spond to a more general case of our problem. Assuming perfect stoichiometry and noting that Peeble's variable $Q = 2w_{c0}(1 - p)$, the results reduce to:

$$(1-p) = \frac{1}{2\mu - 1}\left\{\mu\left[\frac{w_c}{w_{c0}}\right]^{1/2\mu} + (\mu - 1)\left[\frac{w_c}{w_{c0}}\right]\right\}$$

This expression was also used to find the relationship between p and p^* for various values of μ.[17]

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Effect of Molecular Weight On Excimer Formation of Polystyrenes in Solution

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ABSTRACT: The fluorescence quenching of monomer and excimer emission bands of polystyrenes in 1,2-dichloroethane solution by oxygen was measured under steady-state and non-steady-state conditions as a function of molecular weight. These measurements permitted calculation of such parameters as the rate constants for excimer formation, dissociation, radiative and nonradiative deactivation processes, and other parameters such as the quenching constant for the monomer emission band and the migration coefficient. These parameters showed molecular weight dependence below 1.0×10^4 but were constant above it. These phenomena revealed that the intramolecular interaction of adjacent chromophores in the polymer chains of high molecular weight polystyrenes was very effective and favored excimer formation, but the interaction in low molecular weight polystyrenes was not so effective for excimer formation because of the isolating tendency of phenyl rings.

There have been many studies made of the intramolecular excimer formation of 1,3-diphenylpropane, 1,3,5-triphenylpentane, and polymers containing aromatic chromophores.[1-5] The "$n = 3$" rule of Hirayama reveals that excimers can be formed between two chromophores separated by three carbon atoms along the alkane chain. The preferred spatial alignment of a pair of chromophores for excimer formation is assumed to be a parallel sandwich type, but strict adherence to this conformational orientation is not necessary.[6,7]

It has been shown that intramolecular excimer formation for polymers is controlled by both configuration and conformation in a polymer chain.[8,9] In addition, the intramolecular dynamics of macromolecules is important for the transient phenomena of excimer formation in the excited state.

The dynamic processes for macromolecules in solution, especially at high frequencies, have been probed by using such methods as dielectric dispersion, NMR, EPR, depolarized Raman and Rayleigh spectroscopy, and fluorescence depolarization.[10-15] The relaxation time obtained from the dynamic processes agrees well with the time of excimer formation for polystyrene of molecular weight above 1.0×10^4.

This paper reports studies of the molecular weight effect on excimer formation of polystyrenes by using the rate parameters of excimer formation calculated from fluorescence quenching as a function of molecular weight measured under steady-state and non-steady-state conditions.

Experimental Section

Materials. The polystyrene samples were monodispersed standard polymers (Pressure Chem. Co.) of molecular weight 600, 900, 2.1×10^3, 4.0×10^3, 1.0×10^4, 3.7×10^4, 1.1×10^5, and 3.9×10^5.

The 1,2-dichloroethane solvent (DCE) used for fluorescence measurements was purified by the fractional distillation procedure prescribed for the guaranteed reagent grade.[16]

Measurements. Fluorescence spectra were measured with a MPF-4 type Hitachi fluorescence spectrophotometer. Fluorescence measurements were conducted at an excitation frequency of 255 nm with an emission slit width of 4 nm and an excitation slit width of 8 nm. Conditions were the same for all measurements. The concentration of all polymer solutions was 3 mmol/L (chromophore unit).

The relative fluorescence quantum yields of the polymers were determined from the area of the fluorescence spectra relative to the area of the spectra for standard anthracene solution in aerated alcohol, assuming that its quantum yield was 0.23.[17]

The quenching measurements were carried out after confirming that the dissolved air in the sample solution had been completely replaced with gaseous nitrogen or oxygen, which were bubbled through the solution.[18] This confirmation was obtained from the fact that after aeration the fluorescence intensity was constant.

The oxygen concentration in an aerated DCE solvent at room temperature was determined by gas chromatography, in which the separation of oxygen was carried out on molecular sieve column (13-X, Nishio Kogyo). The oxygen concentration in the aerated and oxygenated DCE was determined to be 2.3×10^{-3} mol/L and 12.9×10^{-3} mol/L, respectively.

The effect of temperature on fluorescence intensity was measured between −15 and 60 °C. Temperature regulation was accomplished

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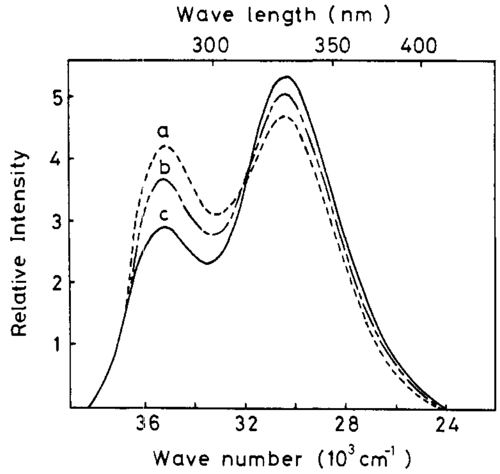

Figure 1. Fluorescence spectra of polystyrenes in DCE: (a) - - - , mol wt = 600; (b) - · -, mol wt = 2.1×10^3; (c) —, mol wt = 1.1×10^5.

by circulating a temperature-controlled aqueous solution of ethylene glycol in the cell holder. Measurements of the fluorescence decay time were made at room temperature by the pulse method with a Hitachi time-resolving spectrophotometer. The excitation light source was a deuterium pulsed discharge lamp with a half-width less than 12 ns. The critical decay time of this apparatus was longer than 7 ns without using the deconvolution method.

