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Diffusion and Reaction Rates of End-Labeled Polystyrenes in Semidilute Solution Studied with Luminescent Triplet Probe

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ABSTRACT: The diffusion-controlled quenching rate constants, k_q, between two end-labeled macromolecules (polystyrylbenzil and polystyrylanthracene) in the presence of inert polystyrene in benzene or cyclohexane have been measured for polymer concentrations, C, up to 0.30 kg/dm^3 with a luminescent triplet probe method. The k_q in benzene increases with increasing C until C reaches about 0.05 kg/dm^3, while k_q in cyclohexane decreases monotonously with increasing C. The k_q in benzene begins to decrease with further increases in C at the point corresponding to the crossover from the dilute to the semidilute region. In the semidilute region, k_q in benzene is proportional to $C^{-\alpha}$, with α = 1.7–1.9. This value of α coincides with the prediction of $D_{\mathrm{self}} \propto C^{-1.75}$ by de Gennes' dynamic scaling theory with a reptation model. The importance of probing distance, d, regulated by the time scale of the measurements, for the interpretation of diffusion data is emphasized. The present results suggest that the onset of the gel effect in radical polymerization corresponds to the point where molecular diffusion of the reacting species becomes restricted to reptation.

Luminescence spectroscopy is a powerful research tool in the study of structure, mobility, and reaction of both synthetic and biological macromolecules.[1] In comparison with fluorescence spectroscopy, information from excited triplet-state probes detected by phosphorescence, delayed fluorescence, or triplet-triplet absorption is of special importance, since much longer lifetimes of excited triplet states compared with fluorescence lifetime allow study of mobility and reactions reflecting the large-scale motions of the whole polymer chain in solution[2–5] and slow motions in solid state.[6]

In previous papers,[2,3] quenching rates of phosphorescence of the benzil group at a chain end of polystyrene (PS-B) by the anthryl group at a chain end of another polystyrene (PS-A) were measured in dilute benzene, butanone, or cyclohexane solution. The effects of molecular weight and solvent power on the intermacromolecular quenching rates have been discussed. In the present paper, the measurements of the quenching rates are extended to the reactions in the semidilute region, i.e., in benzene and cyclohexane solutions with polymer concentration C = 0.05–0.30 kg/dm^3, by using a 10-ns nitrogen laser pulse.

The measurements of quenching rate constants between two end-labeled monodisperse polymers in the semidilute region are supposed to provide valuable information concerning two recent topics in polymer chemistry and physics.

The first is about dynamics of polymer chains in semidilute and gellike solutions. The dynamic scaling theory and reptation model proposed by de Gennes[7–9] have predicted the concentration and molecular weight dependences of two different modes of diffusion: cooperative diffusion of the pseudogel (D_{coop}) and macroscopic self-diffusion of one labeled chain (D_s). Over the past several years, Adam and Delsanti[10] have revealed that D_{coop} is proportional to $C^{0.67}$ and independent of the number of monomer units, N, by using quasielastic light scattering. Klein[11] and Hervet et al.[12] have ascertained the de Gennes prediction of $D_s \propto N^{-2}C^{-1.75}$ by measuring the molecular weight dependence of macroscopic self-diffusion of deuterated polyethylene and by measuring the concentration dependence of self-diffusion of end-labeled polystyrene with a forced Rayleigh light scattering technique, respectively. The N dependence of the mutual diffusion coefficient in polymer melt has been studied for the poly(vinyl chloride)/poly(ϵ-caprolactone) system.[13] The triplet probe technique also provides another experimental approach for studying self-diffusion and large-scale intramolecular relaxation in the time scale up to 10 ms in semidilute solution. The former is discussed in the present paper.

The second topic related to the present paper is the onset of the gel effect in free-radical polymerization. The sudden increase in the rate of polymerization observed at the intermediate or later stage of polymerization is called the gel effect and has been shown by many investigators to be due to the diffusion control of the termination process caused by the increasing viscosity of the system.[14] With the passage of time this termination process between two polymeric radicals has become widely recognized to be a diffusion-controlled process even in the initial stage of polymerization, in other words, even before the onset of the gel effect.[15] Thus the onset of the gel effect has been studied again recently by several investigators who relate it to the close packing of macromolecules with unperturbed dimensions,[16] to the formation of chain entanglements,[17,18] to a change in the rate-determining step from segmental diffusion to translational diffusion,[19] to the free volume concept,[20,21] and to the onset of reptative motion.[22] The present results with the triplet probe give a general picture for the molecular weight, concentration, and solvent power dependences of the diffusion-controlled rate constants between two end-labeled monodisperse polymers.

