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QUENCHING OF FLUORESCENCE OF POLYESTERS HAVING PENDANT ANTHRYL GROUPS BY POLYESTERS HAVING PENDANT N,N-DIMETHYLANILINO GROUPS *

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Fluorescence of various polyesters prepared from 2-(9-anthryl)-methylpropane-1,3-diol was quenched by various polyesters prepared from 2-(4-dimethylaminobenzyl)propane-1,3-diol. The sequence of quenching constants(K_q) was discussed with special reference to the polymer structures of fluorescers and quenchers. When terephthalate groups were incorporated in the main chain of quencher, K_q increased very much, which was interpreted by cooperative quenching action of donor(amine) and acceptor(terephthalate). This concept was unequivocally evidenced by separate experiments.

We wish to report interactions of polymeric fluorescers with polymeric quenchers taking the Stern-Volmer quenching constant as a measure. The aim of the present study is to find out the effects of fluorescer and quencher structures on the quenching constant(K_q). In the preceding articles, we discussed the structural effects on excimer or exciplex formation in polymeric systems in which pendant fluorophores are ω-(9-carbazyl)butyl[1], 9-carbazyl[2], (1-naphthyl)methyl[3] and (9-anthryl)methyl[4]. General conclusions obtained are as follows. a) Intramolecular excimer formation is facilitated when the fluorophores are congested along a polymer chain. b) Interpolymer association among like polymer molecules participates even at the polymer concentration as low as 10^{-3}-10^{-4}M. Differences of fluorescence quenching from excimer formation may be considered as follows. i) Fluorescence quenching concerns to encounter of two unlike molecules whereas excimer is formed between like molecules. ii) Excimer is a short distance event which requires nearly parallel arrangement of two molecular planes at a distance of 3-5Å whereas the encounter for fluorescence quenching could occur at a distance of ~10Å in configurationally non-specific fashions.

The abbreviation, structure and molecular weight of fluorescers and quenchers are presented in Tables I and II. Preparation of the fluorescers is in the course of publication[4]. The quencher polymers were prepared by ester exchange of 2-(4-dimethylaminobenzyl)propane-1,3-diol(I) with diethyl(4-dimethylaminobenzyl)malonate(II)(PD-1D), diethyl terephthalate(PD-Ph), or with thiophenolates of relevant dibasic acids(PD-2, PD-4 and PD-8). The II was prepared by hydrogenation of diethyl (4-dimethylaminobenbylidene)malonate(m.p. 111-2°C, prepared by condensation of 4-dimethylaminobenzaldehyde with diethyl malonate) on Pd/C under a pressure of 25 Kg/cm^2 at 100°C for 3 hr. Y=75%, 148°C/0.01mmHg, IR(neat) 1730cm^{-1}(C=O stretch), NMR($CDCl_3$) τ 3.06(4H, q, aromatic), 5.80(4H, q, J=7Hz, $-CO_2\underline{CH_2}CH_3$), 6.35(1H, t, J=8Hz, methine), 6.87(2H, d, J=8Hz, benzyl methylene), 7.11(6H, s, $N(CH_3)_2$), 8.83(6H, t, J=7Hz, $-CO_2CH_2\underline{CH_3}$). The II was then reduced to I by $LiAlH_4$ in ether.

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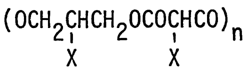
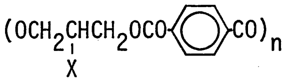
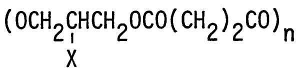
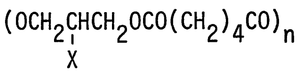
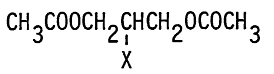
* Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. IV.

