{100} are the intensity of the excitation spectra of polymer I, that corresponding to no transfer (polymer III), and that corresponding to 100% transfer, respectively. The value for the 100% transfer can be estimated from absorption spectra of polymers I with different chain lengths, which were virtually identical. The transfer efficiencies calculated at 290 nm are plotted as a function of the degree of polymerization $\bar{n}$, in Figure 3. The efficiency decreases monotonically with the chain length, but it is noted that the efficiency is still as high as 0.33 at $\bar{n}$ = 60. This finding suggests that a contribution of chain motions to mix up cyclic and extended conformations is significant, since the static probability for such a long chain as $\bar{n}$ = 60 to take cyclic conformations is negligibly small (see below). A plot of log ($T^{-1} - 1$) against log $\bar{n}$ was reasonably linear with a slope of about unity. Since the intrinsic transfer rate constant is inversely proportional to the sixth power of the distance between energy donor and acceptor (eq 3 below), the slope should be 6 when a polymer chain takes a regular conformation. The sixth power dependence has actually been found in oligoprolines in ethanol solution.[11,12] The slope of unity observed in the polysarcosine system indicates that the polymer does not take any regular conformation, as has been reported.[20-23] The same result has also been reported for short oligoprolines (n = 0–5) whose chain lengths are too short to assume any regular conformations of polyprolines.[16] However, there can be no simple explanation for the slope of unity at present, since the total efficiency consists of static and dynamic terms, both of which depend on n in a quite different manner (see below).

It is strange that the efficiency does not reach 100% even at the shortest chain ($\bar{n}$ = 5). The incompleteness of the energy transfer was confirmed by the presence of a weak but definite fluorescence of the naphthylamide moiety for these short chains.

The Static and the Dynamic Intramolecular Energy Transfer. Fluorescence quenching or energy transfer is a typical diffusion-controlled process, and a partial differential equation for such a process in an intramolecular system has been solved.[28,29] However, this equation has been derived only for some idealized chain models and does not seem to apply to the present case. In this study, the above data will be interpreted in a more practical and intuitive manner.

According to Förster's theory, an intrinsic transfer rate constant at a given separation r between the energy donor and the acceptor is,[5,6]

$$k = \frac{1}{\tau}\left(\frac{r_0}{r}\right)^6 \tag{3}$$

where τ is a natural lifetime of the donor in the absence of an acceptor, and r_0 is the critical transfer distance. The above function can be reasonably approximated by

$$k = \infty \quad (r \le r_0); \qquad k = 0 \quad (r > r_0) \tag{4}$$

In the framework of this "active sphere" approximation, the energy transfer is assumed to take place concurrently with the excitation when the donor–acceptor pair is closer than r_0. This type of energy transfer may be called a static transfer, and its efficiency is,

$$T_s = W(r \le r_0) \tag{5}$$

where $W(r \le r_0)$ is a probability that the pair is closer than r_0.

Contrary to the static transfer, the dynamic transfer is a contribution from a donor–acceptor pair which is separated farther than r_0 at the time of the excitation of the donor. If the polymer conformations change frequently enough during the lifetime of the donor, an encounter between the excited donor and the acceptor becomes possible, and as a consequence, the energy transfer occurs. Obviously, the efficiency of the dynamic transfer depends on the lifetime of the donor-excited state and the dynamic flexibility of the intervening polymer chain. Within the framework of the active sphere model (eq 4), the efficiency of the dynamic transfer can be expressed as,

$$T_d = \frac{k_c}{k_c + k_0}[1 - W(r \le r_0)] \tag{6}$$

where k_c is an average rate constant for an extended chain to form a cyclic conformation with $r \le r_0$, and k_0 is the reciprocal of the lifetime of the donor-excited state in the absence of the acceptor. The total efficiency observed in the photostationary state (Figure 3) is the sum of the two contributions:

$$T = T_s + T_d \tag{7}$$

In the following sections, the two terms will be evaluated theoretically and experimentally.