Experimental Procedures

Materials. Benzil or anthracene was attached to the chain end of anionically prepared polystyrene as previously reported.[2] Molecular weights and molecular weight distributions of poly-

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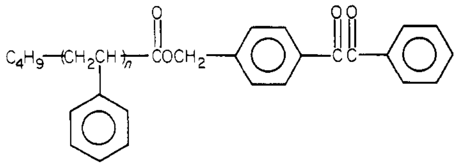
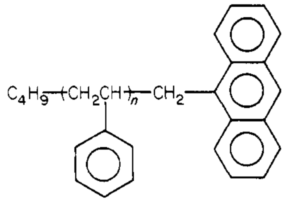
Table I
Characteristics of PS-B, PS-A, and PS

polymer	M_n	M_w/M_n	N of PS chain	% anthryl groups at a chain end	R_g in benzene, nm	C^* in benzene, kg/dm^3
PS60-B	6.40×10^3	1.10	60		2.8	0.52
PS210-B	2.19×10^4	1.06	208		5.7	0.20
PS340-B	3.50×10^4	1.24	336		8.3	0.12
PS640-B	6.60×10^4	1.10	635		11.3	0.083
PS1200-B	1.29×10^5	1.06	1240		16.5	0.051
PS2900-B	2.99×10^5	1.10	2870		27.8	0.025
PS71-A	7.54×10^3	1.13	71	95.9	3.2	0.45
PS400-A	4.20×10^4	1.28	404	51.2	9.5	0.11
PS800-A	8.30×10^4	1.22	798	59.2	13.8	0.064
PS3300-A	3.45×10^5	1.23	3320	72.7	32.3	0.021
PS3900-A	4.11×10^5	1.34	3940	44.0	37.8	0.017
PS98	1.02×10^4	1.02	98		3.6	0.38
PS410	4.28×10^4	1.01	412		8.3	0.12
PS1000	1.07×10^5	1.01	1030		14.3	0.061
PS3800	3.90×10^5	1.10	3750		32.6	0.021

styrene having the benzil or anthryl group at the chain end (PS-B or PS-A, respectively) measured with a gel permeation chromatograph (TSK HLC-802UR) as well as the anthryl group content at the chain end of PS-A measured with an ultraviolet spectrophotometer are shown in Table I. The benzil group content at the chain end in several PS-B samples was determined to be about 80% from visible absorption spectra. Standard polystyrenes (PS) from Pressure Chemical Co. and TSK were used for preparing solutions with definite polymer concentrations C. Characteristics of PS are also given in Table I. Dotite Luminasol grade benzene and cyclohexane were used as solvents for the phosphorescence measurements.



PS-B



PS-A

Measurements of Quenching Rate Constants. The degassed and sealed sample solution was excited by a nitrogen laser pulse (337 nm) with a half-width of 10 ns (Avco C950B). The phosphorescence decay from the sample (λ 560 nm) was detected by a photomultiplier, amplified, and fed into a transient time converter (Riken Denshi TCG-8000) which permitted recording of the decay curve and its semilogarithmic plot on an ordinary pen recorder. The use of cutoff filters for λ <530 nm and a cutoff gate circuit operating for 100 ns after the pulse irradiation enabled us to use the 337-nm pulse from the nitrogen laser with no correction for fluorescence or delayed fluorescence emission from PS-A. Other procedures for the measurements were the same as previously reported.[2]

