Kinetic Study in Intermacromolecular End-to-End Photodimerization of α -Anthrylpolystyrene in Dilute Solution

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ABSTRACT: The rates of an intermolecular photodimerization reaction of 9-methylanthracene (model reaction) and an anthryl group attached to the polymer chain end in various solvents were evaluated from the change in fluorescent or UV absorption intensities of the anthryl group during continuous irradiation by a high-pressure mercury lamp. The assumption that dimerization is diffusion-controlled reaction was confirmed by the fact that the rate constants for photodimerization of 9-methylanthracene were inversely proportional to the solvent viscosity in various mixed hexane-pentadecane solutions. The rates of intermacromolecular photodimerization for α -anthrylpolystyrene with different degrees of polymerization, N , under the conditions of a very dilute solution in benzene (good solvent) were substantially independent of the degree of polymerization over the range of N from about 40 to 550.

KEY WORDS Intermacromolecular End-to-End Reaction / α -Anthrylpolystyrene / Photodimerization / Diffusion-Controlled Reaction / Thermodynamical Equilibrium Behavior of Polymer / Excimer Formation Rate Constant /

Our previous study^{1,2} on intramacromolecular end-to-end photodimerization of α , ω -dianthrylpolystyrene (A-PS-A) in very dilute solution showed that the rate constant k_{intra} for polymer end-to-end cyclization of A-PS-A in benzene (good solvent) was approximately proportional to $N^{-1.4 \pm 0.2}$ for a range of polymerization (N) between 280 and 3000. This is approximately in accord with the theoretical expectation of the equilibrium distribution of the end-to-end distance of polymers based on the thermodynamical equilibrium behavior of polymer chain in activation-controlled reaction system.

The technique based upon photodimeriza-

tion between anthryl groups attached to polymer chain end is very useful for measuring the rates of diffusion-controlled end-to-end reactions of long polymer chains in very dilute solutions, since the rates have been measured as the accumulation of dynamically controlled end-to-end excimer formation processes between polymer chain ends.² Those reactions occur within a very short lifetime ($\tau = 4.6$ — 6.1 ns for 9-methylanthracene (MA)).³ From this point of view, in analogy with the result of the intramacromolecular end-to-end photodimerization reaction of A-PS-A, the N dependence of the intermacromolecular end-to-end reaction rate of α -anthrylpolystyrene (PS-

A) obtained by the photodimerization method in a fluid solution might differ from those reported earlier using the triplet probe method in which lifetimes are of the order of micro- or milli-seconds.⁴⁻¹³

In the present paper, the photodimerization rates of MA were measured in various solvents, and the assumption that the reaction is a diffusion-controlled reaction was proved by the dependence of photodimerization rates of MA on solvent viscosities. The rates for inter-macromolecular end-to-end photodimerizations between the polymer chain ends of PS-A were measured for polymers of various degrees of polymerization, N , in very dilute solution. The molecular-weight dependence of the rate constant for the diffusion-controlled inter-macromolecular end-to-end reaction between PS-A obtained by the photodimerization method is briefly discussed.

EXPERIMENTAL

The characteristics of PS-A used in the present experiment have already been reported (Table I).⁴⁻⁹ Anthracene was attached to the chain end of anionically prepared polystyrene, as previously reported. In the notation of samples, the figures between PS and A mean approximate degrees of polymerization (N).

9-Methylanthracene (MA) was obtained from Wako Pure Chemical Industries Co. and used as received. Pentadecane was obtained from Tokyo Kasei Co. and used after distillation. Dotite-Luminasol-grade benzene, hexane, tetrahydrofuran (THF), and cyclohexane

(from Wako Pure Chemical Industries Co.) were used as solvents for photodimerization measurements.

