

## Rate of Diffusion-Controlled Intramolecular Triplet–Triplet Annihilation between the Terminal Groups of $\alpha,\omega$ -Dianthrylpolystyrene

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**ABSTRACT:** To investigate the rates of diffusion-controlled intramacromolecular reactions between a pair of terminal groups of a flexible polymer, substantially monodisperse  $\alpha,\omega$ -dianthrylpolystyrenes (A–PS–A) were prepared and the decay curves of their P-type delayed fluorescence due to the triplet–triplet interaction (T–T annihilation) of terminal anthryl groups were measured in benzene, butanone, and cyclohexane at 30°C, using 10-ns nitrogen laser pulse. The rate constants for the intramolecular reaction  $k_{TT}^{intra}$  could be obtained by removing the contribution of intermolecular triplet–triplet interaction to the decay curves. They are of the order of  $10^4 \text{ s}^{-1}$  and decreased with the degree of polymerization as  $DP^{-0.53}$  in benzene and  $DP^{-0.60}$  in butanone for  $DP=280\text{--}3000$ . The dependence of  $k_{TT}^{intra}$  on the degree of polymerization found in this work is very small compared with those obtained previously for the range of small  $DP$ . The implication of this result is briefly discussed.

**KEY WORDS**  $\alpha,\omega$ -Dianthrylpolystyrene / Terminal Groups / Diffusion Control / Delayed Fluorescence / Intramolecular Triplet–Triplet Annihilation /

The mechanism of the intramolecular reactions of macromolecules has recently taken on considerable interest. The rates of activation-controlled intramolecular reactions of polymers have been reported by many authors<sup>1–6</sup> and interpreted mainly on the basis of the thermodynamically equilibrated fraction of cyclic conformations having two reactive groups in a proper juxtaposition. As for diffusion-controlled intramolecular reactions between a pair of terminal groups on a polymer, some theories and several experimental works have appeared in recent years. The rate constants of intramacromolecular electron transfer reactions have been determined by electron spin resonance (ESR),<sup>7</sup> and the rate constants of intramacromolecular excimer-formation<sup>8–10</sup> and fluorescence quenching<sup>11,12</sup> were found by optical methods. But the molecular weights studied in these works were very low, because of the intrinsic nature of the techniques used. For example, when one uses a luminescent probe to study the collision rate of the

two end groups of a polymer chain, its lifetime must be similar to or longer than the relaxation time of conformational change of the polymer chain as a whole. Fluorescent probes (singlet probe), however, usually have lifetimes of the order of nanoseconds and are thus too short for studying of high-molecular-weight polymers. The lifetime of pyrene, as a long lifetime singlet probe, is only about 200–400 ns. A similar argument can be made in the case of ESR measurement.

On the contrary, triplet probes have lifetimes of the order of micro- or milli-seconds<sup>14–17</sup> and thus seem useful for studying high-molecular-weight polymers. Furthermore, two triplet anthracene molecules are known to give delayed fluorescence through a diffusion-controlled triplet–triplet annihilation.<sup>13</sup> Consequently, a polymer molecule having anthryl groups at both chain ends may be used to study the intramolecular collision rate by following the decay of delayed fluorescence. Use of a monodisperse polymer is another important factor

Table I. Characterization of A-PS-A

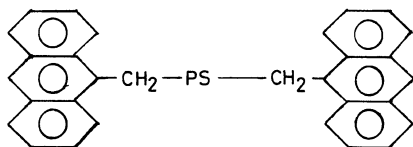
Polymer	$M_n$	$M_w/M_n$	DP of polystyrene moiety	Anthryl group at chain ends
				%
APS280A	$2.95 \times 10^4$	1.59	280	100
APS300A	$3.11 \times 10^4$	1.84	300	92
APS375A	$3.90 \times 10^4$	3.24	375	100
APS640A	$6.68 \times 10^4$	1.45	640	100
APS780A	$8.10 \times 10^4$	1.24	780	100
APS940A	$9.78 \times 10^4$	1.38	940	100
APS1300A	$1.35 \times 10^5$	1.42	1300	100
APS1500A	$1.58 \times 10^5$	1.28	1500	100
APS2600A	$2.78 \times 10^5$	1.19	2600	78
APS3000A	$3.09 \times 10^5$	1.24	3000	91

in this study. Otherwise, the rate constants obtained would be a complex average of polymers having different chain lengths.

In the present work, the time dependence of P-type delayed fluorescence emission due to the triplet-triplet interaction from substantially monodisperse  $\alpha,\omega$ -dianthrylpolystyrene (A-PS-A) in benzene, butanone, or cyclohexane solution was measured at 30°C, and the rate constants for diffusion-controlled intramolecular reactions for polymers with a high degree of polymerization (DP) were obtained as functions of the DP of polystyrene.