The bimolecular rate constant of phosphorescence quenching, k_q, was calculated by using

$$1/\tau = 1/\tau_0 + k_q[\mathrm{A}] \tag{1}$$

where τ and τ_0 are triplet lifetimes of phosphorophore obtained from the decay curves in the presence and absence of quencher, respectively, and [A] is the anthryl group concentration. Three samples with different concentrations of PS-A (0, 1.5×10^{-5}, and 3×10^{-5} M) for each system were prepared in most cases, and the two values of k_q in each system agreed with each other to a degree similar to that of the cases shown in Table II of the previous paper.[3] The range of [B] was from 1×10^{-4} to 1×10^{-3} M. The reciprocal lifetimes $1/\tau_0$ of PS-B in semidilute solutions were between 3×10^4 and 8×10^4 s^{-1} at 40 °C in benzene and between 1×10^4 and 2×10^4 s^{-1} in cyclohexane. The percentage error for k_q was usually about 10% but in some cases reached about 20%.

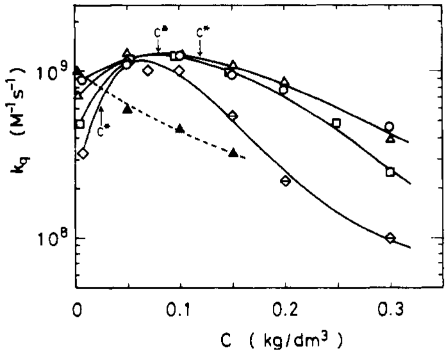


Figure 1. Dependence of k_q at 30 °C on the polymer concentration, C, in benzene (○, △, □, ◇, ◊) and in cyclohexane (▲). The combinations of polymers are PS60B-PS71A-PS98 (○), PS340B (PS210B)-PS400A-PS410 (△, ▲), PS640B-PS800A-PS1000 (□), and PS2900B (PS1200B)-PS3900A (PS3300A)-PS3800 (◇, ◊). Corresponding overlap concentrations C^* are also shown for the systems represented by the symbols ◇, □, and △ (from left to right).

Measurements of Solution Viscosity. The solution viscosity, η, of the sample was measured at 30 °C by using a Ubbelohde-type capillary viscometer. The value of 5.6×10^{-3} kg m^{-1} s^{-1} for the viscosity of benzene was used as a standard for calculation.

Results and Discussion

Rate Constants between PS-B and PS-A in the Dilute and Semidilute Regions. The rate constants, k_q, for quenching of PS-B by PS-A measured in the present work are summarized in Table II. The reduced rate constants, $k_q\eta_0/T$, calculated in order to remove the influence of reaction temperature, T, and solvent viscosity, η_0, on k_q,[3] are also given in Table II. The values of k_q in benzene for polymer concentration C = 0.05–0.10 kg/dm^3 lie in the vicinity of 1×10^9 M^{-1} s^{-1} independent of N and decrease with further increase in C.

Dependences of k_q on C are shown in Figure 1, including the results obtained in the dilute region.[3] In the good solvent (benzene), k_q increases strongly as the solution is changed from the dilute to semidilute region. This increase is more marked for larger N of PS-B and PS-A in the system, and k_q values for different N substantially agree

Table II
Quenching Rate Constants, k_q, and Reduced Rate Constants, $k_q\eta_0/T$, between PS-B and PS-A in Benzene (BZ) and Cyclohexane (CH) in Semidilute Solution