The sample solution was deaerated by several freeze-thaw cycles in a high vacuum system. The sample in a sealed rectangular quartz cell was irradiated continuously by a 450 W high-pressure mercury lamp (Ushio UM-452).² Pyrex glass, as a filter, was set in the apparatus thermostated at $30 \pm 1^\circ\text{C}$. The extent of photodimerization of MA and PS-A was determined from the changes in intensities of UV absorption and fluorescence spectra measured with a Shimadzu MPS-5000 spectrophotometer and JASCO FP-550 spectrofluorometer, respectively. The concentration of the sample solution, 10^{-5} M, was determined from UV absorption spectra, and that at 10^{-6} M, was determined from fluorescence spectra.

RESULTS AND DISCUSSION

Kinetics of Intermolecular Photodimerization Reactions between Anthryl Groups

Plots of the I_F/I_F^0 ratio against irradiation time for MA in air in various solvents are shown in Figure 1, where I_F is the fluorescent intensity of MA at an arbitrary irradiation time t in various solvents and the superscripts 0 is used to designate the initial stage. The curve in THF (No. 5) differs from the other curves in Figure 1, indicating that the photo-

Figure 1. Plots for I_F/I_F^0 of MA against irradiation time t in various solvents in air at $30 \pm 1^\circ\text{C}$: (1) benzene; (2) cyclohexane; (3) tetralin; (4) dioxane; (5) THF.

Table I. Characteristics of α -anthrylpolystyrene

Polymer	M_n	M_w/M_n	N of PS chain	% Anthryl group at a chain end
PS40A	4.63×10^3	1.43	44	83
PS120A	1.22×10^4	1.21	117	68
PS270A	2.85×10^4	1.17	274	90
PS550A	5.73×10^4	1.18	551	90

Figure 2. Plots of the second-order reaction for the photodimerization of MA in benzene. Initial concentration of MA: $[M]_0^0 = 2.3 \times 10^{-5}$ M (detected by UV absorption).

Figure 3. Schematic diagram of photophysical processes for the anthryl group: M, ground state of monomer; M*, singlet excited state of monomer; E*, intermolecular singlet excimer state; D, ground state of dimer; D*, singlet excited state of dimer.

dimerization reaction of MA in THF includes not only the oxidation reaction but certain side reactions with THF. This is supported by the change in the shape of the fluorescence spectra during the photo-reaction. Consequently, all subsequent experiments were carried out in an evacuated system.

Our previous study² showed that irradiation light through the Pyrex glass filter caused partial photo-dissociation of the dianthryl dimer formed by photodimerization of anthryl groups. Plots of the second-order reaction for photodimerization of MA are shown in Figure 2. Under the conditions of the above experimental system, both photo-dimerization and dissociation occurred in this reaction. A schematic diagram of the photophysical processes of the anthryl group as well as a photo-

dissociation process of dianthryl dimer are described in Figure 3. The reaction rate for the above reaction system is expressed by eq 1—5.

$$\frac{d[M]}{dt} = -I_{M^*} + (k_M - k_{EM}[M])[M^*] + (k_{ME} + 2k_E)[E^*] + 2k_{dis}[D^*] \quad (1)$$

$$\frac{d[M^*]}{dt} = I_{M^*} - (k_M + k_{EM}[M])[M^*] + k_{ME}[E^*] \quad (2)$$

$$2\frac{d[E^*]}{dt} = 2k_{EM}[M][M^*] - 2(k_E + k_{ME} + k_{DF})[E^*] \quad (3)$$

$$2\frac{d[D]}{dt} = -2I_{D^*} + 2k_{DF}[E^*] + 2k_D[D^*] \quad (4)$$

$$2\frac{d[D^*]}{dt} = 2I_{D^*} - 2k_D[D^*] - 2k_{dis}[D^*] \quad (5)$$

where M, E*, and D* denote monomer, excimer, and dimer respectively, and the asterisk * represents an excited state. k_{EM} is the rate constant for intermolecular excimer formation; k_M is the sum of the rate constants for fluorescence, non-radiative transition, and the intersystem crossing of singlet monomer; k_E is the sum of the rate constants for excimer emission and non-radiative transition of excimer; k_{ME} , k_{DF} , and k_{dis} are the rate constants for dissociation of the excimer, dimerization, and photo-dissociation of dianthryl dimer, respectively; k_D is the sum of rate constants for fluorescence, non-radiative transition, and the intersystem crossing of excited dimer, and I^* is the rate of formation of excited molecules, with M and D as suffixes denoting the monomer and dimer.

