while conditions 2 and 3 are related to the polymer structure. The carbazole chromophore satisfies the former conditions to some extent, and the present polyurethane has a suitable structure for the latter conditions. Therefore, the conversion efficiency of PU-I-44 is higher than that of PVCz-394 under almost the same experimental conditions.[2]

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# Functionalized Polyionenes. 2. Absorption and Fluorescence Properties of a Polyionene and Relevant Model Compounds Bearing (9-Anthryl)methyl Groups

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ABSTRACT: Aiming at understanding the correlation between polymer conformation and polymer functionality in water-soluble polymers, we have measured the absorption and fluorescence spectra of a polyionene bearing pendant anthryl groups, poly[oxycarbonylmethylene-1,6-hexamethylenebis(dimethyliminio)methylenecarbonyloxy-2-[(9-anthryl)methyl]propylene dichloride] (PIA-6), and relevant low molecular weight model compounds, hexamethylenebis[[[(9-anthrylpropoxy)carbonyl]methyl]dimethylammonium chloride] (DIA) and 2-[(9-anthryl)methyl]-1,3-propanediol bis(triethylammonio)acetate dichloride (MIA). The absorption spectrum of PIA-6 ($^1L_a$ band of the pendant anthryl groups) in water was broader than that of DIA or MIA while the absorption spectra in methanol were nearly the same for all samples, suggesting association between anthryl groups of PIA-6 brought about by hydrophobic interaction. Such ground-state association between pendant anthryl groups was also found in the fluorescence excitation spectra. Fluorescence emission spectra of PIA-6 and DIA in water showed broad excimer emission around 500 nm while excimer emission from MIA was negligible. The excimer emission intensity relative to the monomeric emission of PIA-6 and the model compounds was measured in various media, and these results are discussed from the viewpoint of a polymer conformation–photodimerizability correlation in the polyelectrolyte system.

## Introduction

In previous articles on photodimerization reaction of polyionenes bearing pendant anthryl groups,[1,2] we have shown that (1) the neutral salt effects on photodimerizability of the polyionenes are different from those of the relevant monomeric or oligomeric ionenes, (2) the reactivity of the polyionenes is sensitive to changes in the environments rather than to their chemical structure, indicating that the reactivity is determined by a delicate balance between Coulombic and hydrophobic interaction, and (3) the photoreactivity is not decided only by the local concentration of anthryl groups. In these studies, a polyelectrolyte conformation–functionality correlation for the polyionenes was discussed on the basis of the photodimerization reaction of pendant anthryl groups and the viscosity behavior as indices of functionality and polymer chain conformation, respectively.

In this article, we deal with the correlation between polymer conformation and interchromophore interaction as detected by spectroscopic studies of a polyionene and the relevant low molecular ionenes. In particular, the excimer emission is informative as to the nature of the polymer-bound anthryl groups as already shown for polyesters.[3,4] The results on excimer studies of the ionenes

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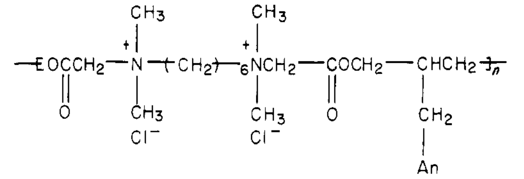
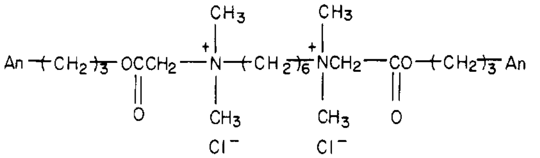
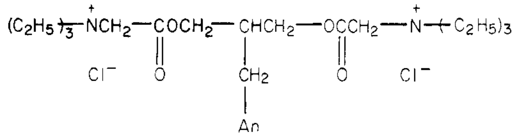
Table I
Structures and Abbreviations of Ionenes[a]