Results

The fluorescence emission spectra of polystyrene with molecular weights of 600, 2.1×10^3, and 1.1×10^5 are shown in Figure 1 as typical cases. Each of them consists of two main bands: one is assigned to the monomer emission band and the other to the excimer emission band.[1,2,4,5] Their maximum peaks are at about 3.5×10^4 and 3.0×10^4 cm^{-1}, respectively.

The molecular weight dependence of the relative quantum yields of monomer and excimer emission bands are shown in Figure 2a. As the molecular weight increases, the relative quantum yields of the excimer emission band increase but those of the monomer emission band decrease until a molecular weight of 1.0×10^4 is reached. But the relative quantum yields of monomer and excimer emission bands are independent of molecular weight above 1.0×10^4. The ratio of the relative quantum yields of excimer to monomer emission band plotted against the molecular weight is shown in Figure 2b. It increases linearly as the molecular weight increases to 1.0×10^4 and becomes constant above it.

The reaction kinetics of excimer formation and dissociation can be given by Scheme I.[4,19,20]

Stern–Volmer plots for quenching monomer and excimer emission bands by oxygen are shown in Figure 3. The Stern–Volmer relation for monomer and excimer emission bands is given by the following equation under steady-state conditions.[4,19,20]

$$(F_0/F)_M = \frac{k_D}{k_M k_D - k_a k_d}\left(k_M + k_{qM}[Q] - \frac{k_a k_d}{k_D + k_{qD}[Q]}\right) \qquad (1)$$

and

$$(F_0/F)_D = \frac{(k_M + k_{qM}[Q])(k_D + k_{qD}[Q]) - k_a k_d}{k_M k_D - k_a k_d} \qquad (2)$$

where F_0 and F are the intensities of monomer and excimer emission bands in the absence and the presence of a quencher, respectively. The rate constant for intramolecular excimer

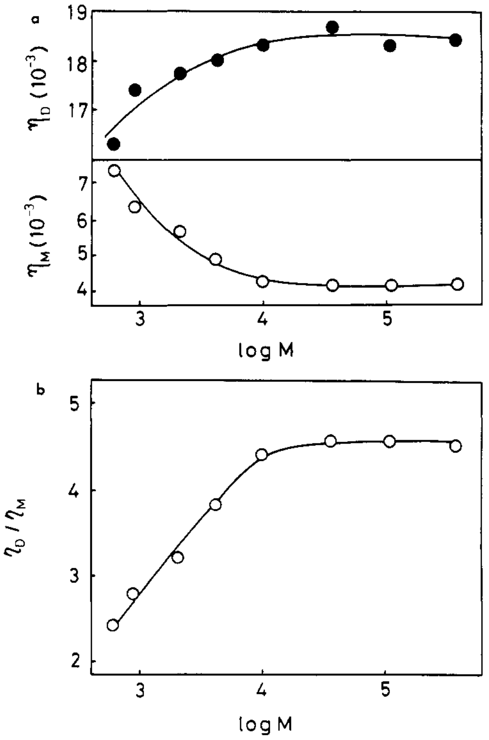

Figure 2. (a) Molecular weight dependence of the relative quantum yields of excimer and monomer emission bands: (●) excimer emission band; (○) monomer emission band. (b) Molecular weight dependence of the ratio of the relative quantum yields of excimer to monomer emission band.

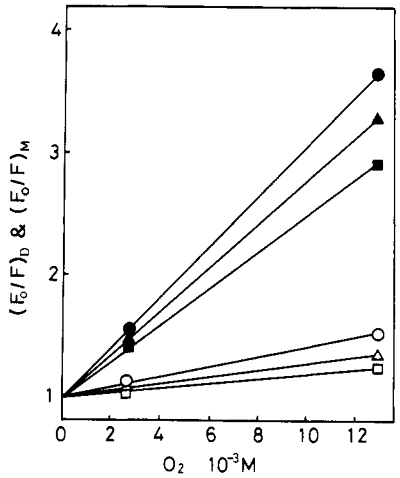

Figure 3. Stern–Volmer plots for the fluorescence quenching of excimer and monomer emission bands by oxygen. Excimer emission band: (●) mol wt = 600, (▲) mol wt = 2.1×10^3, (■) mol wt = 1.1×10^5. Monomer emission band: (○) mol wt = 600, (△) mol wt = 2.1×10^3, (□) mol wt = 1.1×10^5.