## EXPERIMENTAL

$\alpha,\omega$ -Dianthrylpolystyrene (A-PS-A) shown below was prepared in a way similar to that reported previously.<sup>16,17</sup> Styrene was polymerized anionically



(A-PS-A)

in tetrahydrofuran (THF) with sodium-naphthalene as the initiator under high vacuum, the resultant living polystyryl dianion was end-capped with 9-chloromethylantracene prepared in advance from 9-anthraldehyde via 9-hydroxymethylantracene.<sup>18</sup> The reaction seems to broaden a little the molecular-

weight distribution of the products (A-PS-A) as compared with the original living polymers.

The number-average molecular weight and molecular-weight distribution of A-PS-A were measured with a Toyo Soda HLC-802UR gel-permeation chromatograph (GPC) at 40°C in THF. The molecular-weight distribution was corrected according to Pierce *et al.*<sup>19</sup> The content of anthryl group (A) at the chain ends was determined from its absorption spectra obtained with a Shimadzu MPS-5000 spectrophotometer. Pertinent data are shown in Table I.

The procedure and apparatus for measuring the time-dependent delayed fluorescence from polymer solutions are described in Figure 1. The sample

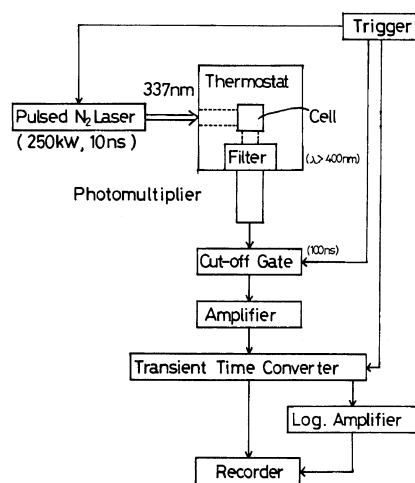


Figure 1. Schematic diagram of apparatus.

solution in a degassed and sealed rectangular quartz cell was set in a thermostat, and irradiated by a 250 kW pulsed nitrogen laser (AVCO C950B) at 337 nm with a pulse having a half width of 10 ns. Luminescence up to 100 ns after irradiation was rejected by a cut-off gate. The signal of the photomultiplier was fed into a transient time converter (Riken Denshi TCGD-8000) which permitted recording of the decay curve on the X-t type pen recorder (Riken Denshi SP-H3C). Semi-logarithmic plots of the decay curve, electronically calculated by a logarithmic amplifier, were also recorded on the chart. Dotite-Luminasol-grade benzene and cyclohexane as well as Dotite-Spectrosol-grade butanone were used as solvents in the delayed fluorescence measurements.

KINETIC ANALYSIS OF TIME  
DEPENDENT P-TYPE DELAYED  
FLUORESCENCE FROM  $\alpha,\omega$ -  
DIANTHRYLPOLYSTYRENE  
SOLUTION

*Kinetics*

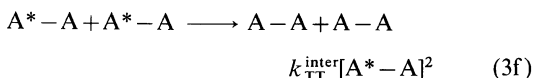
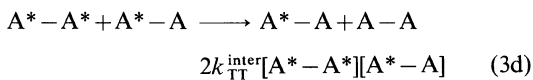
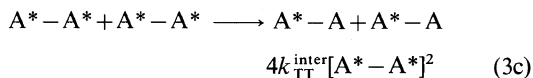
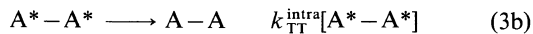
In the case of monoanthrylpolystyrene having an anthryl group at only one of the two chain ends, we have shown that the triplet anthryl group  $A^*$  decays not only because of the radiationless transition (rate constant  $k_d^T$ ), concentration quenching ( $k_{cq}$ ) and intermolecular T-T annihilation ( $k_{TT}^{inter}$ ), but also as a result of quenching by the polystyrene chain intra- and inter-molecularly ( $k_{intra}$  and  $k_{inter}$ ).<sup>16</sup> This decay rate is expressed by eq 1 and 2,

$$-\frac{d[A^*]}{dt} = k_1[A^*] + k_{TT}^{inter}[A^*]^2 \quad (1)$$

$$k_1 = (k_d^T + k_{intra}) + k_{cq}[A] + k_{inter}[St] \quad (2)$$

where  $[A]$  is the concentration of anthryl groups,  $[St]$  is the base molar concentration of polystyrene, and  $k_1$  is an apparent first order (with respect to  $[A^*]$ ) rate constant.

When anthryl groups are attached to the both ends of a chain, excitation by a laser pulse will produce two species (*i.e.*, singly excited and doubly excited), denoted by  $A^*-A$  and  $A^*-A^*$ . In the case of A-PS-A, the kinetic scheme of each species is shown below.



where  $k_{TT}^{intra}$  and  $k_{TT}^{inter}$  are intra- and intermolecular T-T annihilation-rate constants. The rate of disappearance of each species can be expressed by eq 4 and 5.

$$-\frac{d[A^*-A]}{dt} = k_1[A^*-A] + k_{TT}^{inter}[A^*-A]^2 - 2k_1[A^*-A^*] - 4k_{TT}^{inter}[A^*-A^*]^2 \quad (4)$$

$$-\frac{d[A^*-A^*]}{dt} = 2k_1[A^*-A^*] + k_{TT}^{intra}[A^*-A^*] + 2k_{TT}^{inter}[A^*-A^*][A^*-A] + 4k_{TT}^{inter}[A^*-A^*]^2 \quad (5)$$

