Functionalized Polyionenes. 1. Synthesis and Photoreaction of Polyionenes Bearing Pendant (9-Anthryl)methyl Groups

Yasuzo Suzuki*

Research Institute for Polymers and Textiles, Higashi, 1-1-4, Yatabe-cho, Tukuba-gun, Ibaragi, Japan 305

Shigeo Tazuke

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4295, Nagatsuta, Midori-ku, Yokohama, Japan 227. *Received March 16, 1979*

ABSTRACT: Various polyionenes having pendant (9-anthryl)methyl groups and their dimer and monomer model compounds were prepared by the Menschutkin reaction. These polymers bearing both hydrophobic and hydrophilic segments formed micelles at the segment concentration above 10^{-5} mol/dm^3 in aqueous solution as determined by spectral change of fluorescein sodium salt in the presence of the polymer. The effects of polymer structure, molecular weight, concentration, and solvents on photodimerizability of pendant anthryl groups were studied in comparison with the dimer and monomer model compounds. The reaction behaviors of low molecular weight model compounds and polyionene were distinctively different. Increasing hydrophobic interaction and decreasing Coulombic interaction brought about a decrease in the reactivity of the latter whereas the effects were discussed in terms of molecular interactions studied by emission and absorption spectroscopy of anthryl groups and also of expected polymer chain conformation. In particular, the reactivity of polyionene in the micelle was shown to be independent of apparent chromophore concentration whereas the mobility of the chromophore seemed to be a more important factor than the concentration. The reactivity of polyionene is consequently very sensitive to the reaction medium influencing inter- and intrapolymer interactions responsible for the chromophore mobility.

We have been interested in the polymer structure–molecular interactions–polymer functionality correlation and involved in the syntheses and spectroscopic measurements of polyesters or polyurethanes bearing naphthyl,[1] anthryl,[2] pyrenyl,[3] carbazolyl,[4] and other groups.[6-8] These studies provided useful information on the intra- and interpolymer interactions of polymer bound fluorophores based on excimer and exciplex measurements and the polymer–small molecular interactions such as charge transfer complex formation and fluorescence quenching of polymer bound fluorophores. Also photodimerization experiments of polymer bound anthryl groups revealed an interesting structure–functionality correlation that the mobility of the functional groups was more important than the chromophore concentration for bimolecular reactions to proceed in polymer matrices.[3,6] These detailed measurements made in organic dilute solution are governed by collision between chromophores or by exchange interaction between excited and nonexcited chromophores. When there are specific ground-state interactions such as electron donor–acceptor, Coulombic and/or hydrophobic interactions, both intra- and interpolymer interactions are a function of these molecular interactions. We have already demonstrated that weak electron donor–acceptor interactions promote polymer association in dilute solution.[5,8] However, these measurements in organic solvents do not provide any information on Coulombic and hydrophobic interactions. Since we believe that the investigation on Coulombic and hydrophobic interactions in the polymeric system is equally indispensable for the design of water-soluble functional polymers, study on functionalized polyelectrolytes having balanced hydrophobic and hydrophilic properties with functional probes is intended in this series of articles. Since the conformation of the polyelectrolytes is sensitive to the change in the medium, the investigation of molecular interactions in different hydrophobic and Coulombic media is informative with respect to the polymer conformation–polymer functionality correlation.

Recently we have reported the preliminary investigation on water-soluble polyionenes having (9-anthryl)methyl groups.[10] The results indicated that the solution properties such as viscosity, photodimerizability, and fluorescence characteristics were affected by both hydrophobic association of anthryl groups and Coulombic interaction of quarternary ammonium ions. These hydrophobic polyionenes in water should be better considered as a polymer micelles based on the spectroscopic study of hydrophobic probe in the presence of the polyionenes.