phosphorophore	quencher	inert polymer	solvent	polymer concentration, kg/dm^3				$k_q \times 10^{-9}$, M^{-1} s^{-1}			$k_q\eta_0/T$, J/(K·mol)
				C_{PSB}	C_{PSA}	C_{PS}	C_{total}	20 °C	30 °C	40 °C	
PS60-B	PS71-A	PS98	BZ	0.006	<0.0002	0.044	0.05	0.73	1.04	1.40	1.91
				0.006	<0.0002	0.094	0.10	0.99	1.23	1.36	2.20
				0.006	<0.0002	0.14	0.15	0.85	0.95	1.29	1.89
				0.006	<0.0002	0.19	0.20	0.60	0.77	0.84	1.36
				0.006	<0.0003	0.29	0.30	0.40	0.47	0.57	0.88
PS340-B	PS400-A	PS410	BZ	0.018	<0.001	0.032	0.05	1.21	1.37	1.47	2.51
				0.018	<0.001	0.083	0.10	1.11	1.32	1.37	2.35
				0.018	<0.001	0.13	0.15	0.99	1.12	1.35	2.13
				0.018	<0.001	0.18	0.20	0.86	0.89	1.12	1.77
				0.018	<0.001	0.28	0.30	0.40	0.39	0.45	0.77
PS210-B	PS400-A	PS410	CH	0.011	<0.001	0.036	0.05	turbid	0.59	0.72	1.62
				0.011	<0.001	0.087	0.10	turbid	0.45	0.71	1.42
				0.011	<0.002	0.14	0.15	turbid	0.32	0.46	0.95
PS640-B	PS800-A	PS1000	BZ	0.033	<0.003	0.015	0.05	1.07	1.25	1.36	2.27
				0.033	<0.003	0.065	0.10	1.13	1.23	1.51	2.38
				0.033	<0.003	0.12	0.15	0.88	0.98	1.15	1.86
				0.033	<0.005	0.21	0.25	0.39	0.48	0.67	0.85
				0.066	<0.005	0.23	0.30	0.18	0.25	0.33	0.46
PS2900-B	PS3900-A	PS3800	BZ	0.030	<0.009	~0.02	0.05	1.09	1.18	1.23	2.17
				0.046	<0.009	~0.02	0.07	1.00	1.03	1.33	2.06
				0.057	<0.015	~0.03	0.10	0.80	1.03	1.34	1.93
PS1200-B	PS3300-A	PS3800	BZ	0.065	<0.014	~0.07	0.15	0.35	0.54	0.58	0.89
				0.065	<0.019	~0.12	0.20	0.26	0.22	0.35	0.51
				0.065	<0.020	~0.22	0.30	0.10	0.10	0.14	0.21
PS210-B	PS400-A	PS3800	BZ	0.022	<0.003	0.18	0.20	0.49	0.53	0.52	0.96
PS640-B	PS800-A	PS3800	BZ	0.066	<0.006	0.13	0.20	0.38	0.42	0.44	0.77

with one another at $C = 0.05$ kg/dm^3. The overlap concentration, C^*, corresponding to the crossover from the dilute to semidilute region was calculated according to[10]

$$C^* = M/(N_A R_g^3) \tag{2}$$

$$R_g = 1.45 \times 10^{-2} M_w^{0.595} \text{ nm} \tag{3}$$

where M is the molecular weight of the polymer, N_A is Avogadro's number, and R_g is the radius of gyration of the polymer at infinite dilution. The values of R_g and C^* for the present samples in benzene are shown in Table I.

The initial large increase in k_q shows that a simple correlation of k_q with the self-diffusion of the polymer is hardly to be expected, since the viscosity, η, of the solution increases considerably as shown in Figure 2 and hence the self-diffusion of the polymer diminishes with increasing C. North and Reed[23] have reported an increase in termination rate constant, k_t, in the initial stage of radical polymerization with increasing polymer concentration in good solvents, and a theoretical treatment on the concentration dependence of k_t in dilute solution has also been given by Mahabadi and O'Driscoll.[24]

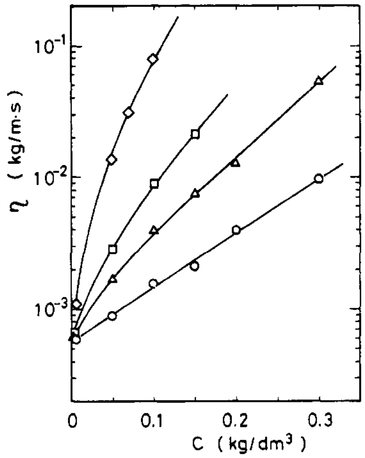


Figure 2. Solution viscosity, η, at 30 °C vs. polymer concentration C. Symbols are the same as in Figure 1.