Evaluation of the Static Transfer Efficiency. To begin with, the critical transfer distance r_0 should be calculated according to Förster's equation,[5,6]

$$r_0^6 = \frac{9000(\ln 10)\kappa^2\eta_0}{128\pi^5 N n_0^4}\int f(\bar{\nu})\epsilon(\bar{\nu})\,\frac{d\bar{\nu}}{\bar{\nu}^4} \tag{8}$$

where κ^2, η_0, N, and n_0 are the orientation factor, the fluorescence quantum yield of the donor, Avogadro's number, and the refractive index of the solvent (ethanol, 1.33). As to the value of κ^2 there have been several studies.[34-36] However, it is certain that it can be taken as $^2/_3$ when rotational motions of the two terminal chromophores are sufficiently fast, as in the present case which has been carried out in a low viscous solvent at room temperature. The quantum yield was measured for N-acetyl-β-naphthylamine with quinine sulfate as a reference substance. The result (0.25, at room temperature) was in good agreement with the literature value[37] (0.24 at 20 °C). The integral in eq 8 was evaluated from the overlap of the normalized fluorescence spectrum of N-acetyl-β-naphthylamine with the absorption spectrum of N-dansylsarcosinedimethylamide. By the use of these parameters, r_0 was calculated to be 24 Å, which is reasonable as compared with analogous donor–acceptor pairs.[11,12,38]

The ring-closure probability $W(r \le r_0)$ should be obtained from the distribution of end-to-end distances of the polysarcosine chain. The distribution cannot be evaluated experimentally, and we can only estimate it by a theoretical calculation. A Monte-Carlo conformational calculation has been carried out for a hard-sphere model of polysarcosine chain allowing cis as well as trans amide bond conformations.[23] The results were consistent with NMR data and also with data from end-to-end reactions[24,25] and interactions.[26,27] Using the distribution obtained by the Monte-Carlo calculation and taking r_0 = 24 Å, we calculated the static transfer efficiency (eq 5). The result is shown in Figure 3 (broken line) as a function of $\bar{n}$. The static-transfer efficiency calculated is substantially smaller than the experimental points of the total efficiency, especially at large $\bar{n}$, indicating an essential contribution of the dynamic transfer.

The static-transfer efficiency can be evaluated more precisely in an alternative way. From eq 3, a probability of the energy transfer for a donor–acceptor pair separated by a given distance r can be expressed as

$$p = \frac{r_0^6}{r^6 + r_0^6} \tag{9}$$

The static-transfer efficiency is

$$T_s = \int_0^\infty pW(r)\,dr \tag{10}$$

where $W(r)$ denotes the distribution of end-to-end distance. Using the distribution calculated by the Monte-Carlo method, we evaluated T_s for r_0 = 24 and 35 Å. The results are shown in Figure 3 by solid lines. The difference between the two curves calculated according to eq 5 and 10, both using r_0 = 24 Å, is not important as it should be. To test the possibility that the static transfer efficiency fits the experimental data of the total efficiency, r_0 was increased to 35 Å and T_s was calculated by eq 10. It is clear that even if one takes r_0 = 35 Å, which is unacceptably large, the experimental data of the total efficiency cannot be reproduced without considering dynamic transfer.

Evaluation of the Dynamic-Transfer Efficiency. The rate of dynamic-energy transfer can be measured as an enhanced fluorescence decay of the energy donor when it is excited by a pulsed light.[5,6] In our experiment, an air-discharge lamp was used as a light source, the line at 294 nm being passed through a band-pass filter. The fluorescence of the donor was monitored by using a band-pass filter at 360 nm. The decay curves for polymers I having different chain lengths are shown in Figure 4, together with the shape of the pulsed light. Even in the shortest chain ($\bar{n}$ = 5), the donor fluorescence shows a finite lifetime, indicating the presence of conformations unfavorable for the energy transfer, at least at the time of the excitation. The lifetime becomes longer when the chain length is increased. The decay curves did not follow first-order kinetics; possible reasons follow: (1) Quenching by oxygen in solution may cause an initial fast drop of the decay curve. (2) The distribution in the cyclization rate constant k_c due to the distribution of the end-to-end distances may appear as a curvature in the decay curve, expecially for short polymers.[14,19,39,40] For relatively long polymers, the decay is expected theoretically to follow