Scheme I
Reaction Kinetics

Reaction			Rate constant
$M \rightsquigarrow M^*$	Excitation	Monomer	
$M^* \rightarrow M + h\nu$	Fluorescence		k_{fM}
$M^* \rightarrow M$	Internal quenching		k_{iM}
$Q + M^* \rightarrow M + Q$	External quenching		$k_{qM}[Q]$
$M + M^* \rightarrow D$	Excimer formation	Excimer	k_a
$D^* \rightarrow M^* + M$	Dissociation		k_d
$D^* \rightarrow 2M + h\nu'$	Excimer fluorescence		k_{fD}
$D^* \rightarrow 2M$	Internal quenching		k_{iD}
$Q + D^* \rightarrow 2M + Q$	External quenching		$k_{qD}[Q]$

Table I
Quenching Constants and Physical Properties of Monomer and Excimer Emission Band of Polystyrenes

Samples	K_Q, L mol^{-1}	k_{qD}, 10^9 L mol^{-1} s^{-1}	E_a, kcal mol^{-1}
600	47.9	9.64	4.60
900	45.2	8.73	4.43
2.1×10^3	36.8	8.26	4.31
4.0×10^3	27.3	8.09	4.12
1.0×10^4	17.2	7.78	4.06
3.7×10^4	17.7	7.79	4.03
1.1×10^5	16.2	7.73	3.93
3.9×10^5	19.3	7.67	4.04

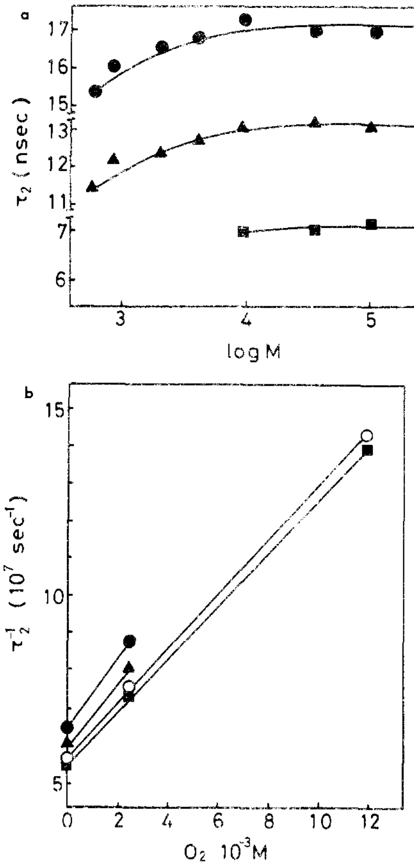

Figure 4. (a) Molecular weight dependence of the excimer fluorescence decay time of polystyrenes in the presence and absence of oxygen. (b) Plots of $1/\tau_2$ against oxygen of polystyrenes: (●) mol wt = 600, (▲) mol wt = 2.1×10^3, (○) mol wt = 1.0×10^4, (■) mol wt = 1.1×10^5.

formation k_a is obviously greater than the rate constant for radiative and nonradiative deactivation of the monomer emission band as shown by Klöpffer and Liptay.[23] Then, the rate constant for the monomer emission band k_M should be set as $k_M = k_a$. Vala, Haebig, and Rice[2] have shown that the absorbed monomer band of polystyrene returns to the ground state directly rather than through the dissociation of the excimer. These conditions have the relation $k_Mk_D \gg k_ak_d$, which can simplify Stern–Volmer plots of monomer emission bands as follows,

$$(F_0/F)_M = 1 + K_Q[Q] = 1 + \tau_M k_{qM}[Q] \qquad (3)$$

The quenching constant for monomer band K_Q can be evaluated from eq 3 as shown in Table I. K_Q decreases linearly as the molecular weight increases to 1.0×10^4 and then remains constant.

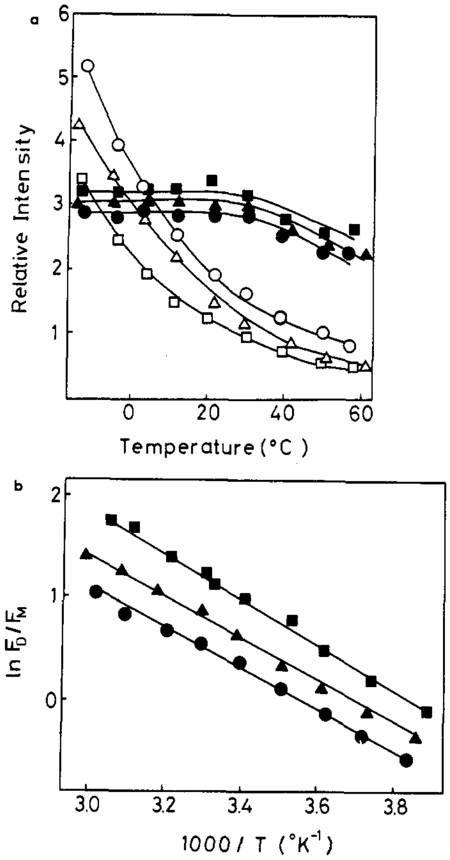

Figure 5. (a) A plot of the temperature change in the relative intensity of excimer and monomer emission bands of polystyrenes. Excimer emission band: (●) mol wt = 600, (▲) mol wt = 2.1×10^3, (■) mol wt = 1.1×10^5. Monomer emission band: (○) mol wt = 600, (△) mol wt = 2.1×10^3, (□) mol wt = 1.1×10^5. (b) Arrhenius plots for the determination of the activation energy of excimer formation of polystyrenes: (●) mol wt = 600, (▲) mol wt = 2.1×10^3, (■) mol wt = 1.1×10^5.