Rehage et al.[25] have reported that the macroscopic diffusion coefficient of polystyrene in a good solvent (toluene) measured under a macroscopic concentration gradient increases strongly with increasing C and passes through a maximum at $C = 0.25$–0.40 kg/dm^3. The macroscopic (mutual) diffusion coefficient, D, in a polymer–solvent system is divided into a hydrodynamic term and a thermodynamic term as in

$$D = (1/f)C(\partial\mu/\partial C)_{T,P}/N_A \tag{4}$$

where f is the friction coefficient of a polymer molecule and μ is the chemical potential of the polymer. Rehage et al.[25] attributed the remarkable increase in D to an increase in the thermodynamic term $C(\partial\mu/\partial C)_{T,P}$ with increasing C. The chemical potential is related to the osmotic compressibility by

$$(\partial\mu/\partial C)_{T,P} = (1 - vC)(M/C)(\partial\pi/\partial C)_{T,P} \tag{5}$$

where v is the specific volume of the polymer. Then the combination of eq 4 with eq 5 gives[26]

$$D = (k_B T/f)(1 - vC)(M/N_A k_B T)(\partial\pi/\partial C)_{T,P} = D_s(1 - vC)(M/N_A k_B T)(\partial\pi/\partial C)_{T,P} \tag{6}$$

with the definition of the self-diffusion coefficient, D_s, given as

$$D_s = k_B T/f \tag{7}$$

where k_B is the Boltzmann constant. Roots et al.[26] have observed an increase in D by concentration gradient measurements and a decrease in D_s by sedimentation measurements for increasing polystyrene concentration in toluene up to 0.12 kg/dm^3. They also ascertained that the D_s calculated from the observed values of D and $(\partial\pi/\partial C)_{T,P}$ with eq 6 agreed with the observed D_s from the sedimentation measurements. Laser light scattering spectroscopy gives information on the diffusion coefficient reflecting the local concentration fluctuation in a macroscopically homogeneous polymer–solvent system, with spatial scales (probing length) ranging from 0.1 to 10 μm. The results of Adam and Delsanti[10] for the polystyrene–benzene system with this technique show an increase in diffusion coefficient with increasing C up to 0.1 kg/dm^3. The results for D_s by forced Rayleigh scattering[12] might be said to show a little increase with increasing C for $C < C^*$.

These results suggest the importance of a probing distance, d, defined by the distance the molecules diffuse during the observation time. The mass diffusion coefficient for polymers in the absence of a macroscopic concentration gradient would increase in good solvents with increasing C for $C < C^*$, so long as the probing distance is not large in comparison with the correlation length for the local concentration fluctuation. Our experimental conditions with k_q also meet this prerequisite.

In the case of quenching between PS-B and PS-A in cyclohexane, k_q decreases monotonously with increasing C as is shown in Figure 1. The concentration dependence of the diffusion coefficient of polystyrene in poor solvents (cyclohexane and decalin) has been measured by Rehage et al.[25] under the concentration gradient and by Nose and Chu[27] with laser light scattering, respectively. In both measurements, D decreases with increasing C and passes through a minimum at $C \simeq 0.1$ kg/dm^3. The increase in $(\partial\pi/\partial C)_{T,P}$ is shown to be negligible with increasing C in decalin for $C < C^*$,[27] and therefore, the change of the hydrodynamic term D_s in eq 6 is presumed to contribute predominantly to the concentration dependence of D of polystyrene in poor solvents. Thus the results with k_q in the poor solvent show a concentration dependence similar to those of both D and D_s.

From the above qualitative comparison of the observed concentration dependence of k_q with that of various kinds of diffusion coefficients, it would be suggested that k_q reflecting the diffusion in the absence of a macroscopic concentration gradient depends on the polymer concentration C in a similar manner for $C < C^*$ as D does, due to the microscopic concentration fluctuation in the scale of probing distance of the present cases ($d \simeq$ 40–50 nm). The probing distance is estimated from

$$d \simeq (N_A[\mathrm{P}])^{-1/3} \tag{8}$$

where [P] is the molar concentration of the quencher.

However, the difference between the concentration dependence of k_q and that of D or D_{coop} becomes clear for regions of higher polymer concentration. The k_q begins to decrease with further increase in C, as is shown in Figure 1. This critical point appears earlier for systems with larger N and roughly corresponds to C^*, denoting the crossover from the dilute to semidilute region, with the exception for the highest molecular weight polymer (◊). The deviation might be due to the failure of the condition $d \gg R_g$ for this system. The implication of this condition will be discussed in the next section. There may exist another possible explanation for the deviation, namely, that the dynamic effect of chain entanglement appears at a concentration higher than the static overlap concentration C^*.[28] Moreover, it should be noted that there is some arbitrariness in the choice of numerical factors in eq 2, which causes deviation in the case of the numerical estimation of C^*.[27] The concentration dependence of k_q for the case $C > C^*$ will be discussed in the next section.