Strictly speaking, the constituents of  $k_1$  appearing in eq 1, 3a, and 3e are not the same. But, in previous papers,<sup>16,17</sup> it has already been proved that the rate of intramolecular concentration quenching between the terminal groups of  $A^*-PS-A$  involved in  $k_1$  in eq 3e is negligibly small compared with the rate of intramolecular quenching of  $A^*$  by the polystyryl chain ( $k_{cq}^{intra} \ll k_{intra}$ ) and that each of the two triplet terminal groups in  $A^*-PS-A^*$  are quenched by the polystyryl chain independently at the same rate as  $A^*$  in PS- $A^*$ . So, we may assume the same values for  $k_1$  in eq 1, 3a, and 3e.

The intramolecular T-T annihilation-rate constant  $k_{TT}^{intra}$  is the one we want to find out about. In the following, we will show that only the first two terms in each equation are important under our experimental conditions. When the concentration of sample polymer is known, the value of  $k_1$  can be calculated by eq 1 and 2, since we have already determined all rate constants constituting  $k_1$  for monoanthrylpolystyrene in benzene, butanone, and cyclohexane.<sup>16,17</sup> The rate constant  $k_{TT}^{inter}$  may have a value similar to that of the quenching reaction of

benzil-terminated polystyrene by monoanthryl-polystyrene,<sup>14,20</sup> both being the rate constants for the diffusion-controlled polymer-polymer reactions of terminal triplet groups. The initial concentration of  $A^*-A$  and  $A^*-A^*$  can be estimated in the following way. When the fraction of anthryl group, excited to the triplet state by laser pulse, is given by  $f$ , then  $[A^*-A]_0 = f[A]$  and  $[A^*-A^*]_0 = (f[A])^2/2$ . By knowing the intensity of laser pulse which is  $4.3 \times 10^{-6}$  Einstein/l, the molar extinction coefficient of anthryl group  $\epsilon$  is  $4.7 \times 10^3$  at 337 nm in benzene and its triplet quantum yield  $\phi$  is 0.72, the value of  $f$  at the onset of decay is thus calculated to be of the order of  $3.4 \times 10^{-2}$  for  $[A-PS-A] = 3.0 \times 10^{-5}$  M. Introduction of these values as well as the values of rate constants to each term shows that the third, fourth, and fifth terms in eq 4 and the third and fourth terms in eq 5 can be disregarded even at the initial stage. For example, in the case of APS640A in benzene at 30°C with  $[A] = 6.2 \times 10^{-5}$  M ( $[A-PS-A] = 3.1 \times 10^{-5}$  M), the following values were calculated:

$$\begin{aligned} k_1[A^*-A]_0 &= 5.7 \times 10^{-3} \text{ M s}^{-1}, \\ k_{TT}^{\text{inter}} [A^*-A]_0^2 &= 2.4 \times 10^{-3} \text{ M s}^{-1}, \\ 2k_1[A^*-A^*]_0 &= 1.9 \times 10^{-4} \text{ M s}^{-1}, \\ 2k_{TT}^{\text{inter}} [A^*-A^*]_0[A^*-A]_0 &= 8.2 \times 10^{-5} \text{ M s}^{-1}, \\ 4k_{TT}^{\text{inter}} [A^*-A^*]_0^2 &= 2.8 \times 10^{-6} \text{ M s}^{-1}. \end{aligned}$$

As the relative values of the third through fifth terms in eq 4 and the third and fourth terms in eq 5 to the first and second terms become smaller with time, especially at lower concentration, they may be disregarded in the rate equation. This means that two species decay almost independently.

Thus, eq 4 and 5 can be integrated separately to give,

$$[A^*-A^*] = [A^*-A^*]_0 \exp[-(2k_1 + k_{TT}^{\text{intra}})t] \quad (6)$$

and

$$[A^*-A] = \frac{k_1[A^*-A]_0 e^{-k_1 t}}{k_1 + k_{TT}^{\text{inter}}[A^*-A]_0(1 - e^{-k_1 t})} \quad (7)$$

$$\begin{aligned} &\longrightarrow \frac{k_1[A^*-A]_0}{k_1 + k_{TT}^{\text{inter}}[A^*-A]_0} e^{-k_1 t} \quad (8) \\ &\quad \quad \quad \text{(at large } t) \end{aligned}$$

This latter is the same function as that in the case of monoanthrylpolystyrene (PS-A), and at large,  $t$ , it becomes a simple exponential function.