| structure | name |
|---|---|
|  $-\!\!\left[\!\begin{array}{c}OCCH_2\\ \Vert\\ O\end{array}\!\!-\overset{+}{N}(CH_3)_2\,Cl^- -(CH_2)_6-\overset{+}{N}(CH_3)_2\,Cl^- \,CH_2-\!\begin{array}{c}COCH_2\\ \Vert\\ O\end{array}\!\!-CH(CH_2An)CH_2\right]_n\!\!-$ | PIA - 6 |
|  $An-(CH_2)_3-\!\begin{array}{c}OCCH_2\\ \Vert\\ O\end{array}\!\!-\overset{+}{N}(CH_3)_2\,Cl^- -(CH_2)_6-\overset{+}{N}(CH_3)_2\,Cl^- \,CH_2-\!\begin{array}{c}CO\\ \Vert\\ O\end{array}\!\!-(CH_2)_3-An$ | DIA |
|  $(C_2H_5)_3\overset{+}{N}CH_2\,Cl^- -\!\begin{array}{c}COCH_2\\ \Vert\\ O\end{array}\!\!-CH(CH_2An)CH_2-\!\begin{array}{c}OCCH_2\\ \Vert\\ O\end{array}\!\!-\overset{+}{N}(C_2H_5)_3\,Cl^-$ | MIA |

[a] An represents the 9-anthryl group.

suggest the presence of ground-state association between anthryl groups in water. To confirm this possibility, we also study the absorption and excitation spectra of the ionenes in water and methanol. These spectra are discussed from the viewpoint of the polymer entanglement–hydrophobic or Coulombic interaction correlation by comparing with the results of viscosity and photodimerization behavior. Although steric requirements for photodimerization and excimer formation by anthryl groups are not identical, the study on molecular interaction under the influence of hydrophobic and Coulombic interaction to different degrees would be indispensable for the design of water-soluble functional polymers.

## Experimental Section

**Materials.** The polyionene (PIA-6) and its model compounds (DIA and MIA) were synthesized as already reported.[2] The polyionene for spectroscopy was used without molecular weight fractionation. Distilled water having a conductance of $3 \times 10^{-6}$ $\Omega^{-1}$ at 20 °C was used as solvent. Sodium fluorescein, methanol, urea, and potassium chloride of guaranteed reagent grade were used without further purification.

**Fluorescence and Absorption Spectroscopy.** A Hitachi MPF-2A fluorescence spectrometer and an EPS-3T and a Shimadzu UV-220 spectrometer were used for fluorescence and absorption spectroscopy, respectively. The sample solution for fluorescence measurements was purged with argon for 30 min immediately before measurement. The fluorescence excitation spectra were corrected for the wavelength dependence of the exciting light intensity to an accuracy of 5% (from 300 to 450 nm). To minimize the effect of reabsorption of fluorescence by the sample solution, the incident light angle to the cell was kept at 45° and the emission from the sample solution was monitored at right angles to the exciting light.

**Determination of Critical Micelle Concentration (CMC).** The CMC was determined by the spectral changes of sodium fluorescein dye as a function of the concentration of the polyionene and its model compounds as already reported.[2] The CMC of PIA-6 and DIA were $3 \times 10^{-5}$ and $2.5 \times 10^{-4}$ mol/dm$^3$, respectively. No tendency of micelle formation by the monomer model (MIA) was detected up to $3 \times 10^{-3}$ mol/dm$^3$.

## Results and Discussion

**Absorption Spectra of the Ionenes.** The structures and abbreviations of the ionenes are listed in Table I and their absorption characteristics are summarized in Table II. Although the peak wavelengths of the ionenes are nearly same in water, there is a little, but significant, difference in $\epsilon_{max}$ between DIA or PIA-6 and MIA. Similar phenomena have already been reported for polyesters bearing pendant anthryl[3] or pyrenyl[5] groups and pyrenyl-*N*,*N*-dimethylaniline exciplex-forming pairs.[6] Furthermore, the extent of broadening of the spectra for PIA-6 and DIA as indicated by the peak/valley ratio was greater than that of MIA. The broadening of the absorption band was most prominent when the anthryl groups were linked by a short and rigid polyester chain but was not so great for polyesters in which anthryl groups were linked by a flexible chain. PIA-6 showed relatively large broadening of the absorption band in spite of the fact that the interchromophore distance of PIA-6 was large. This difference is attributed to the presence of hydrophobic interaction between anthryl groups in PIA-6. In fact, the absorption spectra of the ionenes in methanol are sharper than those in water and the extent of broadening in methanol is nearly the same for all ionenes as shown in Table IIIB and also by the $\epsilon_{max}$ values in Table II, indicating that ground-state interaction between anthryl groups is negligible in the absence of hydrophobic interaction.