Table II
Rate Constants and Efficiencies for Dynamic Energy Transfer

$\bar{n}$	k_{obsd}, s^{-1}	k_c, s^{-1}	$W(r \leqslant 24$ Å$) =$ T_s	T_d	T_{calcd}	T_{obsd}
5	5.3×10^8	3.1×10^8	1.0		1.0	0.85
20	3.8×10^8	1.7×10^8	0.28	0.32	0.60	0.63
30	3.4×10^8	1.3×10^8	0.14	0.33	0.47	0.47
40	3.1×10^8	1.0×10^8	0.08	0.29	0.37	0.43
60	2.9×10^8	0.7×10^8	0.04	0.25	0.29	0.33
AcNA[a]	2.1×10^8					
40[b]	2.2×10^8					

[a] *N*-Acetyl-β-naphthylamine. [b] Polymer II. [c] Relative errors for k_{obsd} and k_c are within 10%, and those for T_{obsd} are within 5%.

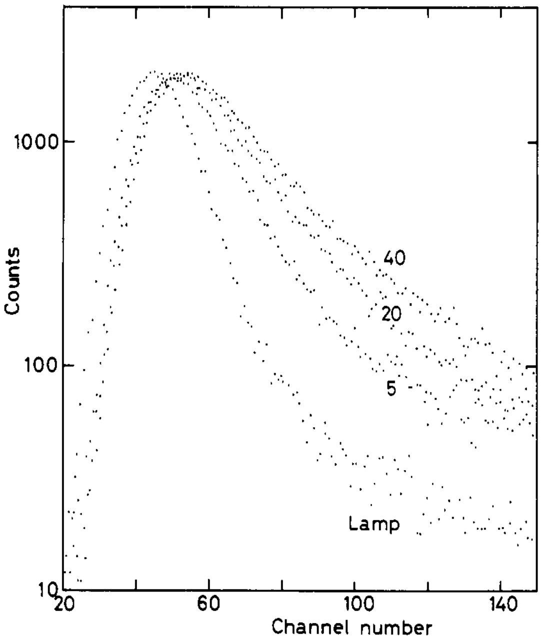


Figure 4. Fluorescence decay curve of polymer I. Numbers indicate the degree of polymerization. "Lamp" denotes the shape of pulsed light (6.65 channels = 1 ns).

first-order kinetics.[28,29] At the present stage, it seemed most appropriate to take an "average" rate constant k_{obsd} of the donor fluorescence decay at the medium region of the decay curve (count number = 1000–200). The width of the light pulse has been taken into account by using a simulation method. The average rate constants are listed in Table II. In the same table, the average rate constants for polymer II and *N*-acetyl-β-naphthylamine are also shown. With the introduction of a dansyl group at the second end of the polymer, the donor fluorescence becomes quenched, and its rate is faster for shorter chains. The observed quenching rate should be composed of two terms as

$$k_{obsd} = k_c + k_0 \qquad (11)$$

where k_c and k_0 are rate constants as defined in eq 6. k_0 is evaluated from the decay of polymer II and *N*-acetyl-β-naphthylamine. From eq 11, the cyclization rate constants k_c were calculated and are listed in Table II. They are of the order of 10^{-8} s^{-1} and decrease with an increase in the chain length. These rate constants are in a reasonable region as compared with similar data obtained from the electron transfer,[17,18] excimer formation,[8] and triplet–triplet annihilation on long polystyrene chains.[41]

The data in Table II and the Monte-Carlo values of $W(r \leq r_0)$ are used to calculate the dynamic-energy-transfer efficiency according to eq 6, and results are listed in Table II. The contribution of the dynamic transfer is larger for longer chains. The total transfer efficiency was obtained as a sum of the static term calculated by eq 5 and the dynamic term in Table II. Results are in excellent agreement with the data obtained in a photostationary state, indicating a consistency of data in Table II.

Conclusion

In the present study, the importance of chain motions to determine the efficiency of intrachain energy transfer on a long chain was demonstrated. The average rate constant for the chain motion was evaluated from the fluorescence decay rate and was found to be consistent with the data from the photostationary state.