Self-Diffusion of a Labeled Macromolecule in the Semidilute Region. It has been thought that in dilute solution a collision between two polymer chain ends is controlled by the segment diffusion step in the individual coils, bringing the reactive sites together.[29] In semidilute solution, as the polymer chains overlap with one another and the screening length ξ[30] becomes small, it is difficult to distinguish the intramolecular diffusion of a chain end segment from its diffusion in a medium of average polymer concentration C. The translational diffusion coefficient of a chain end segment with the cell-fixed frame of reference, D_e, depends on the probing distance, d, regulated by the time scale of measurements, since the time dependence of the mean-square displacement of a certain moiety in the polymer chain differs for a time scale smaller or larger than the relaxation time, τ_r, of the polymer coil.[31] When d is large enough for the time scale of the measurement to be larger than τ_r, D_e coincides with the translational diffusion coefficient of the center of gravity of the polymer, which is equal to D_s in the absence of concentration gradient.

The theory of polymer diffusion in the semidilute region has been advanced recently by several investigators.[7-9,32] de Gennes[7] has defined two different diffusion processes for $C > C^*$. The cooperative diffusion (D_{coop}) is associated with the long-wavelength fluctuation of the polymer concentration and has been detected by the laser light scattering.[10] The self-diffusion of one labeled chain (D_s) is associated with its reptative motion in a solution of chemically identical (but unlabeled) other chains and has recently been detected in the semidilute region[12] and in the melt.[11] The scaling law together with the reptation and tube models gives[8,33]

$$D_s \simeq R^2(C)/(3\pi^2 T_r) \tag{9}$$

where the coil radius at concentration C, $R(C)$, and the renewal time of the coil, T_r, are expressed by

$$R^2(C) \simeq R_g^{\,2}(C/C^*)^{-0.25} \tag{10}$$

$$T_r \simeq (6\pi\eta_0/k_B T)R_g^{\,3}(C/C^*)^{1.5} \tag{11}$$

$$R_g \simeq bN^{0.6} \tag{12}$$

By combining eq 9 with eq 2, 10, 11, and 12, we arrive at

$$D_s \simeq (k_B T/18\pi^3\eta_0)m_0^{\,1.75}b^{-6.25}N^{-2}C^{-1.75} \tag{13}$$

where $m_0 = M_0/N_A$ is the molecular mass of a monomer unit and b in eq 12 can be calculated from eq 3. The important conclusion of eq 13 is the dependence of D_s on N and C in the power law $D_s \propto N^{-2}C^{-1.75}$, and the numerical factors are introduced only for the rough estimation of the order of magnitudes of D_s.

The reduced rate constants, $k_q\eta_0/T$, for the reaction of PS-B with PS-A in benzene are plotted against polymer concentration, C, on a log–log scale in Figure 3. The linear decrease in $k_q\eta_0/T$ with C on logarithmic scales for $C >$ 0.1 kg/dm^3 corresponds to a power law $D_s \propto C^{-\alpha}$, with α = 1.7–1.9. The agreement of α with eq 13 is quite good and shows that D_e of the chain end segment reflects the reptation movement of the polymer molecule with the increase in C. The values of $k_q\eta_0/T$ for the reaction of benzil with anthracene in a polystyrene–benzene system[34] are also shown in Figure 3.