Table I. Structures of Polymer Fluorescers

Name	Structure	M.W.	n	τ_f(ns)
PA-1A	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO\underset{X}{C}HCO})_n$	1000	2	8
PA-Ph	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO{-}C_6H_4{-}CO})_n$	690	2	8
PA-2	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO(CH_2)_2CO})_n$	830	2-3	8
PA-4	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO(CH_2)_4CO})_n$	2450	6-7	7
MA	 $\mathrm{CH_3COOCH_2\underset{X}{C}HCH_2OCOCH_3}$	350		8

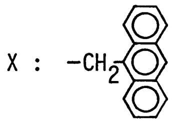
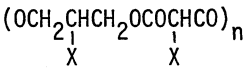
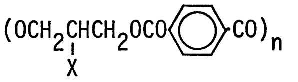
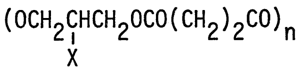
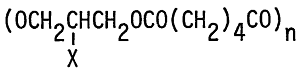
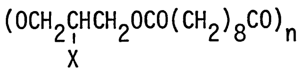
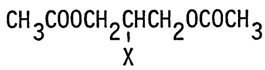
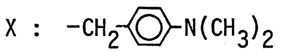


Table II. Structures of Polymer Quenchers

Name	Structure	M.W.	n
PD-1D	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO\underset{X}{C}HCO})_n$	3900	9-10
PD-Ph	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO{-}C_6H_4{-}CO})_n$	1500	4- 5
PD-2	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO(CH_2)_2CO})_n$	5900	18-20
PD-4	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO(CH_2)_4CO})_n$	2900	9-10
PD-8	 $(\mathrm{OCH_2\underset{X}{C}HCH_2OCO(CH_2)_8CO})_n$	5400	14-15
MD	 $\mathrm{CH_3COOCH_2\underset{X}{C}HCH_2OCOCH_3}$	293	



Y=81%, m.p. 95-6°C(from toluene), IR(KBr disk) 3350cm^{-1} (OH), NMR($\mathrm{CDCl_3}$) τ 3.10(4H, q, aromatic), 6.30(4H, 2d $-\underline{\mathrm{C}}\mathrm{H_2OH}$), 7.07(6H, s, $\mathrm{N(CH_3)_2}$), 7.30(2H, broad, OH), 7.48 (2H, d, benzyl methylene). Found: C 68.40, H 9.21, N 6.60. Calcd for $\mathrm{C_{12}H_{19}O_2N}$: C 68.86, H 9.15, N 6.69. The I was acetylated to MD. Viscous oil, IR(neat) 1740cm^{-1}(C=O stretch). Molecular weight of the polyesters were determined by GPC(elutant: THF) calibrated for analogous polyesters.[3]

The quenching experiments were conducted in THF at room temperature. Examples of the Stern-Volmer plots are shown in Fig. 1 and the values of K_q are tabulated in Table III. There are considerable differences in K_q depending upon the combination of the F-Q pair. Identity of absorption maxima as well as fluorescence maxima of anthryl groups indifferent to the structure of polymers indicates that the difference in K_q does not originate from the difference in energy levels of anthryl groups under different environments. Furthermore, the lifetime of monomer emission of anthryl group(τ_f) shown in Table II which was determined by a time resolved photometer(an attachment to Hitachi MPF-4 fluorescence spectrometer) in a dilute THF solution is the same for all anthryl polymers The decay processes of the singlet excited state of anthryl groups are not much affected by the environments except certain differences in the probabilities of excimer formation.[4] Consequently, the difference in K_q should

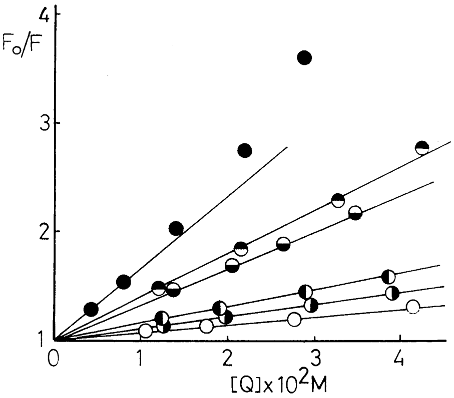


Figure 1. Stern-Volmer plots. fluorescer: [MA] = 1x10^{-4}M in THF.
●: PD-Ph, ◓: MD, ◒: PD-4,
◐: PD-8, ◑: PD-2, ○: PD-1D.