The intensity of observed delayed fluorescence,  $I_{DF}^{\text{obs}}$  is the sum of the contributions from intra- and inter-molecular T-T annihilations and, in the limit of the approximations used, is given by eq 9,

$$\begin{aligned} I_{DF}^{\text{obs}} &= I_{DF}^{\text{inter}} + I_{DF}^{\text{intra}} \\ &= z(k_{TT}^{\text{inter}}[A^*-A]^2 + k_{TT}^{\text{intra}}[A^*-A^*]) \quad (9) \end{aligned}$$

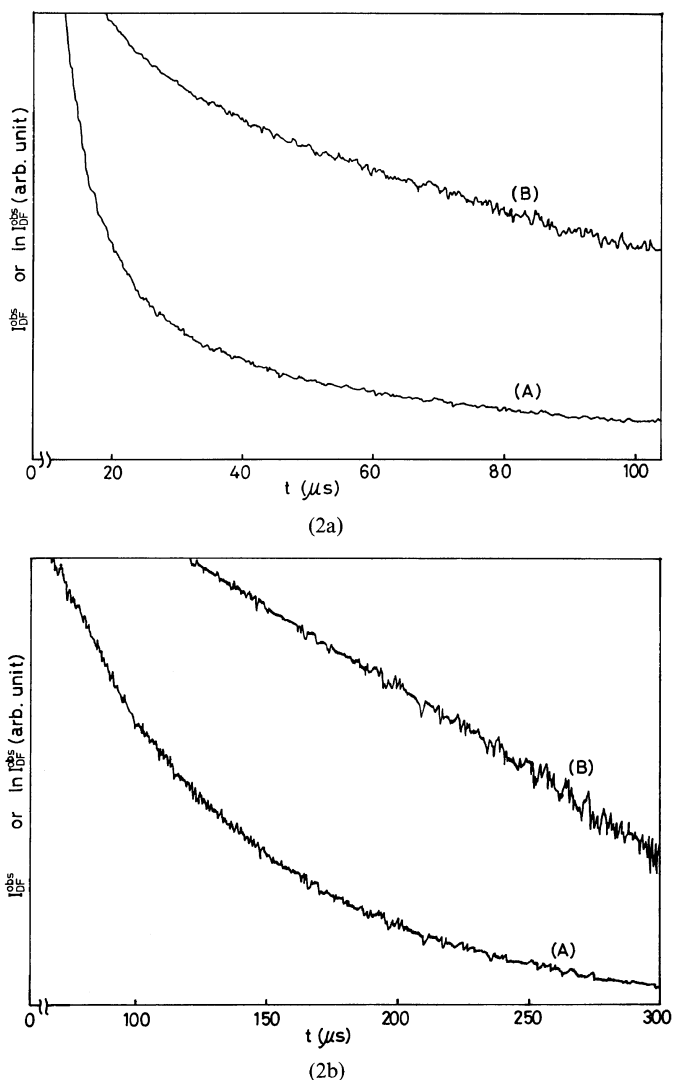
Consequently, except for a very early stage at which the second-order intermolecular T-T annihilation contributes strongly to the decay of  $A^*-A$ ,  $I_{DF}^{\text{obs}}$  must be the sum of two exponential functions, and  $I_{DF}^{\text{obs}}$  approaches  $I_{DF}^{\text{inter}}$  at a later stage since  $I_{DF}^{\text{intra}}$  decays faster than  $I_{DF}^{\text{inter}}$ . Thus, a semilogarithmic plot of  $I_{DF}^{\text{obs}}$  against  $t$  must be linear, with a slope of  $-2k_1$  at the later stage and its linear extrapolation into the short time region can be used to obtain  $I_{DF}^{\text{intra}}$  by subtraction. Replotting again semilogarithmically,  $I_{DF}^{\text{intra}}$  thus obtained against  $t$ , we obtain the rate constant  $2k_1 + k_{TT}^{\text{intra}}$  and consequently  $k_{TT}^{\text{intra}}$ . It must be noted that the identity of the subtracted intensity  $I_{DF}^{\text{intra}} = I_{DF}^{\text{obs}} - I_{DF}^{\text{inter}}$  (extrapolated) with  $I_{DF}^{\text{intra}}$  does not hold at a very early stage.

#### Analysis of Data

Decay curves and their semilogarithmic plots registered on the chart are shown in Figure 2 for the P-type delayed fluorescence of a dianthryl-polystyrene sample (APS280A) in benzene at 30°C in the range from  $t \leq 100 \mu\text{s}$  and  $t \leq 300 \mu\text{s}$ . A smooth semilogarithmic decay curve of the above data and another one for a butanone solution are shown in Figure 3 as examples.

We have shown that most of the decay curves for PS-A are straight lines for  $t \geq 20 \mu\text{s}$ .<sup>16</sup> On the other hand, as is seen in Figures 2 and 3 the decay curves for A-PS-A are linear only after  $t \approx 120 - 160 \mu\text{s}$ . Hence, it can be presumed that  $I_{DF}^{\text{intra}}$  is observed on the decay curves of A-PS-A between  $t \approx 20 \mu\text{s}$  and  $t \approx 160 \mu\text{s}$ .  $I_{DF}^{\text{intra}} = I_{DF}^{\text{obs}} - I_{DF}^{\text{inter}}$  (extrapolated) for APS280A in benzene and butanone at 30°C are replotted in a semilogarithmic scale in Figure 4. As expected, they are linear for  $t \geq 20 \mu\text{s}$ .