The solution of Scheme I under conditions of pulsed excitation for the excimer fluorescence decay of polystyrene in the presence of oxygen is given as follows[19-22]

$$F_D(t) \propto \exp(-\lambda_2 t) - \exp(-\lambda_1 t) \qquad (4)$$

$$\lambda_{1,2} = 1/\tau_{1,2} = \tfrac{1}{2}[k_M + k_D + (k_{qM} + k_{qD})[Q] \pm \{(k_M - k_D + (k_{qM} - k_{qD})[Q])^2 + 4k_ak_d\}^{1/2}] \qquad (5)$$

Since λ_1 is always greater than λ_2, for a small t the decay curve is dominated by $\exp(-\lambda_1 t)$, whereas for a large t the dominant term is $\exp(-\lambda_2 t)$. The negative gradient of excimer fluorescence decay when t is large yields the value of λ_2. When $[Q] = 0$, eq 5 is simplified because $k_Mk_D \gg k_ak_d$,

$$1/\tau_{01} \text{ or } 1/\tau_{02} = \tfrac{1}{2}[(k_M + k_D) + (k_M - k_D)] = 1/\tau_M \text{ or } 1/\tau_D \qquad (6)$$

When the decay time of the excimer emission band is reduced by a quencher, the decay time will be given as follows.[19-22]

$$1/\tau_2 = 1/\tau_{02} + k_{qD}[Q] = (1/\tau_D) + k_{qD}[Q] \qquad (7)$$

The excimer fluorescence decay time τ_2 in oxygenated, aerated, and nitrogenated solutions has been shown in Figure 4a as a function of molecular weight. The excimer fluorescence decay time of the excimer emission band in nitrogenated and aerated solutions increases as the molecular weight increases to 1.0×10^4 and then becomes constant above it. But the decay time for molecular weights below 1.0×10^4 for the oxygenated solution is shorter than 7 ns.

τ_2^{-1} vs. [Q] plots give the linear relation shown in Figure 4b.

Table II
The Rate Constant of Excimer Formation, Dissociation, and Its Related Rate Parameters for Various Molecular Weights of Polystyrenes in DCE Solution

Sample	k_a, 10^9 s^{-1}	k_d, 10^7 s^{-1}	k_{fD}, 10^5 s^{-1}	k_{iD}, 10^7 s^{-1}	f_E, 10^{-4}
600	1.24	1.31	7.53	5.10	4.80
900	1.29	1.08	7.37	5.05	6.38
2.1×10^3	1.51	1.05	8.51	4.90	7.78
4.0×10^3	1.74	0.89	8.75	4.97	10.7
1.0×10^4	1.95	0.78	9.25	4.88	11.8
3.7×10^4	1.93	0.58	8.72	5.18	12.4
1.1×10^5	1.96	0.57	8.51	5.23	14.6
3.9×10^5	1.95	0.57	8.88	5.18	12.2

The quenching constant for excimer emission band k_{qD} can be evaluated by using equation 7 as shown in Table I. k_{qD} decreases as the molecular weight increases to 1.0×10^4, and becomes constant above it.

The dependence of the intensities of the excimer and monomer emission bands on temperature is shown in Figure 5a for mol wt = 600, 2.1×10^3, and 1.1×10^5, respectively. For all samples, the intensity of the monomer emission band decreases as the temperature increases, while the intensity of the excimer emission band does not change below about 30 °C and decreases above it.

The activation energy of intramolecular excimer formation has been obtained from the relation $\ln (F_D/F_M) = -E_a/RT$, where F_D and F_M are the respective excimer and monomer fluorescence intensities in the aerated solution.[19] Arrhenius plots are shown in Figure 5b. The dependence of the activation energy on molecular weight is shown in Table I. The activation energy of excimer formation decreases from 4.6 to 4.0 kcal/mol as the molecular weight increases to 1.0×10^4 above which it is constant.