The rate constant k_q can be related to the diffusion coefficient, D, by using a modified Smoluchowski equation[2]

$$k_q = 8\pi\gamma R_e D \tag{14}$$

with the radius of triplet–triplet energy transfer R_e = 1.37

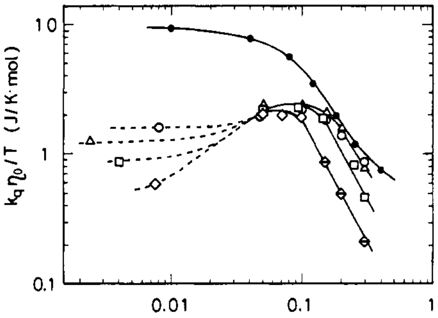


Figure 3. Reduced rate constants, $k_q\eta_0/T$, vs. polymer concentration, C, for polymer–polymer reactions in benzene (○, △, □, ◇, ◇) and for the model reaction between small molecules[32] (●). Symbols for the former are the same as in Figure 1.

nm[35] and the steric hindrance factor $\gamma = 1$ for the case of reactions between small molecules. In the case of diffusion-controlled reactions between polymers in the dilute region, various modifications on eq 14 have been already presented.[15,24] Another more orthodox attack for these subjects has been given by Doi.[36] For the semidilute region, we might roughly estimate D_e from eq 14 by setting $D = D_e$, $R_e = 1.37$ nm,[35] and $\gamma = 0.61$.[3] The value of $D_e \simeq 2 \times 10^{-11}$ m^2/s for $N = 1200$ and $C = 0.20$ kg/dm^3 is about 6 times larger than the corresponding D_s observed by Hervet et al.[12] and about 10^2 times larger than the predicted value of D_s from eq 13. These differences can be attributed to differences in the time scales of the measurements, that is, to the small probing distance of the present experiments (d = 40–50 nm) compared with $d \simeq 1$ μm for mass diffusion in the forced Rayleigh scattering experiments.[12] The expression of the self-diffusion coefficient in the form of eq 9 corresponds to the case of large time scale motion with a fixed tube. The average distance between adjacent contact points or screening length, ξ, for $C = 0.20$ kg/dm^3 was supposed to be 1.6 nm from

$$D_{\mathrm{coop}} \simeq k_B T/(6\pi\eta_0\xi) \qquad (15)$$

together with the result of D_{coop}.[10] Equation 16 was used to calculate a value about 24 for the mean number of monomer units between contact points, g.[30]

$$g \simeq (\xi/b)^{5/3} \qquad (16)$$

The values $d/\xi \simeq 30$ and $d/R_g \simeq 3$ for the present case with $N = 1200$ and $C = 0.20$ kg/dm^3 suggest that reptation of chain end segments is required for their collision but that it does not last sufficiently long for D_e to be equal to D_s. d in the present system is restricted by the lifetime τ_0 of the triplet probe. Therefore a measurement with a probing distance larger than the present case would be achieved by using a triplet probe with a lifetime longer than that of benzil.

The dependence of k_q on the number of monomer units, N, of PS-B and PS-A in the semidilute solution of PS3800 with $C = 0.20$ kg/dm^3 is shown in Figure 4. The values of $\xi = 1.6$ nm and $g = 24$ are obtained for this case as mentioned above. k_q begins to decrease markedly for $N > N_c$, with the number of monomer units at the critical entanglement formation, N_c, being equal to 300. This value is compared to an estimate of $N_c \simeq 200$ from neutron scattering experiments.[37] This indicates a change in the mode of diffusion of chain end segments at this point. The N dependence of k_q for $N > N_c$ in the present range of experiments, however, does not reach the −2 power predicted by eq 13.

The above results show that the mode of diffusion is affected much by the technique which detects the diffusion coefficient over a certain probing distance. By using a probe with a much longer lifetime, one would be able to attain the onset of reptation at a smaller polymer concentration and to detect the pure reptation behavior of labeled macromolecules in the semidilute region.

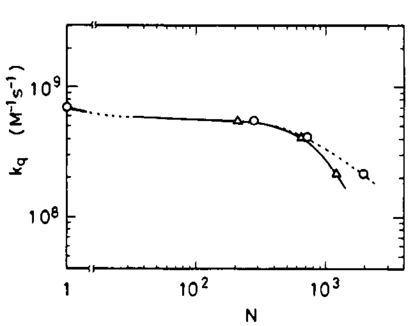


Figure 4. Dependence of k_q on the number of monomer units, N, of the probing polymers in PS3800 solution with $C = 0.20$ kg/dm^3 at 30 °C. The mean value of N for PS-B and PS-A (○) or the smaller value of N among them (△) for each system is adopted.