Experimental Section

2-[(9-Anthryl)methyl]trimethylene Dibromide I. The solution of 10.78 g (4.11×10^{-2} mol) of triphenylphosphine in 30 cm^3 of acetonitrile was cooled with stirring. To this solution was added dropwise 6.37 g (3.99×10^{-2} mol) of bromine, followed by a solution of 3.00 g (1.13×10^{-2} mol) of 2-[(9-anthryl)methyl]-1,3-propanediol (II)[2] in 80 cm^3 of acetonitrile. Cooling was continued until the addition of II was completed. After the reaction had continued for 2 h, acetonitrile was evaporated to dryness, and to the residue was added 10 cm^3 of benzene. The remaining crystals were filtered and then washed with aqueous 60% ethanol to remove triphenylphosphine oxide; 0.14 g of I was obtained. The filtrate was chromatographed on SiO_2–benzene, and 3.78 g of I was obtained from the effluent. The combined products were recrystallized from 70 cm^3 of 2-propanol: yield 3.69 g (88.9%); mp 112–113 °C; NMR ($CDCl_3$) δ 2.4–2.9 (1 H, m, CCHC), 3.6–3.9 (6 H, 2 d, $BrCH_2$ and CH_2An), 7.2–8.5 (9 H, m, aromatic). Anal. Calcd for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 54.54; H, 3.87.

2-[(9-Anthryl)methyl]trimethylene Bis(dichloro ethanoate) III. To the solution of 2.74 g (1.03×10^{-2} mol) of II on 10 cm^3 of chloroform was added dropwise 4.5 g (4.0×10^{-2} mol) of chloroacetyl chloride. After standing overnight, the mixture was washed with aqueous sodium bicarbonate, and the suspension was extracted with chloroform. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was recrystallized from a benzene–cyclohexane mixture (1:1): yield of III 2.35 g (58.6%); mp 108–109 °C; NMR ($CDCl_3$) δ 2.8 (1 H, m, CCHC), 3.9 (2 H, d, CH_2An), 4.2 (4 H, d, $ClCH_2COO$), 4.8 (4 H, 2 d CCH_2OOC), 7.6–8.7 (9 H, m, aromatic). Anal. Calcd for $C_{22}H_{20}Cl_2O_4$: C, 63.02; H, 4.81. Found: C, 63.54; H, 5.05.

2-[(9-Anthryl)methyl]trimethylene Bis(5-bromo pentanoate) IV. The mixture of 1.50 g (5.64×10^{-3} mol) of II and 2.44 g (1.22×10^{-2} mol) of 5-bromopentanoyl chloride was dissolved in 10 cm^3 of benzene. After standing overnight, the reaction mixture was washed with aqueous sodium bicarbonate and then extracted with ether. The organic layer was dried over potassium carbonate and evaporated to dryness. The residue was recrystallized from ether–petroleum ether: yield 2.81 g (83.8%); mp 64–67 °C; NMR ($CDCl_3$) δ 1.8 (8 H, m, CCH_2C), 2.3 (5 H, m, $OOCCH_2$ and CCHC), 3.8 (4 H, m, CH_2Br), 3.7 (2 H, d, CH_2An), 4.1 (4 H, d, CH_2O), 7.2–8.5 (9 H, m, aromatic). Anal. Calcd for

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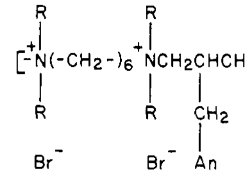
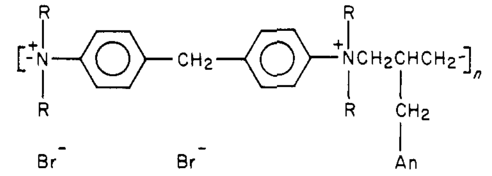
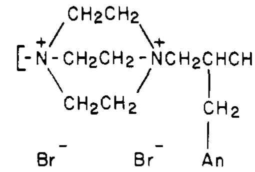
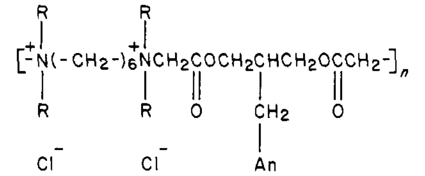
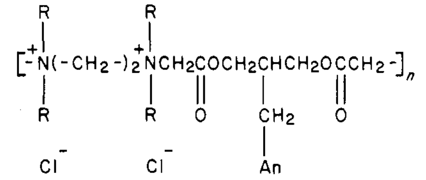
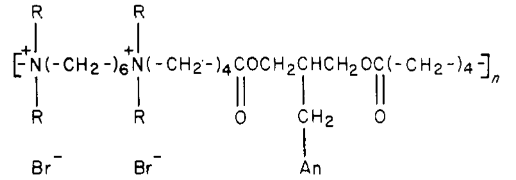
Table I
Preparation of Polyionenes Having (9-Anthryl)methyl Groups[a]

name	structure	halide	reduced viscosity (concn, g/100 cm^3)
IA-6		I	0.052 (0.25)
IA-DM		I	0.054 (0.28)[b]
IA-ACO		I	0.077 (0.30)[b]
PIA-6		III	0.256 (0.26)
PIA-2		III	0.10 (0.28)
PIA-4,6		IV	0.19 (0.33)

[a] The viscosity was measured in water unless otherwise noticed. R is the methyl group; An is the 9-anthryl group. The polymerization reaction was run in DMF. [b] Measured in DMF.