The rate parameters for intramolecular excimer formation, dissociation, and radiative and nonradiative deactivation are calculated by using the following kinetic equations.[4,23,24] The rate constant of excimer formation k_a and dissociation k_d in a steady-state condition can be given as follows,

$$\frac{k_a}{k_{fM}} = \left[\frac{(k_{iD})_q - (k_{iD})_v}{k_{fD}}\right]\left[\left(\frac{F_M}{F_D}\right)_q - \left(\frac{F_M}{F_D}\right)_v\right]^{-1} \quad (8)$$

$$\frac{k_d}{k_{fD}} = \left(\frac{F_M}{F_D}\right)_v \frac{k_a}{k_{fM}} - \frac{(k_{id})_v}{k_{fD}} - 1 \quad (9)$$

where F_M and F_D represent the fluorescence intensities of monomer and excimer emission bands for polymers and v and q the absence and presence of a quencher, respectively. The rate constants can be calculated from the following equations,

$$\frac{(k_{iD})_v}{k_{fD}} = \left[\left(\frac{F_E}{F_D}\right)_v - \left(\frac{F_M}{F_D}\right)_v\right]\frac{1}{\eta_v} - 1 \quad (10)$$

$$\frac{(k_{iD})_q}{k_{fD}} = \left[\left(\frac{F_E}{F_D}\right)_q - \left(\frac{F_M}{F_D}\right)_q\right]\frac{1}{\eta_q} - 1 \quad (11)$$

where F_E is the fluorescence intensity of the unit chromophores of a polymer, that is, ethylbenzene, and η_v and η_q are the relative fluorescence quantum yields of ethylbenzene in the absence and presence of a quencher, respectively.

Here, we assume that the following condition is satisfied in the presence of a quencher:

$$(k_{iD})_q = (k_{iD})_v + k_{qD}[Q] \quad (12)$$

Equation 12 can be transformed into:

$$\frac{(k_{iD})_q - (k_{iD})_v}{k_{fD}} = \frac{k_{qD}[Q]}{k_{fD}} \quad (13)$$

The quantities on the right-hand side of eq 10 and 11 were obtained from experimental data. Equations 10, 11, and 13 make it possible to calculate k_{fD}.

Knowing the value of k_{fD}, other rate parameters, such as the rate constant of excimer formation k_a and dissociation k_d, can be calculated by using eq 8 and 9. The calculated values are shown in Table II.

The rate constant of excimer formation k_a is on the order of 10^9 and increases as the molecular weight increases to 1.0×10^4 and becomes constant above it. It means that excimers can be formed more easily in high molecular weight polystyrenes than in low ones.

The rate constant of excimer dissociation k_d is on the order of 10^7 or 10^6 and its molecular weight dependence is inverse to the rate constant for excimer formation. The rate constant for excimer dissociation decreases as the molecular weight increases to 1.0×10^4 and becomes constant above it. The rate constants of the excimer emission band k_{fD} and the internal quenching k_{iD} are on the order of 10^5 and 10^7, respectively. The dependence of k_{iD} and k_{fD} on molecular weight is not as distinct as for those of the other rate parameters.

Discussion

The Effect of the Reorientational Correlation Time on Excimer Formation. It has been known that excimer formation of intermolecular and intramolecular interactions can occur with a coplanar sandwich-like orientation affording the maximum π-orbital overlap and an interchromophore separation in the range of 3.0 and 3.7 Å.[1,3,4,25] In addition to these geometrical requirements, excimer formation is controlled by the dynamic processes of chromophores, including the surrounding viscosity and the intrachain dynamics.[15,24–27]

The intramolecular dynamics of macromolecules are controlled by the relaxation process, which has been found to consist of two components: (1) a molecular weight dependent component that can be associated with the overall tumbling motion of the whole molecule, and (2) a molecular weight independent component which can be associated with local relaxation. The observable relaxation time is considered to be the sum of these two separate mechanisms.[10]

The reorientational correlation time of phenyl groups of polystyrenes yields information on the rotational diffusion constant which is related to the friction constant of the molecular motion of phenyl groups in a polymer chain. The larger the molecular weight, the greater the interaction between the phenyl groups. The large interaction induces long reorientational correlation times. At sufficiently high molecular weights, the segmental distribution of a polymer chain reaches a constant distribution, which brings about the interaction between phenyl groups. This constant interaction results in a constant reorientational correlation time.[13]

Our experimental results show that the excimer formation time (the reciprocal of the rate constant for excimer formation) decreases as the molecular weight increases to 1.0×10^4, then becoming constant. The rate constant for excimer for-

Table III
The Rate Constant, Quenching Constant, and Related Parameters for Various Molecular Weights of Polystyrene in DCE Solution

Sample	k_M, 10^9 s^{-1}	k_{qM}, 10^{10} L mol^{-1} s^{-1}	k_{qM}/k_{qE}	Λ, 10^{-5} cm^2 s^{-1}	l,[a] Å
600	1.31	6.26	3.89	15.6	48.8
900	1.46	6.35	3.94	15.7	46.4
2.1×10^3	1.62	5.64	3.50	13.4	40.7
4.0×10^3	1.81	4.72	2.93	10.6	34.2
1.0×10^4	2.02	3.51	2.18	6.87	26.1
3.7×10^4	2.00	3.48	2.16	6.81	26.4
1.1×10^5	2.08	3.62	2.25	7.29	26.4
3.9×10^5	2.03	3.27	2.03	6.26	25.7

[a] $l = (2\Lambda\tau_M)^{1/2}$.