Table III. The Values of K_q(M^{-1})

Q \ F	MA	PA-1A	PA-2	PA-4	PA-Ph
MD	39	26	31	20	34
PD-1D	8	7	6	6	7
PD-2	11	8	9	-	9
PD-4	35	29	-	29	28
PD-8	18	14	14	-	15
PD-Ph	65	53	58	-	60

Measurements in THF at 17 ± 1°C.

be interpreted by the change in the local concentration of relevant functional groups influenced by their linear density along a polymer chain and also by entanglement of polymer chains. Another important factor will be the mobility of polymer molecules.

Quenching of fluorescence of aromatic hydrocarbons by amines is generally considered as a diffusion controlled process.[5] The simple Stern-Volmer equation(1) is then converted to (2), indicating upward curvature of the Stern-Volmer plots at the higher concentration range of quencher.

$$F_0/F = 1 + K_q[Q] \qquad (1)$$

$$F_0/F = (1 + k_0\tau_f[Q])\exp(V_d(F/F_0)^{1/2}[Q]) \qquad (2)$$

$$\text{where } k_0 = 4\pi N''D(\gamma R_0), \quad V_d = 4\pi N''(D\tau_f)^{1/2}(\gamma R_0)^2$$

γR_0, D and N" are the effective action diameter, the sum of diffusion constants for F and Q, and the Avogadro number $\times 10^{-3}$, respectively. γ is the probability of the decomposition of $(F^*\cdots Q)$ expressed by $k_3/(k_2 + k_3)$ for the reaction path (3).

$$F^* + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (F^*\cdots Q) \xrightarrow{k_3} \cdots\cdots \rightarrow F + Q \qquad (3)$$

Although some of the Stern-Volmer plots in Fig. 1 do not fall on straight lines, the initial slope of the plots corresponds to $K_q(\equiv k_0\tau_f)$. The values of K_q thus obtained for polymer quenchers are smaller than those of MD with exceptions of PD-Ph. The smaller K_q values of polymer quenchers are explained by following two factors. 1) The diffusion constants of polymer quenchers are smaller than that of MD. 2) Since the quencher groups in polymers are congested, there will be overlap of quenching diameter as depicted in Fig. 2. When $K_q = 30\text{M}^{-1}$ and $\tau_f = 8\times10^{-9}$sec, k_0 is $4\times10^{-9}\text{M}^{-1}\text{sec}^{-1}$ and then D is to be in the order of $10^{-6}\text{cm}^2\text{sec}^{-1}$, assuming γR_0 to be ~10Å. This is about the critical value of k_0 for polymers having molecular weight of 10^3-10^4 to react via diffusion controlled processes. However, there seems to be no relation between the magnitude of K_q and the degree of polymerization of Q. The sequence of DP is PD-2 > PD-8 > PD-1D ≈ PD-4 > PD-Ph whereas the sequence of K_q determined for a fixed fluorescer - variable quenchers pairs is PD-Ph > MD > PD-4 > PD-8 > PD-2 > PD-1D. The finding that K_q of congested polymer quenchers(PD-1D, PD-2) are small is indicative of the factor 2) to be more important. The reversed sequence of PD-8 and PD-4 will be due either to the smaller molecular weight of PD-4 than that of PD-8 or to different degrees of entanglement of polymer chains. Concerning to polymer entanglement, the results of photodimerization of anthryl groups attached to the polyesters having identical backbone structures to the PD series are suggestive.[4] When N,N-dimethylanilino groups in PD-8 are substituted by 9-anthryl groups(according to the nomenclature in Tables I and II, this is named PA-8), intramolecular photodimerization of the polymer is faster than that of PA-4, indicating that the encounter probability of anthryl groups is larger for a polymer in which chromophores are separated by a long, polymethylene chain. Consequently, the time averaged overlap of quenching groups in PD-8 may also be more than that in PD-4.

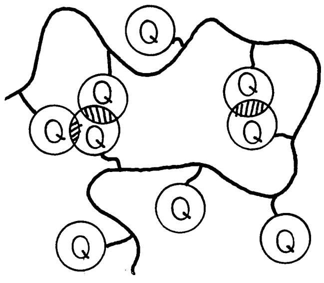


Figure 2. Overlap of quenching diameters.