In the case of $\epsilon_M[M]$ and $\epsilon_D[D]$ less than about 0.1, the rate of formation of excited molecules by incident light in the light path within 1 cm can be adequately approximated by eq 6 and 7,

$$I_{M^*} = I_M^0 \{1 - \exp(-\epsilon_M[M])\} \cong I_M^0 \epsilon_M[M] \quad (6)$$

$$I_{D^*} = I_D^0 \{1 - \exp(-\epsilon_D[D])\} \cong I_D^0 \epsilon_D[D] \quad (7)$$

where I^0 and ϵ are the intensity of the incident light and molar extinction coefficient multiplied by 2.3 (for example, $\epsilon_M = 5.3 \times 10^3$ M⁻¹ cm⁻¹ at 389 nm in benzene).

Using the steady state approximation and relation $[M]_t = [M]_i^0 - 2[D]_t$, where $[M]_t = [M] + [M^*] + 2[E^*]$ and $[D]_t = [D] + [D^*]$, with the superscript 0 for designating the initial concentration of anthryl group, the rate of decrease in the fluorescent intensity of the anthryl group can be obtained from eq 1—7 as follows,

$$\begin{aligned} -d[M]_t/dt &= 2d[D]_t/dt \\ &= 2(d[D]/dt + d[D^*]/dt) \\ &= 2k_{DF}[E^*] - 2k_{dis}[D^*] \\ &= K_F[M]^2 - 2K_B[D] \\ &= K_F[M]_t^2 + K_B[M]_t - K_B[M]_i^0 \end{aligned} \quad (8)$$

$$K_F = 2k_{EM}k_{DF}\epsilon_M I_M^0 / \{k_M(k_M + k_{DF} + k_{ME}) + k_{EM}(k_E + k_{DF})[M]\} \quad (9)$$

$$K_B = k_{dis}\epsilon_D I_D^0 / (k_D + k_{dis}) \quad (10)$$

where K is the apparent rate constant with the suffixes F and B denoting the forward (photodimerization process) and backward (photo-dissociation process) reactions of the anthryl group photo-reaction. To determine the change in $[M]_t$ with irradiation time t , eq 8 can be integrated to give eq 11, assuming the (as to chromophore) solution ($k_{EM}[M] \ll k_M$) to be dilute.

$$\begin{aligned} 2(4L[M]_i^0 - L^2)^{-1/2} [\arctan \{(2[M]_i^0 - L) \\ \times (4L[M]_t^0 - L^2)^{-1/2}\} - \arctan \{(2[M]_t - L) \\ \times (4L[M]_i^0 - L^2)^{-1/2}\}] \\ = G([M]_t) = K_F t \end{aligned} \quad (11)$$

At equilibrium between photodimerization and photo-dissociation ($d[M]_t^e/dt = 0$) with the superscript e designating equilibrium, the equation relating the apparent rate constant of the forward reaction with that of backward is simplified as follows,²

$$L = K_B/K_F = ([M]_t^e)^2 / ([M]_i^0 - [M]_t^e) \quad (\text{mol l}^{-1}) \quad (12)$$

In we may assume $K_{EM}[M] \ll k_M$, K_F can be adequately approximated as

$$\begin{aligned} K_F &= 2k_{EM}k_{DF}\epsilon_M I_M^0 / \{k_M(k_E + k_{DF} + k_{ME})\} \\ &= 2k_{EM}\tau_S\Phi_D\epsilon_M I_M^0 \end{aligned} \quad (13)$$

where τ_S is the singlet excited lifetime of the anthryl group (MA: 4.6—6.1 ns) and Φ_D , the dimer yield of the anthryl group from a singlet excimer state.