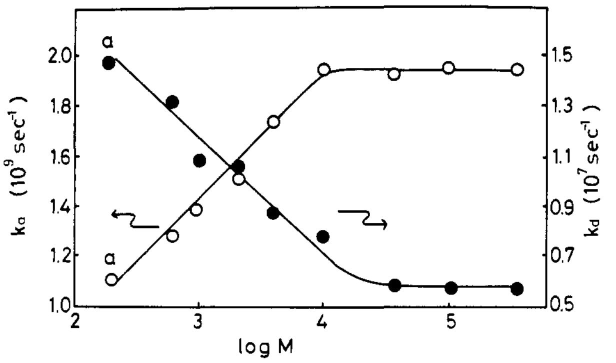

Figure 6. Molecular weight dependence on the rate constant of excimer formation and dissociation of polystyrene: (○) the rate constant of excimer formation; (●) the rate constant of excimer dissociation; (a) the rate constant of excimer formation and dissociation of 1,3-diphenylpropane.[24]

mation vs. molecular weight is shown in Figure 6.

It should be noted that for polystyrene with molecular weights above 1.0×10^4 both the excimer formation time and the reorientational correlation time are constant and have the same order of magnitude, that is, 10^{-10} s.[10-15] This result indicates that the excimer formation of high molecular weight polystyrene is related to local relaxation. On the other hand, at molecular weights below 1.0×10^4, the rate constant for excimer formation does not correlate to the reorientational correlation time. This discrepancy is characteristic of intramolecular excimer formation.

The excimer formation time of toluene is 1.6×10^{-12} s in a concentrated solution[28,29] and its reorientational correlation time is 2.9×10^{-12} s in CCl_4 obtained from Raman line shape analysis.[13] It may be concluded that there is a good agreement between them, taking into account the solvent viscosities of toluene and carbon tetrachloride at 30 °C which are 0.520 and 0.845 cP, respectively.[16]

The excimer formation time of 1,3-diphenylpropane,[1,4,24] the simplest compound for intramolecular interaction, is 9.1×10^{-10} s, which is found on the extrapolated segment of the uncolored curve in Figure 6. This value is about 240 times larger than that of the reorientational correlation time (3.8×10^{-12} s) of dibenzyl.[13] There is a large observational discrepancy between the excimer formation time and the reorientational correlation time in the intramolecular interaction at the lowest molecular weight. If the intramolecular excimer formation of low molecular weight polystyrene was influenced only by the tumbling motion and intermolecular excimer formation, the excimer formation time and the reorientational correlation time should be in good agreement. So, some other agency must have an effect on intramolecular excimer formation.

Fraction of Excimer Forming Sites. Longworth,[3] Klöpffer,[4] David et al.,[30] and the authors[8,9] studied the rate constant for excimer formation k_a of isotactic and atactic polymers of polystyrenes and poly(p-methylsytrenes) and revealed that the k_a of isotactic polymers were larger than those of atactic polymers both in solid film and in solution.

According to x-ray analysis of isotactic PS,[31] the distance of the nearest parallel aromatic rings in isotactic polystyrenes is 6.63 Å, which is too far for the formation of excimers through nearest neighbor intramolecular interactions. On the other hand, Fourche and Lemaire[32] have shown that atactic PS have the same helical structure in a polymer chain as that of isotactic PS, but the succession of the sequences of helices in atactic PS is not as long as that of isotactic PS.

These results indicate that excimer formation of polystyrenes can be attained more effectively at trapping sites such as crystalline or structural defects rather than intermolecular interaction.

The fraction of excimer forming sites, f_E, can be calculated by using the following equation, which was proposed by Frank and Harrah[27] using the activated migration model,

$$f_E = \frac{W_E \exp(-E_a/RT)}{W_G + W_E \exp(-E_a/RT)} \qquad (14)$$

where W_E and W_G are the degeneracies of the excimer and ground states, respectively. The calculated values are shown in Table II. f_E is on the order of 10^{-4} at low molecular weights and increases to 10^{-3} as the molecular weight increases to about 1.0×10^4 and remains constant above it. Although these values are small when compared with the those for poly(2-vinylnaphthalene) and poly(4-vinylbiphenyl) in solid films,[27,33] they are about the same as those for poly(N-vinylcarbazole) (PVK),[34] where it is known that excimer formation cannot be attained through the nearest neighbor interaction of carbazole chromophores.

It can be concluded that the excimer trapping sites in a polymer chain play an important role in the excimer formation of polystyrene.

The Quenching Constant and Energy Migration. The quenching constant of the monomer emission band k_{qM} for polystyrene can be calculated from the relation $K_Q = k_M^{-1}k_{qM}$, where the rate constant for the monomer emission band k_M is the sum of k_{fM}, k_{iM}, and k_a.[20] The calculated values of k_{qM} and k_M are shown in Table III. The value of k_{qM} decreases as the molecular weight increases to 1.0×10^4 and becomes constant above it.