Table II
Absorption Properties of the Ionenes

| ionene | concn, mol/dm$^3$ | $\lambda_{max}$ (nm) at $^1L_a$ band | | | | | $\epsilon_{max}$[a] |
|---|---|---|---|---|---|---|---|
| PIA-6 | $1.0 \times 10^{-5}$ (<CMC in water) | 316 | 334 | 351 | 369 | 390 | 5700 |
| | $4.1 \times 10^{-5}$ (>CMC in water) | 317 | 335 | 352 | 370 | 390 | 5600 |
| | $5.2 \times 10^{-5}$ (in methanol) | | 332 | 348 | 367 | 387 | 8100 |
| DIA | $5.0 \times 10^{-5}$ (in water) | 320 | 333 | 350 | 368 | 388 | 4900 |
| | $5.7 \times 10^{-5}$ (in methanol) | 316 | 331 | 348 | 366 | 386 | 7400 |
| MIA | $5.0 \times 10^{-5}$ (in water) | 317 | 333 | 350 | 368 | 388 | 7000 |
| | $4.6 \times 10^{-5}$ (in methanol) | 317 | 332 | 344 | 367 | 387 | 8000 |

[a] $\epsilon_{max}$ is based on a unit anthryl group.

PIA-6 is considered to be a polysoap. Besides the spectroscopically observed intrapolymer interaction, a critical micelle concentration (CMC) was observed. However, the peak wavelengths and $\epsilon_{max}$'s do not change below and above CMC. Furthermore, the peak/valley ratio of the polyionene below CMC is almost identical with or slightly smaller than that above CMC as shown in Table III. The broader absorption spectrum below CMC indicates that the ground-state association between anthryl groups is stronger than that above CMC. This is in accordance with the observation with 9-dodecylanthracene-10-methanesulfonate (SDAS) which forms micelles.[7] The absorption spectra of the surfactant at the anthracene absorption region are even broader below CMC, indicating the formation of anthracene stable dimers as premicelle states. Above CMC the specific aggregate structure seems to be destroyed owing to micelle formation and, consequently, the spectra resemble those in ethanol. PIA-6 would behave in a similar manner as SDAS. Micelle formation does not necessarily bring about interchromophore interaction detectable by absorption spectroscopy.

**Fluorescence Emission Spectra of the Ionenes.** The fluorescence spectra of the ionenes are shown in Figure 1. The spectra of PIA-6 and DIA consist of a broad excimer band around 500 nm together with monomeric emission by anthryl groups while the spectrum of MIA is almost all monomeric emission. Excimer formation by anthryl groups

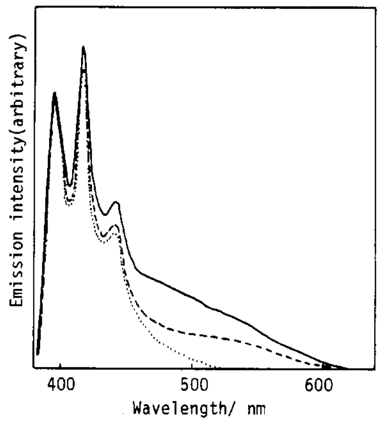


**Figure 1.** Fluorescence spectra of PIA-6 (——), DIA (- - -), and MIA (···) in water. [PIA-6] = 5.8 × $10^{-5}$ mol/dm$^3$, [DIA] = 5.6 × $10^{-5}$ mol/dm$^3$, and [MIA] = 5.4 × $10^{-5}$ mol/dm$^3$. All spectra were normalized to the peak intensity at ≃396 nm.