Photodimerization of 9-Methylantracene in a Fluid Solution

Plots of eq 11 for the photodimerization of MA at various initial concentrations are shown in Figure 4. That the plots in Figure 4 are linear suggests the analytical method with eq 11 to actually be valid in the our experimental system. K_F defined by eq 13 can easily be obtained from the slope of the straight line, and the value of K_B is calculated from eq 12 and K_F .

The solvent viscosity dependence of the reciprocal of the apparent forward rate constant for the photodimerization of MA is shown in Figure 5. K_F is inversely proportional

Figure 4. Plots using eq 11 for the photodimerization of MA in benzene at $30 \pm 1^\circ\text{C}$. Initial concentrations of MA: ($\bullet$), $[M]_i^0 = 2.3 \times 10^{-5} \text{ M}$ (detected by UV absorption); ($\bullet$), $[M]_i^0 = 8.2 \times 10^{-6} \text{ M}$ (detected by fluorescent intensity); ($\blacktriangledown$), $[M]_i^0 = 4.4 \times 10^{-6} \text{ M}$ (detected by fluorescent intensity);

$$\begin{aligned} G(M) &= 2/H [\arctan \{(2[M]_i^0 - L)/H\} \\ &\quad - \arctan \{(2[M]_t - L)/H\}] \end{aligned}$$

where $H = (4L[M]_i^0 - L^2)^{1/2}$

Table II. Rate constants for the photodimerization of 9-methylanthracene in a semi-concentrated polystyrene solution at $30 \pm 1^\circ\text{C}$

Chromophore	Solvent	Polystyrene		K_F $\text{M}^{-1} \text{s}^{-1}$	K_F/K_F^0 ^a
		M_n	Concentration		
			g dl^{-1}		
MA	benzene	—	—	$4.7 \times 10^2 \pm 50$	1.0
MA	benzene	3.8×10^4	2.0	$4.0 \times 10^2 \pm 50$	0.85
MA	benzene	3.8×10^4	5.2	$1.7 \times 10^2 \pm 50$	0.36
MA	benzene	3.8×10^4	9.1	$1.5 \times 10^2 \pm 50$	0.32
MA	benzene	1.1×10^5	8.9	$2.0 \times 10^2 \pm 50$	0.43
MA	benzene	3.9×10^5	8.4	$1.9 \times 10^2 \pm 50$	0.40

^a K_F^0 , rate constant value for photodimerization of 9-methylanthracene (MA) without polystyrene in benzene ($K_F^0 = 4.7 \times 10^2 \text{ M}^{-1} \text{s}^{-1}$).

Figure 5. Solvent-viscosity dependence of K_F^{-1} for the photodimerization of MA in hexane-pentadecane mixtures or cyclohexane at $30 \pm 1^\circ\text{C}$.

to the viscosity of each solvent in various mixed hexane-pentadecane and cyclohexane solutions. Doing on the assumption that the singlet excited lifetime of MA is equal in various hydrocarbon solvents (hexane-pentadecane and cyclohexane), the result in Figure 5 leads to the conclusion that photodimerization of MA is a diffusion-controlled reaction *via* a excimer formation process, as reported by Tanaka and Osugi.¹⁴

Photodimerization 9-Methylanthracene in Semi-Dilute Polystyrene Solution

Plots using eq 11 for the photodimerization

Figure 6. Plots using eq 11 for the photodimerization of MA in semi-dilute polystyrene solutions of benzene at $30 \pm 1^\circ\text{C}$: (●), without polystyrene; (▼), in addition of 9.1 g dl^{-1} PS of $N=370$