$C_{28}H_{32}Br_2O_4$: C, 56.77; H, 5.45. Found: C, 55.40; H, 5.12.

Monomer Model Compound (MIA). The solution of III and triethylamine in dimethylformamide (DMF) was heated at 60 °C. After the reaction had continued for 8 h, DMF was distilled off, and to the residue was added dry ether with stirring. The precipitated yellowish powder of MIA was filtered: IR (KBr) 1750, 1220 cm^{-1}; NMR (CD_3OD) δ 1.3 (18 H, t, CH_3), 2.7–4.5 (23 H, m, aliphatic), 7.4–8.7 (9 H, m, aromatic). Anal. Calcd for $C_{34}H_{50}Cl_2N_2O_4$: C, 65.69; H, 8.11; N, 4.51. Found: C, 63.89; H, 8.82; N, 4.86.

Dimer Model Compound (DIA). 3-(9-Anthryl)propyl chloro ethanoate V was prepared by chloroacetylation of 3-(9-anthryl)-1-propanol[11] in chloroform. The yield of V was 67%, mp 99–100 °C. Anal. Calcd for $C_{19}H_{17}Cl_1O_2$: C, 72.96; H, 5.48. Found: C, 73.74; H, 5.47. The solution of 1.98 g (6.33 × 10^{-3} mol) of V and 0.5 g of N^1,N^1,N^6,N^6-tetramethyl-1,6-hexanediamine (VI) in 2 cm^3 of DMF was stirred for 2 days at room temperature, and then DMF was evaporated. The oily residue was stirred in dry ether. The crude DIA was filtered and then dissolved in water. After filtration, the filtrate was subjected to freeze-drying: yield 2.06 g (92.8%); IR (KBr) 1750, 1250–1210 cm^{-1}; NMR (CD_3OD) δ 1.2–2.5 (12 H, broad, CCH_2C), 3.2–4.7 (28 H, broad, aliphatic and NCH_3), 7.4–8.6 (18 H, m, aromatic). Anal. Calcd for $C_{48}H_{58}Cl_2N_2O_4$: C, 72.33; H, 7.33; N, 3.51. Found: C, 68.69; H, 7.55; N, 3.32.

Polymerization. In a typical experiment, the mixture of 0.3416 g (8.148 × 10^{-4} mol) of III and 0.1404 g (8.142 × 10^{-4} mol) of VI in 0.5 cm^3 of DMF was heated at 60 °C with stirring. After the reaction had continued for 23 h, DMF was evaporated to dryness. Dry ether (5 cm^3) was added to the residue and the mixture was stirred overnight. A fine powder of polyionene (PIA-6) was filtered and dried under vacuum on P_2O_5. Anal. Calcd for $C_{32}H_{44}Cl_2N_2O_4$: C, 64.97; H, 7.50; N, 4.74. Found: C, 58.15; H, 7.56; N, 4.74. Other polymers were similarly prepared, as shown in Table I.

Photoreaction. A 3 cm^3 sample solution in a 1 cm^2 quartz cell was purged with argon for 30 min. The solution was irradiated at the wavelength of 366 nm by a Jasco spectroirradiator (CRM-FA) which was composed of a 2000 W xenon lamp as the light source and a grating monochromator. The optical density of the sample solution at the irradiated wavelength was above 0.8 all through the course of photoreaction. The disappearance of the (9-anthryl)methyl groups was monitored by measuring the absorbance at the lowest energy bottom of the ^1L_a band of the anthryl groups. The incident light intensity was simultaneously monitored at 603 nm and determined by a digital photometer (IL-600-620, International Light Inc.). The recorded count number gave the