In a dilute solution, it can be assumed that the collisional quenching process between solvent and quenching molecules is accomplished through molecular diffusion. The quenching constant for diffusion-controlled processes in ethylbenzene for the unit chromophore of polymers is given by the Smoluchowski-Einstein equation as follows,[20,35-39]

$$k_{qE} = 4\pi N(D_E + D_Q)(1 + C_{qE})PR \times 10^{-3} \qquad (15)$$

where C_{qE} is the transient term and is given as follows,

$$C_{qE} = R[(D_E + D_Q)\tau_E]^{-1/2} \qquad (16)$$

where R is the sum of the radii of colliding molecules, D_E is the diffusion coefficient of ethylbenzene, D_Q is the diffusion coefficient of the quenching molecule, and τ_E is the decay time of ethylbenzene in the absence of a quencher. P is the quenching probability per molecular encounter, and N is Avogadro's number. Here we use the interaction radius of R as 4.5 Å, which is the sum of the interaction radii of hydrogen and oxygen (2.5 and 2.0 Å, respectively).[20,40,41] The diffusion coefficients of ethylbenzene D_E and oxygen D_Q are 1.53×10^{-5} and 4.0×10^{-5} cm^2/s, respectively.[20,40]

The quenching constant of ethylbenzene k_{qE} is calculated as 1.61×10^{10} L mol^{-1} s^{-1} from the Stern–Volmer diagram and by using τ_E (obtained from another experiment). The calculated value of k_{qE} from eq 15 is $1.88P \times 10^{10}$ L mol^{-1} s^{-1}. P is calculated to be 0.86.

The quenching constant for the monomer emission band k_{qM} by bimolecular quenching can be expressed as follows,[37–39]

$$k_{qM} = 4\pi N(\Lambda + D_p + D_Q)(1 + C_{qM})PR \times 10^{-3} \qquad (17)$$

where Λ is the migration coefficient, introduced because k_{qM} exceeds the rate constant of the diffusion-controlled reaction k_{qE}. D_p is the diffusion coefficient of the polymer. C_{qM} is the transient term and is given as follows,[38]

$$C_{qM} = R[(\Lambda + D_p + D_Q)\tau_M]^{-1/2} \qquad (18)$$

The migration coefficient Λ can be calculated from eq 15 and 17 as follows,

$$\Lambda = (D_E + D_Q)\left(\frac{k_{qM}}{k_{qE}}\right)\frac{1 + C_{qE}}{1 + C_{qM}} - (D_p + D_Q) \qquad (19)$$

C_{qM} in eq 18 gives the largest values under the condition of $\Lambda = 0$, while the smallest C_{qM} values are obtained under the condition of $\Lambda = \infty$. The average value of C_{qM} ranged from 0.13 to 0.16 for molecular weights 600 to 3.9×10^5. C_{qE} is calculated as 0.05 from eq 16. The values of $(1 + C_{qE})/(1 + C_{qM})$ decrease from 0.93 to 0.91 as the molecular weight increases from 600 to 1.0×10^4 and becomes constant above 1.0×10^4. D_P of low molecular weight polystyrenes in CCl$_4$ is calculated from the relation $D_p = 8.31 \times 10^{-5} \times M^{-0.48}$.[14] The diffusion coefficient for D_P ranged from 0.39 to 0.10×10^{-5} cm^2/s for molecular weights 600 to 1.0×10^4. The calculated values of the migration coefficient Λ are shown in Table III. It decreases as the molecular weight increases to 1.0×10^4 and becomes constant above it.

During the life time of the monomer emission band τ_M, singlet excitation migration occurs through the molecules in a polymer chain. The average distance of the exciton migration l can be calculated from $l = (2\Lambda\tau_M)^{1/2}$ [19] as shown in Table III. The exciton of lower molecular weights can migrate much longer distances than those of higher molecular weights without being trapped by the excimer-forming sites. The constant value l for molecular weights above 1.0×10^4 indicates that high molecular weight polystyrenes have a constant distribution of the excimer-forming sites in the polymer chain.

The Rate Constant of Excimer Dissociation. The rate constant for excimer dissociation k_d of polystyrenes has been shown in Figure 6 to be a function of molecular weight. k_d decreases as the molecular weight increases to 1.0×10^4 and becomes constant above it. The rate constant for excimer dissociation of 1,3-diphenylpropane is 1.5×10^7 s^{-1},[4,24] which is found on the extrapolated linear line of the rate constant of excimer dissociation vs. molecular weight plots, as shown in Figure 6. On the other hand, the rate constants for excimer dissociation for aromatic hydrocarbons such as benzene and toluene are 8.3×10^{11} and 12×10^{11} s^{-1}, respectively,[19,21,22] and are much larger than those of intramolecular ones.

Birks et al.[19,28] have proposed that the quenching of excitations of concentrated aromatics occurs collisionally in a similar manner to solvent–solute transfer. Further evidence for excitation migration exists in the fact that the rate parameter for the quenching of solvent excitation by an efficient quencher (e.g., biacetyl) exceeds the rate parameter for collisional quenching of solute excitation in the same solvent. Birks et al. have also proposed that excimer formation and dissociation provide the mechanism for excitation migration in aromatic liquids as follows,[19,28]

$${}^1M^*_A + {}^1M_B \rightleftarrows {}^1D^*_{AB} \rightarrow {}^1M_A + {}^1M^*_B$$

The rms displacement $\overline{\alpha}$ of excitation migration in the three-dimensional random-walk process is related to the migration coefficient as $\overline{\alpha}^2 = 6\Lambda\bar{t}$, where $\bar{t}$ is the mean time. The calculated values of $\overline{\alpha}$ are 3.3 and 3.6 Å for benzene and toluene, respectively.[19] It means that the excitation migration of concentrated aromatic liquids is controlled by short-range excimer interaction.