$$G(M) = 2/H [\arctan \{(2[M]_t^0 - L)/H\} - \arctan \{(2[M]_i - L)/H\}]$$

$$\text{where } H = (4L[M]_i^0 - L^2)^{1/2}.$$

of MA in a semi-dilute polystyrene solution is shown in Figure 6. The apparent rate constants K_F for photodimerization of MA in benzene at $30 \pm 1^\circ\text{C}$ are shown in Table II along with the polymer concentrations studied. In Table II, K_F for MA solution containing 9.1 g dl^{-1} polystyrene (PS) ($M_n = 3.8 \times 10^4$) roughly agrees with that of a solution containing 8.9 g dl^{-1} PS ($M_n = 1.1 \times 10^5$) or 8.4 g dl^{-1} PS ($M_n = 3.9 \times 10^5$) regardless of increasing solution viscosity with molecu-

lar weight of PS. The bimolecular rate constant for a diffusion-controlled reaction, k_{dif} , is given according to Debye¹⁵ as,

$$k_{\text{dif}} = 4\pi RD = 8k_B T / 3\eta \quad (14)$$

where R is the sum of the hydrodynamic radii of the reacting species, D , the sum of the diffusion coefficients, η , the viscosity of the medium, k_B , Boltzmann's constant and T , temperature. In Table II, the apparent rate constant K_F for the photodimerization of MA depends as a first approximation only on the polystyrene concentration and not the DP of the polymer used. Hence, D for the photodimerization of MA may be related, not to the solution viscosity η_{sol} but to the volume fraction of polystyrene. A similar situation was reported for benzil-anthracene triplet-triplet energy transfer in polystyrene-benzene solution in our previous work.¹⁶ Moreover, by the NMR spin-echo technique, at a fixed polystyrene concentration, [PS], the self-diffusion coefficient of benzene in polystyrene-benzene solution was found to be independent of molecular weight in the region $M > 10^4$.¹⁷

Molecular-Weight Dependence of K_F of α -Anthrylpolystyrene

Plots for the intermacromolecular end-to-end photodimerization of PS-A are shown in Figure 7. The apparent rate constants K_F for the intermacromolecular end-to-end photodimerizations of PS-A in benzene (good solvent)

at $30 \pm 1^\circ\text{C}$ are shown in Table III together with the values of K_B and polymer concentrations studied.

Figure 7. Plots using eq 11 for the intermacromolecular end-to-end photodimerization of PS270A in benzene at $30 \pm 1^\circ\text{C}$:

$$G(M) = 2/H [\arctan \{(2[M]_t^0 - L)/H\} - \arctan \{(2[M]_t - L)/H\}]$$

where $H = (4L[M]_t^0 - L^2)^{1/2}$. Initial concentration: (○), 3.8×10^{-6} M; (●), 5.0×10^{-6} M.

Figure 8. Molecular-weight dependence of K_F/K_F^{MA} for the intermacromolecular end-to-end photodimerization of α -anthrylpolystyrene in benzene at $30 \pm 1^\circ\text{C}$.

Table III. Rate constants for the intermacromolecular end-to-end photodimerizations of α -anthrylpolystyrene in benzene at $30 \pm 1^\circ\text{C}$

Polymer	Concentration		K_F $\text{M}^{-1} \text{s}^{-1}$	$K_F/K_F^{\text{MA}}^a$	K_B s^{-1}
	M	g dl^{-1}			
PS40A	3.6×10^{-6}	1.7×10^{-3}	$9.7 \pm 0.5 \times 10^1$	0.21	$1.4 \pm 0.5 \times 10^{-4}$
PS120A	3.4×10^{-6}	4.1×10^{-3}	$9.5 \pm 0.5 \times 10^1$	0.20	$1.3 \pm 0.5 \times 10^{-4}$
PS270A	3.8×10^{-6}	1.1×10^{-2}	$7.0 \pm 0.5 \times 10^1$	0.15	$1.4 \pm 0.5 \times 10^{-4}$
PS550A	2.9×10^{-6}	1.7×10^{-2}	$1.2 \pm 0.5 \times 10^2$	0.25	$1.2 \pm 0.5 \times 10^{-4}$

^a K_F^{MA} , rate constant value for the photodimerization of 9-methylanthracene (MA) in benzene ($K_F^{\text{MA}} = 4.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$).