Table II
Polymerization Reactions of PIA-6 in Different Solvents

run no.	solvent	temp, °C	reaction time, h	reduced viscosity (concn, g/100 cm^3)
1	DMF	60	23	0.27 (0.26)
2	DMA	60	55	0.20 (0.25)
3	Me_2SO	40	20	0.23 (0.29)
4	sulfolane	40	19.5	0.03 (0.25)
5	DMF:MeOH (4:1)	40	126	0.03 (0.23)

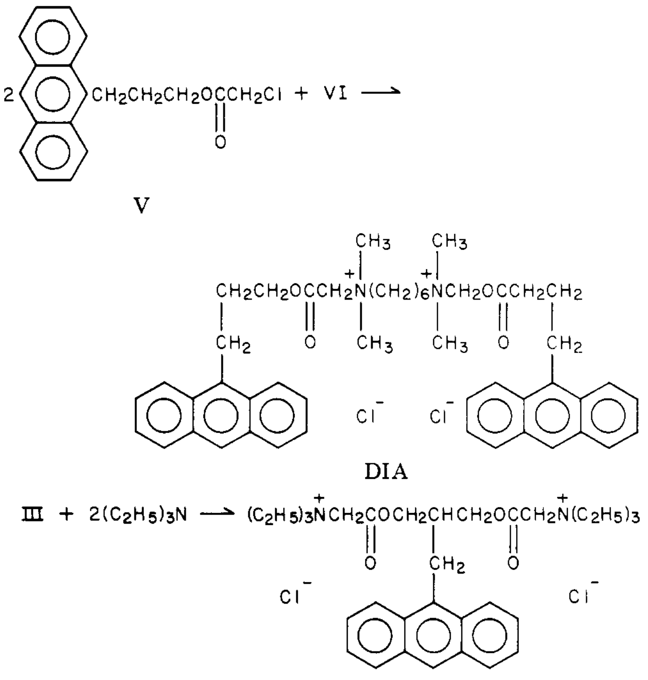
relative input energy to the sample solution.

Results and Discussion

Preparation of Polyionene. The results of the polymerization reaction are summarized in Table I. The high molecular weight polyionenes were obtained from III and IV, whereas the polyionenes made from I were of low molecular weight. Such low reactivity of I would be caused by steric hindrance due to anthryl groups because high molecular weight polyionene having identical main chain structure but without anthryl groups has been obtained from 1,3-trimethylene dibromide.[12] The use of bis(chloro ethanoate) III was effective for the preparation of polyionenes, as shown in Table I. There are two considerable reasons for this high reactivity of III. First, the insertion of ester groups to the 1 and 3 positions would reduce steric hindrance owing to anthryl groups. Second, the halide at the α position of the carbonyl group has high reactivity.[13] However, since a nonactivated monomer, IV, also showed high reactivity in the preparation of PIA-4,6, giving a high molecular weight polymer, it seems to be more important to keep the reaction site away from the bulky pendant group rather than to activate the reaction sites.

The degree of polymerization of polyionenes was somewhat affected by reaction solvents as shown in Table II. Methanol and sulfolane were not suitable for polyionene preparation, whereas dipolar aprotic solvents having high donor number (DN)[14] are suitable solvents. DMF (DN = 26.6), dimethylacetamide (DMA, DN = 32.3), and dimethyl sulfoxide Me_2SO, DN = 29.8) were proved to be good solvents for the present polymer preparation. The solvent effects are not only to accelerate the Menschutkin reaction but also to solvate the polyionenes formed in the polymerization reaction. Since the polyionenes precipitate with progression of polymerization, the chain propagation will not continue unless the polymers are sufficiently swollen by the solvents. DMF, DMA, and Me_2SO are favorable with respect to the polymer–solvent affinity. The earlier work by Rembaum discussed side reactions during polyionene formation in DMF,[12] yielding presumably cyclic quarternary ammonium salts.[15] Our results in Table II indicate that the polyionene formation proceeds equally well in all dipolar aprotic solvents as jugded by the quantitative yield and considerably high viscosity of the polyionenes. Furthermore, since the participation of side reactions is known to be marginal, we did not care about the probable side reactions. The family of polyionenes having identical backbone structures with the present polymers exhibits typical polyelectrolyte properties as coagulant and precipitant, although the reduced viscosity in 0.1 N NaCl solution is as low as 0.1–0.2,[13] the figure being comparable with the values in Table I. There should be no objection to considering the present polymers as polyelectrolytes as discussed already.[10]