To make sure that the analysis of data given above is reasonable, the decay curves for APS280A in solutions were reconstructed by computer calculation, using rate equations 6, 7, and 9, with the

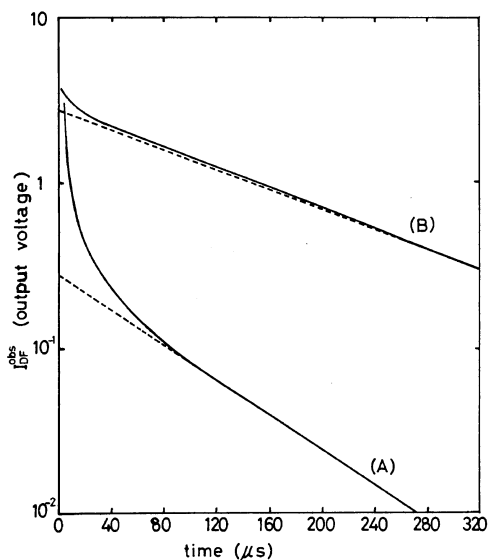


**Figure 2.** P-type delayed fluorescence decay curves of APS280A in benzene at 30°C and their semilogarithmic plots: 2a,  $t < 100 \mu\text{s}$ ; 2b,  $t < 300 \mu\text{s}$ ; concentration of APS280A,  $3.0 \times 10^{-5} \text{ M}$ ; (A),  $I_{\text{DF}}^{\text{obs}}$  vs.  $t$ ; (B),  $\ln I_{\text{DF}}^{\text{obs}}$  vs.  $t$ .

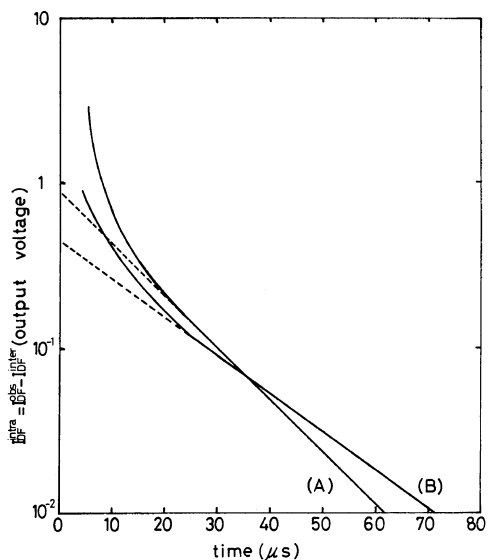
values of rate constants obtained ( $k_1$  and  $k_{\text{TT}}^{\text{intra}}$ ) and the data mentioned already. Since we do not know the emission efficiency of delayed fluorescence  $z = I_{\text{DF}}^{\text{obs}}/R_{\text{TT}}$  ( $R_{\text{TT}}$ , rate of T-T annihilation) and the conversion factor  $r$  from  $I_{\text{DF}}^{\text{obs}}$  to the real output reading  $V$ , ( $V = rI_{\text{DF}}^{\text{obs}} = rzR_{\text{TT}}$ ), the calculated and the observed curves are fitted so as to make them equal at  $t \approx 160 \mu\text{s}$ . The agreement between the calculated and observed curves is very good except at a very

early stage (Figure 5).

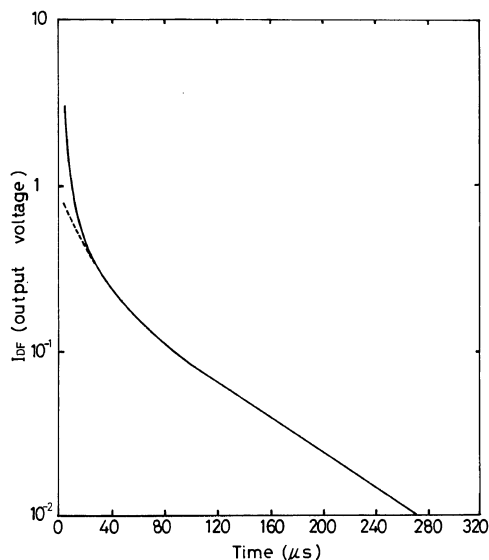
Disagreement between calculated and observed intensities at a very early stage seems to be caused by the direct fluorescence of anthracene. Though the direct fluorescence decays quite rapidly ( $\tau \approx 5 \text{ ns}$ ), its very strong intensity seems to induce some effect on the observed output reading due to the response characteristics of the photomultiplier.



**Figure 3.** Smooth semilogarithmic decay curves for P-type delayed fluorescence for the range of  $t=4\text{--}360\ \mu\text{s}$ : concentration of APS280A,  $3.0 \times 10^{-5}\ \text{M}$ ; (A), APS280A in benzene at  $30^\circ\text{C}$ ; (B), APS280A in butanone at  $30^\circ\text{C}$ .