Change in K_q for a quencher with varying fluorescer is not prominent. We expected a sudden change in K_q for a specific F - Q pair so that we could discuss interpolymer association between different polymer molecules. More elaborated design of polymer syntheses would be required to realize specific interpolymer association as occurring in antigen - antibody interactions.

Unexpectedly large values of K_q of PD-Ph are interpreted by considering the enhancement of k_3 in eq.(3). Evidence is as follows. Firstly, the quenching constants of N,N-dimethylaniline(DMA) and dimethylterephthalate(DMT) to the fluorescence of anthracene were determined as $56.9M^{-1}$ and $16.9M^{-1}$ in THF, respectively, whereas K_q determined for equimolar mixture of DMA and DMT was $84.6M^{-1}$. Synergic effect of DMA and DMT in fluorescence quenching should therefore be considered. Secondly, the fluorescence of polyesters having both N,N-dimethylanilino and anthryl pendant groups arranged in an alternative sequence(PA-1D, prepared by ester exchange of II with 2-(9-anthryl)methylpropane-1,3-diol according to the same recipe as employed for preparing samples in Table II.[3] M.W. 2000, $\overline{DP}$ 4 - 5) was studied in the presence of DMA or DMT. As shown in Fig. 3, the fluorescence of PA-1D shows the maximum emission at 415nm(monomer emission) and 525nm(exciplex emission) in THF. By the addition of DMT, the exciplex emission is strongly quenched(Fig. 4,○⊕) whereas the monomer emission is scarcely affected(●). The exciplex emission is scarcely affected by the addition of DMA(□) while the monomer emission is quenched(■).

These results indicate unequivocally that a weak acceptor, DMT, interacts effectively with the exciplex state which is apparently a stronger donor than the singlet excited state of anthry group. Although we do not know the exact mechanism of this unique cooperative quenching action of donor and acceptor, the participation of terephthalate group in process(3) must be taken into account. Phenomenologically, this effect should be observed as an enhancement of k_3, an enhancement of , resulting in a larger value of K_q as well as the prominent upward curvature of the plots for PD-Ph in Fig. 1.

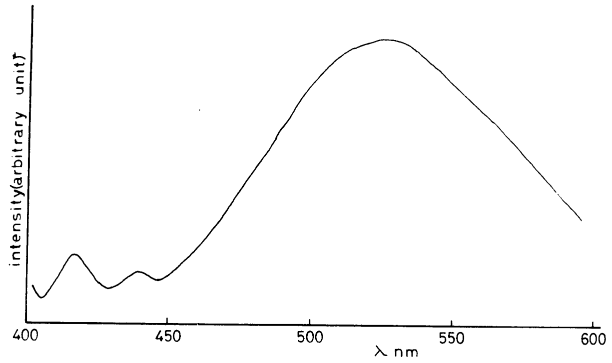


Figure 3. Fluorescence spectrum of PA-1D in THF. [PA-1D] = $2x10^{-5}$M, excitation at 390nm.

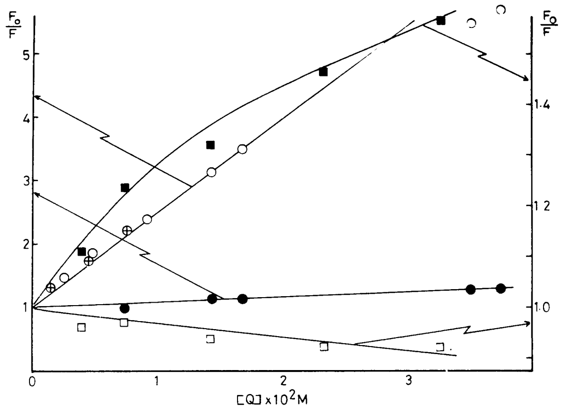


Figure 4. Quenching of exciplex and monomer emission of PA-1D in THF(Stern-Volmer plots). ○:Q=DMT, exciplex, ⊕:Q=DMT, exciplex(τ_0/τ), ●:Q=DMT, monomer, □:Q=DMA, exciplex, ■:Q=DMA, monomer.

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