Scheme I



The dimer ionene compound (DIA) corresponding to PIA-6 was also obtained by the Menschutkin reaction, and the monomer ionene compound (MIA) was prepared similarly as shown in Scheme I. The polyionenes and their model compounds were hygroscopic powders and dissolved in water, methanol, and dipolar aprotic solvents such as DMF and Me_2SO. Poor agreement of elemental analysis is attributed to the hygroscopic nature of the samples. However, the ratio of carbon to nitrogen (the value is independent of the amount of absorbed water) coincided with the calculated ratio. The C/N ratios for MIA, DIA, and PIA-6 were 13.2 (calcd 14.5), 20.7 (calcd 20.6), and 13.6 (calcd 13.7), respectively. The molecular weight of PIA-6 was about 2000, as determined by the low angle light scattering method in methanol. For photochemical study, we chose the PIA series of polyionene having comparatively high molecular weight.

Comparison of Photoreactivity of Anthryl Groups in Polymers and Their Model Compounds. The photoreaction of polyionenes and their model compounds having (9-anthryl)methyl groups under argon atmosphere was studied in water. Photoirradiation at the wavelength longer than 340 nm brought about the disappearance of the ^1L_a band as a result of photodimerization of anthryl groups. The dimerization reaction was confirmed by quantitative thermal recovery of anthryl groups by heating the photofaded solution at 80 °C for 20 min.

The photodimerization rates were fitted in pseudo-first-order plots as shown in Figures 1 and 2 and as previously reported for polyesters having pendant anthryl groups.[2] The first-order rate constant (k) apparently increased with a decrease in the initial segment concentration (M_0). Typical results for PIA-6 and MIA were shown in Figure 3. To compare the photoreactivity of polyionenes and their model compounds as a function of structure, the relation between the initial rate (R_0) calculated from the initial slope of time–conversion curves and M_0 was plotted in Figure 4. The values of R_0 were nearly constant at varing M_0, except for MIA. The other polyionenes, PIA-2 and PIA-4,6, also showed similar reaction behaviors with PIA-6, whereas MIA photodimerized by a normal fashion of bimolecular reaction. These results were different from those of polyesters bearing anthryl groups in which R_0 increased with increasing M_0. These data imply the facts that the photodimerization of PIA-6 and DIA occurred

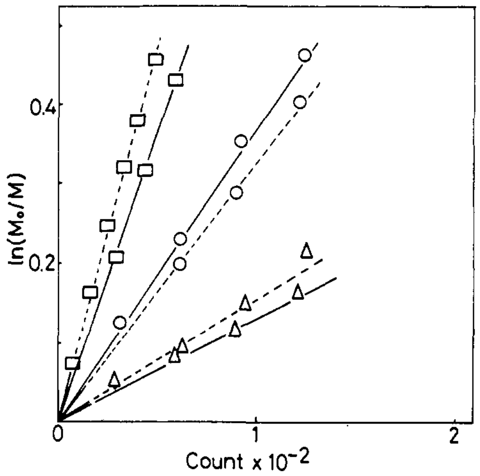


Figure 1. First-order plots for photodimerization of (9-anthryl)methyl groups in polyionene and their model compounds in water and 0.25 N aqueous KCl solution: real lines in water; dotted lines in the salt solution; PIA-6 (○) 2.24 × 10^{-4} mol/dm^3; DIA (□) 2.50 × 10^{-4} mol/dm^3; MIA (△) 2.13 × 10^{-4} mol/dm^3.

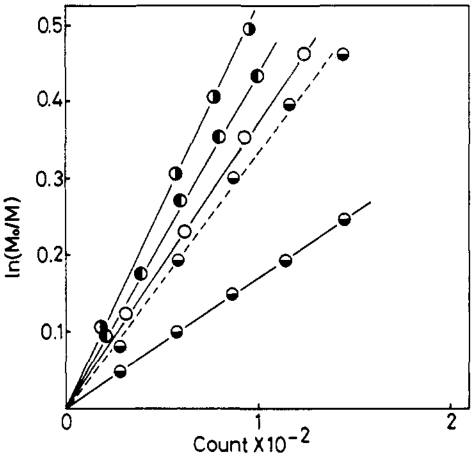


Figure 2. First-order plots for photodimerization of (9-anthryl)methyl groups of polyionenes in water and 0.03 N aqueous KBr solution: real lines in water; dotted lines in the salt solution; PIA-6 (○) 2.24 × 10^{-4} mol/dm^3; PIA-2 (◐) 2.29 × 10^{-4} mol/dm^3; PIA-4, 6 (◑) 2.10 × 10^{-4} mol/dm^3; IA-6 (◒) 3.35 × 10^{-4} mol/dm^3.