Onset of the Gel Effect in Radical Polymerization. The discussion on the concentration dependence of D_e in the foregoing sections provides some insight into the nature of the onset of the gel effect at the intermediate or later stage of the free-radical polymerization. As the termination reaction between two polymer radicals is controlled by the collision between two polymer chain ends in solution without a macroscopic concentration gradient, the quenching reaction between PS-B and PS-A can be regarded as a reasonable model for the termination reaction. The possible differences in the effective collision radius, R_e, and the probing distance, d, for these two cases should be noted. The influence of R_e on the absolute values of the rate constants for these reactions has been already discussed,[2] and the dependence of the rate constants on C will not be influenced much by the difference in R_e.

The existence of a marked change in k_q in Figure 1 at a critical concentration corresponding to C^* suggests that the onset of the gel effect corresponds to the point where molecular diffusion becomes restricted to reptation. This critical concentration for the onset of the gel effect, C_c, will be expressed by

$$C_c \simeq C^* = m_0 N R_g^{-3} \simeq m_0 b^{-3} N^{-0.8} \qquad (17)$$

Equation 17 holds for polymers with $N > N_c$ in good solvents since the entanglement formation is presumably a prerequisite for the occurrence of the gel effect. Another limitation for eq 17 is that the condition $d \gg R_g$ should be fulfilled. The marked deviation of C_c from C^* for the case of the highest molecular weight polymers might be due to the failure of the second condition ($d/R_g \simeq 2$). A typical condition for the radical polymerization with a rate of initiation of 10^{-9} M/s and a termination rate constant of 10^7 M^{-1} s^{-1} gives an estimate of [P] $\simeq 10^{-8}$ M for the steady-state radical concentration,[38] which corresponds to $d \simeq 550$ nm, using eq 8.

Turner et al.[16] have proposed the onset of the gel effect as the point of close packing of macromolecules with unperturbed dimensions, and an effective radius of the polymer coil, r, supposed from entanglement formation[39] has been used in this estimation of C_c, eq 18 and 19, where $\langle r_0^2\rangle$ is the unperturbed mean-square end-to-end distance and p is the packing factor. The last two terms in eq 18

$$C_c = 3m_0 N p/(4\pi r^3) \simeq 0.37 m_0 N^{1.3} R_g^{-1} \simeq 0.37 N^{0.3} C^* \qquad (18)$$

$$r = (5.11/6\pi)(\langle r_0^2\rangle/M)^{0.5} M^{0.5} \qquad (19)$$

were derived for the case of polystyrene in benzene. Klein[28] has calculated a critical point for the onset of macroscopic entangled behavior in semidilute polymer solution. Using his critical condition of $N/g = (18\pi^2)^{0.5} \simeq 13.3$ for the onset of reptation, we give C_c by

$$C_c \simeq (18\pi^2)^{0.4} m_0 b^{-3} N^{-0.8} \simeq 7.9C^* \qquad (20)$$

where eq 16 and 21 are used for the transformation.

$$\xi = R_g(C/C^*)^{-0.75} \simeq m_0^{0.75} b^{-1.25} C^{-0.75} \qquad (21)$$

The values of C_c from eq 18 and 20 are larger than C_c from eq 17.

It is clear from the present results and from the results of Hervet et al.[12] that a rapid decrease in D_s with increasing C occurs at $C \simeq C^*$ in the case of large d with monodisperse polymers of $N > N_c$. Nevertheless, it should be noted that the observed values of Turner et al.[16] for C_c for radical polymerization seem nearer to C_c from eq 18 and 20 than to C_c from eq 17. In the real polymerization experiments, termination between polymer radicals with different chain lengths, primary radical termination, and chain transfer as well as the radical concentration affecting the probing distance are presumed to give substantial effects on the process of the gel effect. Detailed results for real polymerization systems is left to further investigation.

In conclusion, the concentration dependence of diffusion-controlled quenching rate constants, k_q, between two end-labeled macromolecules in semidilute solution has been measured with a luminescent triplet probe method and explained by using dynamic scaling theory and a reptation model. The importance of probing distance, regulated by the time scale of the measurements, is emphasized for the interpretation of various kinds of diffusion data and diffusion-controlled reactions.

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