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(38) As to the active sphere radius r_0' for intermolecular electron transfer, there are some arguments. If one assumes a uniform distribution of energy acceptors around an energy donor, the condition that the total transfer efficiency calculated by the active sphere model is the same as that for the exact case, yields,

$$\int_0^{r_0'} 4\pi r^2\,dr = \int_0^{\infty} \frac{r_0^6}{r_0^6 + r^6} 4\pi r^2\,dr$$

where r_0 denotes the Förster distance. Integration gives $r_0' = 1.16r_0$. The above equation means the radius of the active sphere should be a little larger than the Förster distance. Jabłoński (A. Jabłoński, *Bull. Acad. Pol. Sci., Ser. Sci. Math., Astron. Phys.*, **6**, 663 (1958)) reported a similar calculation and suggested $r_0' = 1.33r_0$. On the other hand, in the intramolecular case, the distribution of acceptors cannot be uniform and, strictly speaking, there can be no simple way to define r_0'. In fact, a comparison of static transfer efficiency for the active sphere model (broken line in Figure 3) with that for the exact case (solid line, $r_0 = 24$ Å) indicates that r_0' should be smaller than r_0 for $n < 12$ but larger than r_0 for $n < 12$. However, since the difference between the two lines is not significant, it is sufficient to use the Förster distance as an active sphere radius in our approximate analysis. A small change in the active sphere radius did not change any conclusions in the text. The authors wish to thank the referee for informing us of this point.
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Phase Transition Behavior of the Isolated Polymer Chain

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ABSTRACT: A mean field theory of chain dimensions is formulated which is very similar to the van der Waals theory of a simple fluid. In the limit of infinite chain length, the chain undergoes a Landau-type second-order phase transition. For finite chains, the transition is pseudo-second-order. At low temperatures, the chain is in a condensed or globular state, and the mean square gyration radius $\langle S^2 \rangle$ varies as $r^{2/3}$ where r is proportional to chain length. At high temperatures, the chain is in a gaslike or coil state where $\langle S^2 \rangle$ varies as $r^{6/5}$. In the globular state, fluctuations in $\langle S^2 \rangle$ are very small, whereas they are very large in the coiled state. A characteristic feature of the theory is that ternary and higher order intramolecular interactions are approximated. At high temperatures, only binary interactions are important, but at low temperatures, many of the higher order terms contribute. An important conclusion of this study is that a polymer chain does not obey ideal chain statistics at the Θ temperature. Although the second virial coefficient vanishes at Θ, the third virial coefficient does not; its presence is responsible for the perturbation of the chain statistics. For an infinite chain, Θ and the second-order phase-transition temperature are identical. For finite chains, the pseudo-second-order transition temperature is less than Θ. When generalized to d dimensions, the theory yields at low temperatures $\langle S^2 \rangle^{d/2} \sim r$ for all d and at high temperatures $\langle S^2 \rangle \sim r^{6/(d+2)}$, $d < 4$, and $\langle S^2 \rangle \sim r$, $d > 4$.

Historical Perspective

Recently, there has been a spate of theoretical papers dealing with the "collapse transition" of a flexible polymer chain in a poor solvent.[1-12] As early as 1960, Stockmayer[13] suggested that "even atatic chain molecules must collapse to a rather dense form if the net attraction between their parts becomes sufficiently large". However, theoretical interest in this subject remained relatively restrained until experiments gave evidence of the transition not only in synthetic polymers,[14-18] but also in biopolymers such as DNA.[19-21] Interest in this subject has also been stimulated by the recent arrival of neutron scattering as an analytical tool for the investigation of chain configurations and dynamics[22,23] and by theoretical advances (renormalization group methods) in treating phase-transition phenomena.

In 1972, in a terse note of less than 500 words, deGennes[24] made the remarkable observation that a correspondence exists between the self-excluded volume problem in polymers and critical point phenomena. He showed that renormalization group methods were applicable to polymers in dilute solution. Later, deGennes[2] also noted that the Θ point of a polymer solution was probably not an ordinary second-order critical point, but a *tricritical* point. His argument for a tricritical point is somewhat indirect. The evidence is based on the observation that at the Θ point the third virial coefficient cannot be ignored. This has the theoretical implication that in a Landau free-energy expansion near the Θ point, terms to sixth order have to be retained because the coefficient of the sixth-order term is proportional to the third virial coefficient.[2] It is this form of the free energy that is capable of yielding a tricritical point.[25,26]

The identification of the Θ point as a probable tricritical point and the extension of deGennes ideas to the semi-