**Figure 4.** Semilogarithmic decay curves for  $I_{\text{DF}}^{\text{intra}} = I_{\text{DF}}^{\text{obs}} - I_{\text{DF}}^{\text{inter}}$  (extrapolated) due to intramolecular T-T annihilation: concentration of APS280A,  $3.0 \times 10^{-5}\ \text{M}$ ; (A), APS280A in benzene at  $30^\circ\text{C}$ ; (B), APS280A in butanone at  $30^\circ\text{C}$ .



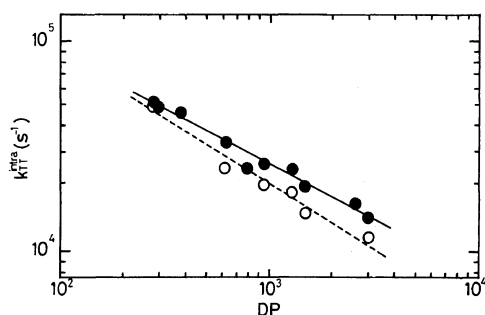
**Figure 5.** Comparison of a measured decay curve ( $I_{\text{DF}}^{\text{obs}}$ , solid line) with calculated curve ( $I_{\text{DF}}^{\text{cal}}$ , dotted line) in the case of APS280A ( $3.0 \times 10^{-5}\ \text{M}$ ) in benzene at  $30^\circ\text{C}$ . Both solid and dotted lines fully overlap after about  $20\ \mu\text{s}$ .

## RESULTS AND DISCUSSION

The values of  $k_{\text{TT}}^{\text{intra}}$  in benzene, butanone, and cyclohexane at  $30^\circ\text{C}$  obtained by the method described above are shown in Table II together with the polymer concentrations studied. Several experiments were made at higher concentrations (1–4%) and we found that  $k_{\text{TT}}^{\text{intra}}$  at higher concentrations is always a little larger than that at lower concentrations. The concentration effect of  $k_{\text{TT}}^{\text{intra}}$  is an interesting problem and a subject for further study. But our study is confined only to dilute solutions (less than 1%) where the effect of concentration is not important. The plots of  $k_{\text{TT}}^{\text{intra}}$  in benzene and butanone at  $30^\circ\text{C}$  against  $DP$  on a log-log scale are shown in Figure 6. An almost straight line can be drawn and these slopes are about  $-0.53$  (benzene) and  $-0.60$  (butanone), *i.e.*,  $k_{\text{TT}}^{\text{intra}}$  is approximately proportional to  $DP^{-0.53}$  (benzene) and  $DP^{-0.60}$  (butanone) within the range of  $DP=280\text{--}3000$ . Comparison of the data in Table II shows that the values of  $k_{\text{TT}}^{\text{intra}}$  in poor solvents for polystyrene (butanone and cyclohexane) are a little lower than those in good solvent (benzene). But the difference between in good and poor solvents is not very much.

**Table II.** Intramacromolecular-reaction rate constant  $k_{TT}^{intra}$  between the terminal groups of  $\alpha,\omega$ -dianthrylpolystyrene in benzene, butanone, and cyclohexane at 30°C

Polymer	Concn, $\times 10^{-5}$	Polymer concn	$2k_1$ , $\times 10^3$	$k_{TT}^{intra}$ , $\times 10^4$
	M	g dl <sup>-1</sup>	s <sup>-1</sup>	s <sup>-1</sup>
Benzene				
APS280A	3.0	0.09	9.6	5.2
APS300A	3.0	0.09	10	4.9
APS375A	3.0	0.12	13	4.5
APS640A	3.1	0.21	5.3	3.3
APS780A	3.0	0.24	6.4	2.5
APS940A	3.1	0.30	6.7	2.7
APS1300A	2.9	0.39	3.7	2.5
APS1500A	2.8	0.44	6.6	2.0
APS2600A	2.7	0.78	4.5	1.7
APS3000A	2.6	0.81	5.7	1.5
Butanone				
APS280A	3.1	0.09	6.9	5.0
APS640A	3.1	0.21	5.2	2.5
APS940A	3.1	0.30	8.7	2.1
APS1300A	2.9	0.39	8.8	1.9
APS1500A	2.8	0.44	16	1.5
APS3000A	3.0	0.94	6.9	1.2
Cyclohexane				
APS1500A	2.8	0.44	9.4	1.7

**Figure 6.** Dependence of  $k_{TT}^{intra}$  on the degree of polymerization  $DP$  in benzene (●, solid line) and butanone (○, dotted line) at 30°C.

The activation energy of  $k_{TT}^{intra}$  could not be obtained because of the relatively large experimental error. From the data of  $k_{TT}^{intra}$  at 20°C and 40°C, however, it is certain that the activation energy must be very low, perhaps of the order of or less than that of the solvent viscosity (10.6 kJ for benzene).