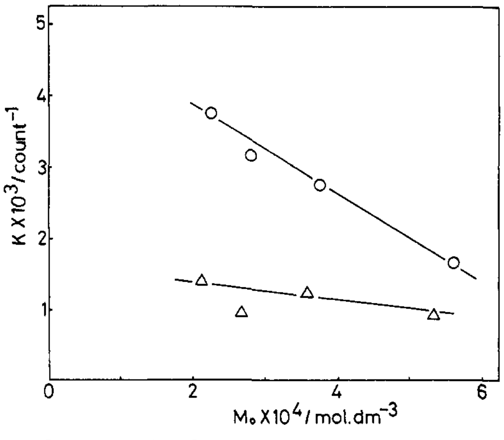


Figure 3. Concentration dependence of the apparent first-order rate constant (k) for PIA-6 and MIA: PIA-6 (○), MIA (△).

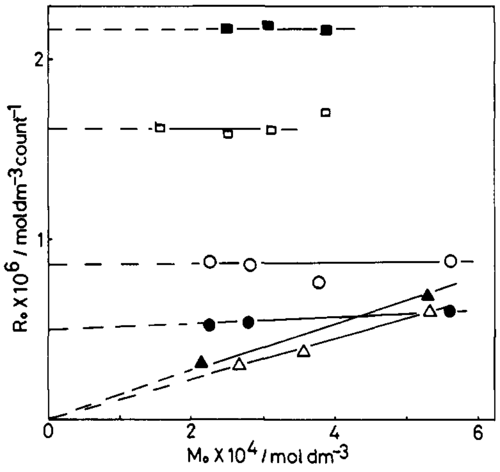


Figure 4. Concentration dependence of R_0 in water and aqueous KCl solution: PIA-6 (○), DIA (□), MIA (△) in water; PIA-6 (●), DIA (■), MIA (▲) in 0.25 N aqueous KCl solution.

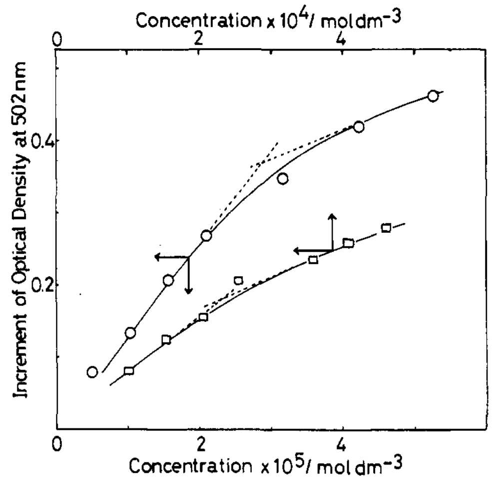


Figure 5. Cmc of PIA-6 and DIA in water as determined by change in the absorption spectrum of flourescein sodium salt: PIA-6 (○), DIA (□).

either intramolecularly or in the aggregate state, namely in the micellar state. The concentration regions shown in Figure 4 are higher than the critical micelle concentrations (cmc) of PIA-6 and DIA which were determined to be 3 × 10^{-5} and 2.5 × 10^{-4} mol/dm^3, respectively, by the spectral change of sodium fluorescein dye, as shown in Figure 5. MIA has a much weaker micelle forming ability, and the cmc of MIA is at least higher than 2.9 × 10^{-3} mol/dm^3.

The reaction features mentioned above fit nicely to the general trends of reactions in micelles. An increase in surfactant concentration above the cmc results in an increase in the number of micelles, the aggregation number being kept nearly constant.[16] Furthermore, intermicelle interactions will not take place due to repulsion between particles bearing a cationic atmosphere.[17] The photodimerization rate above cmc is consequently independent of polymer concentration as shown in Figure 4. Intramicellar bimolecular reactions are, however, kinetically indistinguishable from intramolecular reactions when more than one reacting group are bound to a surfactant molecule.