On the other hand, the calculated values of $\overline{\alpha}$ for polystyrenes are so large that the mechanism of aromatics cannot be adapted to them. The large values of α mean that the excimer cannot dissociate quickly to the excited monomer state, since phenyl groups in a polymer chain cannot move as quickly as in an aromatic liquid. This restriction of molecular motion induces the long resident time of the pair of excimers in polymer systems, during which they dissipate energy through nonradiative deactivation. These results show that the restricted phenyl groups in a polymer chain cannot move as quickly as the free molecules. An excimer in a polymer chain dissipates energy mainly through nonradiative deactivation rather than by returning to the excited monomer state. It means that singlet energy is trapped efficiently at excimer-forming sites and localized in a polymer chain.

Conclusion

The rate parameters and the quenching parameters for high molecular weight polystyrene are constant, but those for low molecular weight polystyrene are dependent upon molecular weight. The rate constants of excimer formation of polystyrenes are on the order of 10^9 s^{-1}. These values agree well with the reorientational correlation time of polystyrenes at high molecular weights above 1.0×10^4, but a discrepancy occurs between them at lower molecular weights. These results show that the interaction of nearest neighbors in a polymer chain of high molecular weight polystyrene is effective and favorable for excimer formation, but that of low molecular weight polystyrene is less effective and unfavorable for excimer formation: phenyl rings in low molecular weight polystyrene move independently, while those in the high molecular weight polymers form clusters.

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Size and Density of Fibrin Fibers from Turbidity[1]

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ABSTRACT: In agreement with earlier observations that the angular dependence of light scattering by fibrin gels obeys the theory for light scattering by very long and thin rigid rodlike particles (intensity proportional to the square of half the scattering angle), we find that the turbidity, τ, of the less opaque gels varies as the inverse third power of the wavelength, λ. Mass–length ratios of the fibers calculated from these two measurements closely agree. For fibrin gels containing fibers with a very high mass–length ratio (of which we had not been able to obtain interpretable scattering data), the turbidity is found not quite to vary as $1/\lambda^3$. For these opaque gels, the fiber diameter is no longer negligible with respect to the wavelength. It is shown how the radius of gyration of the fiber cross section (and therefore the radius of cylindrical fibers) can be obtained from the ratio of slope and intercept of a plot of $1/\tau\lambda^3$ vs. $1/\lambda^2$. The square of the radius of the fibers is found to be proportional to the mass–length ratio. The density of the fibers is calculated to be 0.28. This corresponds to a ratio of fiber volume to volume of protein contained in the fiber of 5.0.

When the plasma protein fibrinogen is acted upon by the enzyme thrombin, it is irreversibly converted to fibrin monomer. Fibrin monomers rapidly form a network of fibrin fibers which, in vitro, turn the solution into a gel, and, in vivo, form a hemostatic plug at a lesion of the circulatory system. (For successive reviews see ref 2–4.)

The gelation of fibrin can be followed by a variety of methods. The most direct of these is the detection or measurement of the rigidity of the gel. The detection of rigidity is often qualitative since its measurement requires the use of equipment that is not widely available. Hence, less direct methods are used more commonly. Of these methods, one is to determine the amount of fibrin fiber as the fraction of insoluble material (clottability). Another is to follow the increase in turbidity or light scattering due to the formation of the fibers. The work reported below was begun with the intention of examining the physical basis of this last method.

All our experiments were done with purified fibrinogen of high clottability and gelation was obtained by addition of thrombin. It is well known that the properties of fibrin gels vary markedly as the solutions in which they are formed are changed, for example, as to ionic strength or pH.[5–8] In particular, the diameter of the fibers is variable; the mass–length ratio of the fibers varies by a factor of at least 100, depending on the solvent.[9] We have used this fact in order to prepare fibrin gels with fibers of different mass–length ratio. Of these gels, we measured the turbidity and the light scattering.

Electron micrographs of fibrin show that the fibers are not bent significantly over distances of several microns.[10–14] One expects that the light scattering by such fibers is the same as that predicted theoretically for very long and thin rodlike particles. We have recently confirmed that this is the case for relatively transparent fibrin gels.[9] The scattering of the more opaque gels (which are typical of gels formed under physiological conditions) is hopelessly affected by their high turbidity, at least when measured in our instrument. Since the turbidity is simply the scattering integrated over all directions, it should be possible to test also if the turbidities of the opaque gels are in agreement with the theory for scattering by very long rods.

As a result of this work, we conclude that one can use the turbidity of a fibrin gel in order to calculate a reliable average mass–length ratio of the fibers in the gel. Furthermore, for very massive fibers, the wavelength dependence of the turbidity can be used to calculate also the average radius of the fibers.

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