The exponent  $n$  in the relation  $k_{TT}^{intra} \propto DP^{-n}$  for the range of relatively large  $DP$  obtained in the

present work is very small compared with that in the low  $DP$  region as reported by other authors for different diffusion-controlled intramolecular reactions. Nishijima *et al.*<sup>8</sup> reported the value of  $n = 1.5$  for the intrachain excimer formation of two terminal pyrene groups connected by an oligomethylene chain with a carbon number up to 20. Perico *et al.*<sup>9</sup> and Winnik *et al.*<sup>10</sup> have also studied the formation of the excimers of pyrene groups, but in these cases, the groups are connected by poly(oxyethylene) and polystyrene chains with  $DP$  up to 443 and 255, respectively. Since Perico *et al.* presented their data in a different form, we used them to calculating the first-order rate constants and obtained an exponent of  $-1.0^*$ , disregarding the very inaccurate value of  $k^{intra}$  for the highest  $DP$ . The exponent of Winnik *et al.* is *ca.*  $-1.35$ . These data are all plotted on log-log scale in Figure 7. In the same figure are shown also, as references, the

\* This exponent value was calculated by the use of values of Table I, eq 5 in reference 9,  $p=1$ , and  $r_M^{-1}$  as singlet life time of pyrene with reported by the other author.<sup>13</sup>

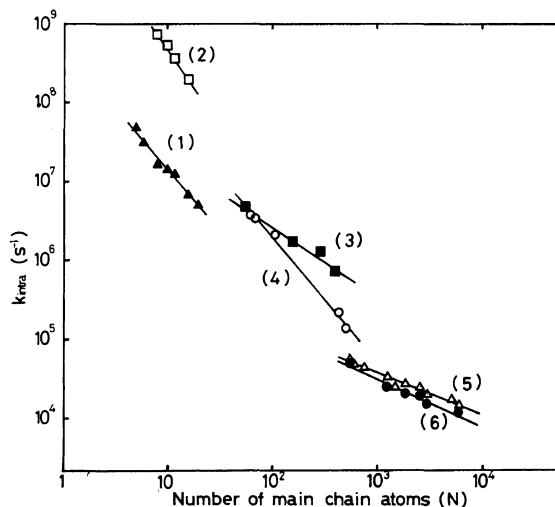


Figure 7. Rate constants for intramolecular reactions between chain ends against number of main chain atoms ( $N$ ): (1), ref 7; (2), ref 8; (3), ref 9; (4), ref 10; (5), present data (benzene); (6), present data (butanone).

Table III. Dependence of intramolecular reactions between chain ends on chain length of polymer

Method	Polymer	Solvent	Temp °C	$N^a$	$n^a$	Reference No.
ESR (Singlet probe)	$N-(CH_2)_m-N^\cdot$	DME <sup>b</sup>	15	3—20	1.5	7
Excimer	$Py-CH_2OCO(CH_2)_m-COOCH_2Py$	MTHF <sup>c</sup>	25	8—16	1.5	8
Excimer	$PyCOO-(C_2H_4O)_m-COPy$	THF	20	90—1300	1.0	9
Excimer	$Py(CH_2)_3COO-PS-OCO(CH_2)_3Py$	Toluene		65—510	1.35	10
Photodimerization (Triplet probe)	A-PS-A	Butanone	30	220—5200	0.12—0.83	28, 29
T-T annihilation	A-PS-A	Benzene	30	560—6000	0.53	
T-T annihilation (Theory)	A-PS-A	Butanone	30	560—6000	0.60	
$k_1$					1.5, 2.0	21—23
$\tau_1$					2.0, 1.8	26, 27
(Computer simulation)						
Monte Carlo ( $k_1$ )				10—70	2.0	24
Monte Carlo ( $\tau_1$ )				8—64	2.0	25

<sup>a</sup>  $N$ , number of main chain atoms;  $n$ , the exponent  $n$  in the relation of  $k^{intra} \propto N^{-n}$  and  $\tau_1 \propto N^n$ .

<sup>b</sup> DME, dimethoxyethane.

<sup>c</sup> MTHF, methyltetrahydrofuran.

intrachain rate constants obtained by Shimada and Szwarc<sup>7</sup> using ESR method. In this system, the end groups can react repeatedly, while in the other systems, including ours, the first collision leads to an

observable event and leaves the end groups inactive. Consequently, in the former case, reaction observed in an equilibrated system, must be differentiated from the latter cases involving quenching reactions



whose rates are controlled directly by the chain dynamics. Since the polymers (flexibility), solvents (expansion), and reactions (reaction diameter, steric effect) are not the same in these experiments, a direct comparison of the absolute rate constants may not be adequate. As for the slopes, however, when considered as a whole, there is a net trend that the exponent decreases with  $DP$  and our result is not inconsistent with others from this point of view.