On the other hand, to discriminate intra- and intermicellar reactions, photoreaction in the concentration region below cmc is necessary. The photodimerization in extremely dilute solution depends on concentration, as shown in Figure 6. The present results indicate that the mode of reaction is different above and below cmc.

Effects of Chromophore Aggregation on Photoreactivity. To examine the photodimerizability of polyionenes and their model compounds under the condition of enhanced hydrophobic interaction, the photoreaction rates of PIA-6 and the model compounds were also mea-

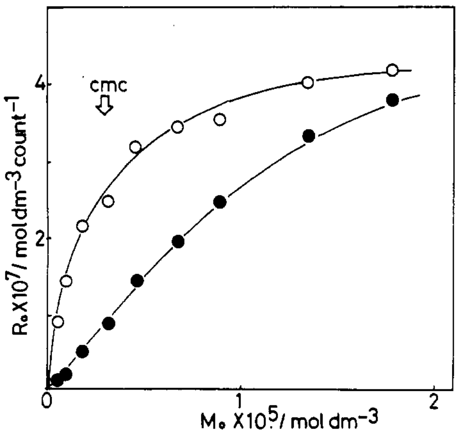


Figure 6. Concentration dependence of R_0 of PIA-6 at a low concentration region in water. The measured rates (●) were corrected for the difference in absorbance at 366 nm (○).

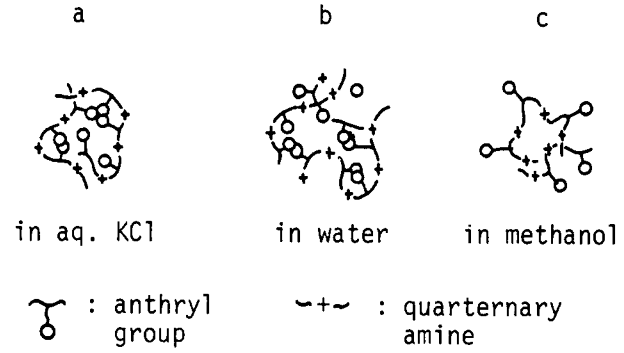


Figure 7. Sketches of polyionene conformation in different environments.

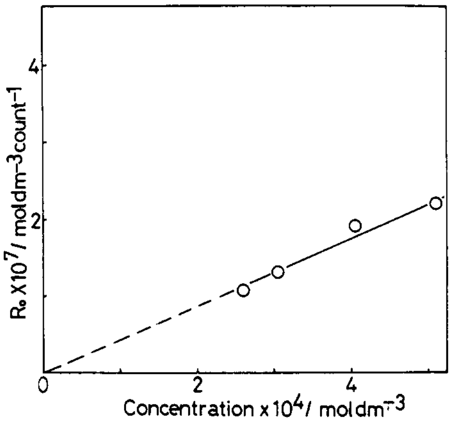


Figure 8. Concentration dependence of the photodimerization reaction of PIA-6 in methanol.

sured in aqueous KCl solution, as shown in Figure 1. The added salt in the polyionene solution would enhance the local concentration of anthryl groups and consequently the rate of photodimerization in micelle. The enhanced rates of photodimerization of DIA and MIA in KCl solution as shown in Figure 1 agree with the expectation. Although MIA does not form micelles at this concentration, the neutral salt effect on reactions between molecules bearing like charge causes an enhanced rate of photodimerization of MIA in KCl solution. Enhanced hydrophobic interaction is a favorable condition for intramicelle photodimerization of DIA, whereas the salt effect is reversed for PIA-6. As judged by the fact that low molecular weight polyionene, IA-6, increases its photodimerizability in the salt solution as shown in Figure 2, the reactivity of polyionenes with respect to salt effects seems to depend largely on the chain length. It is unlikely that the intrinsic photoreactivity of anthryl groups is affected by a neutral salt. The origin of the salt effect is therefore to be sought in the change of environments determining the mobility of the anthryl group and the probability of encounter of anthryl groups. As reported in preceding articles, the photodimerizability of polymer bound anthryl groups is a function of the mobility of the chromophore, both in solution[2] and in solid.[9] When only two chromophores are in a chain as in the case of DIA, volume shrinkage due to dehanced Coulombic repulsion and enhanced hydrophobic interaction will bring about merely an enhanced local concentration of chromophore. For PIA-6, shrinkage of the polymer chain would decrease the mobility of chromophores so that the enhanced local concentration on the anthryl group is over-canceled by the loss of mobility.