The K_F/K_F^{MA} ratio of the apparent forward rate constants obtained by the intermacromolecular end-to-end photodimerization of PS-A in benzene at $30 \pm 1^\circ\text{C}$ are plotted in Figure 8 as a function of the degree of polymerization, N . In Figure 8, the K_F/K_F^{MA} ratio are substantially independent of the degree of polymerization from about 40 to 550.

According to eq 13, the apparent forward rate constant, K_F , is comprised of many constants (k_{EM} , τ_S , Φ_D , ϵ_M , and I_M^0). But among them only k_{EM} for the intermacromolecular end-to-end excimer formation may be influenced by the degree of polymerization, N , of PS-A. The experimental results thus indicate that the rate constant of the intermacromolecular excimer formation k_{EM} is independent of chain length.

Discussion for Molecular-Weight Dependence of the K_F of α -Anthrylpolystyrene

Our previous studies^{11,18} showed the rate constants k_q for the diffusion-controlled quenching of phosphorescence of α -benzylpolystyrene by α -anthrylpolystyrene (triplet probe method) in benzene to decrease with increasing degree of polymerization N at an exponent $n=0.29$ for N^{-n} in the range, $N=23$ –3900. It should be noted that the triplet had a long-excited-lifetime (benzil: $\tau_T=54\ \mu\text{s}$). In our study on activation-controlled reactions between living polystyrene and chloro-ended polystyrene and between polyoxyethylene and chlorosulfonyl-ended polyoxyethylene for $N=24$ –20800, the rate of reaction between polymer chain-ends was independent of the degree of polymerization N .^{19,20} We explained the molecular-weight independence of the rate constant, k_2 , for an activation-controlled intermacromolecular end-to-end reaction by theoretical thermodynamics.²⁰

The present experimental data for intermacromolecular end-to-end photodimerization in a good solvent show the rate constant to be independent of chain length,

though the reactions are diffusion-controlled. The difference between the previous and present diffusion-controlled reactions is in the lifetime of the excited species. We conclude that the molecular-weight dependence of the rate constant for diffusion-controlled intermacromolecular end-to-end reaction is influenced by the excited lifetime of chromophore attached to the polymer chain ends. In the present experiments, excimer formation followed by dimerization should proceed within a very short excited lifetime ($\tau=4.6$ –6.1 ns for 9-methylanthracene). The above-mentioned discussion exactly corresponds to that for the intramacromolecular end-to-end photodimerization reaction of A-PS-A.²

Table III shows that the K_B for an intermacromolecular photo-dissociation reaction is independent of the degree of polymerization N for $N=40$ –550. Thus, K_B should be substantially independent of N in Table III because the PS-A used as a sample was a low molecular-weight polymer. In case of a high molecular-weight polymer, examples of the effects of disentanglement motion are given in the literature.²¹ According to Schnabel *et al.*,²¹ the diffusion rate during degradation of poly(phenyl vinyl ketone) in benzene with laser flash photolysis and pulse radiolysis is proportional to $N^{-0.22 \pm 0.02}$.

In conclusion, the reaction rate for photodimerization of MA in semi-concentrated polystyrene solution is related not to the solution viscosity, but the polystyrene concentration. The diffusivity of small molecules is hardly affected by change in molecular-weight at a certain [PS], but is influenced by the volume fraction of polymer segments in a solution. The K_F for intermacromolecular end-to-end photodimerization between anthryl groups attached to polystyrene chain ends in benzene is independent of the degree of polymerization. Thus the apparent rate for the diffusion-controlled polymer-polymer reaction as determined by the photodimerization method (very short-excited-lifetime

probe) may reflect thermodynamical equilibrium behavior of a polymer chain, as in the case of an activation-controlled reaction system.

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