Recently, Wilemski and Fixman,<sup>21,22</sup> then Doi<sup>23</sup> reported theories on the rate of diffusion-controlled intrachain reactions. Though the former theory does not express the intrachain rate constant as an explicit function of  $DP$  while keeping the reaction diameter constant, their results seem to predict  $k^{\text{intra}} \propto DP^{-1.5}$  for a non-draining bead-spring model and  $k^{\text{intra}} \propto DP^{-2.0}$  for a free-draining model in  $\Theta$ -solvent. In a good solvent, the exponent increases a little. Doi's results are similar. Computer simulations obtained by using the Monte Carlo method have also been reported. According to Sakata and Doi's result<sup>24</sup> the exponent of  $DP$  for  $k^{\text{intra}}$  is ca.  $-2.0$ , and Verdier and Stockmayer<sup>25</sup> have reported that the largest relaxation time,  $\tau_1$ , of the correlation function for the end-to-end vector is proportional to  $DP^{2.0}$ . It must be noted that these computer simulations were carried out with the number of beads only up to 100. These exponents are summarized in Table III.

### CONCLUSION

The rate constant of the intramolecular reaction  $k_{\text{TT}}^{\text{intra}}$  of  $\alpha,\omega$ -dianthrylpolystyrene could be obtained by eliminating the contribution of the intermolecular T-T annihilation to the decay curves. These curves are of the order of  $10^4 \text{ s}^{-1}$  and decreases in proportion to  $DP^{-0.53}$  in benzene and  $DP^{-0.60}$  in butanone for  $DP=280-3000$ .

The experimental results at low  $DP$  reported by Nishijima *et al.* agree with the theories and computer simulations. On the other hand, with increasing  $DP$ , the discrepancy between the theories and the experiments becomes important. The concept of a single exponent throughout the whole range of  $DP$  does not hold. Our results seem to indicate that the dynamical segmental diffusion is faster than expected for the polymer coils with large  $DP$  in which the segmental density becomes lower. Furthermore, there is a possibility of the existence

of intramolecular entangled behavior in polymer coils with large  $DP$ .

In research on high-molecular-weight polymer dynamics in solution, the triplet probe method using delayed fluorescence is of importance. Since the present results are the first data of this sort in a high  $DP$  region, we are now trying to obtain data on different polymers to further support the present results. These data will be reported in near future.

### REFERENCES

1. N. Goodman and H. Morawetz, *J. Polym. Sci., C*, **No. 31**, 177 (1970).
2. N. Goodman and H. Morawetz, *J. Polym. Sci., A-2*, **9**, 1657 (1971).
3. M. Sisido, *Macromolecules*, **4**, 737 (1971).
4. M. Sisido, Y. Imanishi, and T. Higashimura, *Macromolecules*, **9**, 316, 320, and 389 (1976).
5. J. A. Semlyen, *Adv. Polym. Sci.*, **21**, 41 (1976).
6. Y. Imanishi, *J. Polym. Sci., Macromol. Rev.*, **14**, 1 (1979).
7. K. Shimada and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 3313 (1975).
8. M. Yamamoto, K. Goshiki, T. Kanaya, and Y. Nishijima, *Chem. Phys. Lett.*, **56**, 333 (1978).
9. C. Cuniberti and A. Perico, *Eur. Polym. J.*, **13**, 369 (1977).
10. M. A. Winnik, A. E. C. Redpath, and D. H. Richards, *Macromolecules*, **13**, 328 (1980).
11. E. Haas, M. Wilchek, E. Katchlshi-Katzir, and I. Z. Steinberg, *Proc. Natl. Acad. Sci., U.S.A.*, **72**, 1807 (1975).
12. J. A. Nairn, C. L. Braun, P. Cluwe, and M. Szwarc, *Chem. Phys. Lett.*, **54**, 469 (1978).
13. J. B. Birks, "Photophysics of Aromatics Molecules," Wiley-Interscience, New York, N.Y., 1970, Chapters 8, 11.
14. K. Horie and I. Mita, *Polym. J.*, **9**, 201 (1977).
15. H. Ushiki and I. Mita, *Ukōken Hōkoku*, **16**, 689 (1980).
16. H. Ushiki, K. Horie, A. Okamoto, and I. Mita, *Polym. J.*, **11**, 691 (1979).
17. H. Ushiki, K. Horie, A. Okamoto, and I. Mita, *Polym. J.*, **12**, 35 (1980).
18. F. H. C. Stewart, *Aust. J. Chem.*, **13**, 478 (1960).
19. P. E. Pierce and J. E. Amonas, *J. Polym. Sci., C*, **No. 21**, 23 (1968).
20. K. Horie and I. Mita, *Macromolecules*, **11**, 1175 (1978).
21. G. Wilemski and M. Fixman, *J. Chem. Phys.*, **60**, 866 (1974).
22. G. Wilemski and M. Fixman, *J. Chem. Phys.*, **60**, 878 (1974).
23. M. Doi, *Chem. Phys.*, **9**, 455 (1975).
24. M. Sakata and M. Doi, *Polym. J.*, **8**, 409 (1976).

25. P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.*, **36**, 227 (1962).
26. R. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
27. P. G. De Gennes, *Macromolecules*, **9**, 594 (1976).
28. I. Mita, H. Ushiki, A. Okamoto, and K. Horie, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**, 1045 (1979).
29. H. Ushiki, K. Horie, A. Okamoto, and I. Mita, unpublished result.