A very strong salt effect on solution viscosity is in support of this interpretation.[10] The value of $(\eta_{sp}/c)_{KCl=0.1}$ is about one-third of $(\eta_{sp}/c)_{KCl=0}$ for PIH-6, which is a polyionene without pendant anthryl groups, whereas η_{sp}/c of PIA-6 in 0.1 N KCl solution is about one-seventh of that in pure water. In addition to reduced Coulombic repulsion in salt solution, enhanced hydrophobic interaction between anthryl groups endorses extra contraction of the polymer chains, which would result in the restricted mobility of the anthryl groups.

The salt effect on excimer emission[10] also indicates the enhanced excimer formation in salt solution. The excimer intensity of the anthryl group is not an index of the ease of photodimerization[2] since head-to-tail encounter of the anthryl groups is a necessary condition for photodimerization to proceed whereas it will not be for excimer formation. The higher rate of photodimerization of DIA than that of PIA-6 in spite of the lower efficiency of excimer formation by the former is an example suggesting that excimer formation does not run parallel with photodimerization.

All results show that photodimerizability of anthryl groups bound to polyionenes is determined by the mobility of chormophores rather than by the local concentration. The behaviors of macromolecular and small molecular surfactants in micelle are distinctively different. The mobility of functional groups in the polymer micelle seems to be more restricted than those in the usual micelles consisting of small molecular surfactants. The enviromental effects on the conformation of polyionenes are shown in Figure 7.

The photoreaction rate of PIA-6 was also measured in methanol, as shown in Figure 8. From the viscosity measurements in water and methanol, we know that the expansion of PIA-6 molecules in both solvents is about equal. Furthermore, we have shown that the photodimerizability of PIA-6 is determined by the mobility of the chromophores of PIA-6 molecules. From these results, we expect the photodimerizability of PIA-6 molecules in both water and methanol to be nearly equal. However, the reaction rate in methanol is about a quarter of that in water at ca. 5×10^{-5} mol/dm^3. The loss of a hydrophobic interaction in methanol would totally alter the shape of the polymer chain. The expected conformation is shown in Figure 7c together with those in water and KCl solution. The micelle structure is destroyed, and the anthryl groups will no longer stick together while the cationic parts will associate. Such a conformation is certainly unfavorable for intramolecular photodimerization. The kinetics of photodimerization is also different in methanol, as shown in Figure 8. The rate for PIA-6 increases with increasing M_0, indicating participation of only the interpolymer

Table III
Photodimerization Reaction Features of the Ionenes

	photoreaction in				
	salt solution (0.25 N KCl)		water		methanol
PIA-6		<		>	
IA-6	*a*	>		>	
DIA		>		>	
MIA	*b*	>		>	

[a] Measured in 0.03 N KBr solution. [b] The reaction is conducted below cmc.

process even for the polymer, while intra- and intermolecular interactions were observed in the case of the polyesters bearing pendant anthryl groups in tetrahydrofuran. The separation of anthryl groups in methanol was evidenced by the loss of excimer emission from PIA-6. The total features of photoreaction are summarized in Table III.

Conclusion

From the studies of photoreactivity of ionenes, the following three remarks are made. First, the reactivity of the polymer micelle consisting of high polymer is very much different from that of DIA or olgomeric IA-6 micelles. In particular, the direction of the salt effect is opposite for polymer and oligomer (or dimer model) micelles. The details of hydrophobic interactions will be reported elsewhere. Second, the reactivity of polyionenes is sensitive to the change in environments, indicating that the reactivity is determined by the delicate balance between two opposing molecular forces, Coulombic and hydrophobic interactions. This picture is different from that of polyesters with pendant anthryl groups in organic solvents in which no specific interpolymer forces are operative and the chemical structure rather than the surrounding medium is of primary importance. Finally, the photodimerizability is not decided by the local concentration of anthryl groups. With increasing hydrophobic association of the anthryl groups, the excimer intensity of polyionenes increases whereas the photodimerizability does not run parallel with the excimer formation. Although excimer is supposed to be the precursor of anthracene photodimer, all of the excimer forming pairs do not seem to proceed to photodimerization. The same discussions were presented in the study of polyesters with anthryl groups in organic solvents.[2]. Further discussions on the emission characteristics of the present polyionenes, dimer model, and monomer model compounds will be reported elsewhere.

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