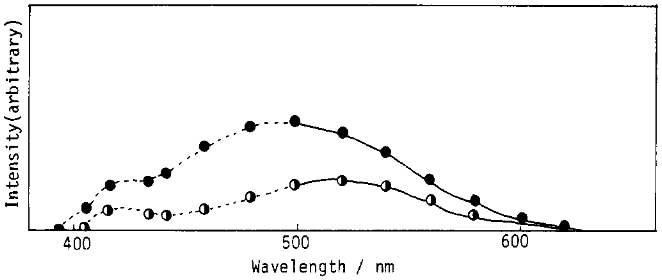


**Figure 2.** Difference fluorescence spectra of PIA-6 (●) and DIA (◐) in water. All spectra were normalized to the peak intensity at 396 nm and then the emission of MIA was subtracted from that of PIA-6 and DIA.

bound to polymer is likely to be a common phenomenon for polymers having various structures.[3,4,8] The excimer emission of the ionenes is different from that of the polyesters in the following three ways. First, the excimer peak wavelengths of PIA-6 and DIA were about 500 and 520 nm, respectively, as shown in Figure 2, while that of the polyester poly[2-[(9-anthryl)methyl]propane-1,3-dioxy-[(9-anthryl)methyl]malonyloxy] [PE(A-1A)] has been estimated to be 450 nm.[3] Second, the ratio of excimer intensity at 500 nm to the monomeric intensity at 417 nm of the ionenes was larger than that of polyesters having chromophore distances similar to that of PIA-6. The ratios for PIA-6, DIA, MIA, and poly[2-[(9-anthryl)methyl]propane-1,3-diyloxysebacyloxy] [PE(A-8)] were 0.22–0.43, 0.10–0.14, 0.02–0.03, and 0.04,[3] respectively. Since the excimer intensity of the polymer is often molecular weight dependent,[9] the excimer intensity of the oligo-PE(A-8) having a degree of polymerization comparable to that of PIA-6 was chosen for comparison. Third, the concentration dependence of $I_E/I_M$ differs between PIA-6 and PE(A-8). The former exhibits a concentration dependence as shown in Table III while the latter shows no concentration dependence, as already reported.[4] The model compound DIA also does not show a concentration dependence of $I_E/I_M$. These results recall that all exciplex-forming polymers consisting of well-defined repeating units exhibit interpolymer association phenomena while the small-molecule model compounds do not.[10] An exciplex-forming pair is essentially an electron-donor–electron acceptor combination so that ground-state interaction is more or less expected. We can then deduce the general principle that polymers of regular structure having weakly interacting groups tend to self-associate in the concentration region where the low molecular weight model compounds do not associate. Enhanced molecular association in polymeric systems is also demonstrated by the lower CMC value of PIA-6 than that of DIA. These differences between PIA-6 and PE(A-8) might indicate a stronger interaction of anthryl groups in PIA-6 than in PE(A-8). We considered that the driving force of such enhanced interaction between pendant anthryl groups in water would be attributed to hydrophobic interaction.

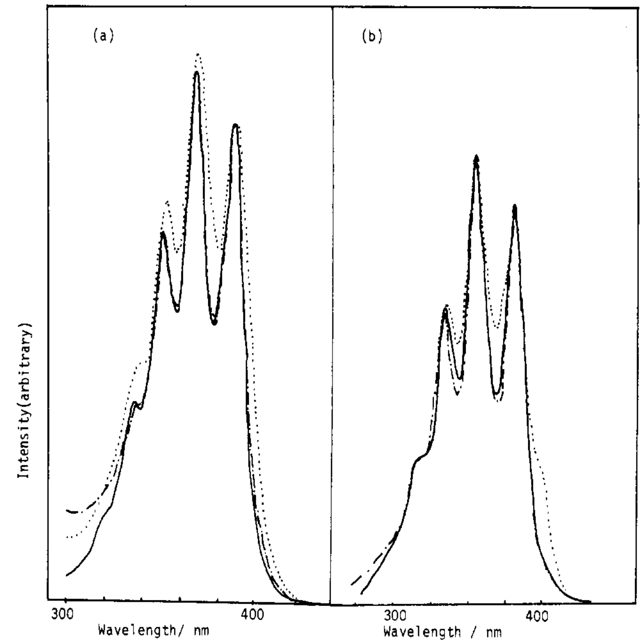


**Figure 3.** Absorption (——) and fluorescence excitation spectra at monitoring emission of ≃417 (-·-) and 500 (···) nm of PIA-6 (a) and DIA (b) in water. [PIA-6] = 5.8 × $10^{-5}$ mol/dm$^3$, and [MIA] = 5.0 × $10^{-5}$ mol/dm$^3$. All spectra were normalized to the peak at ≃390 nm.

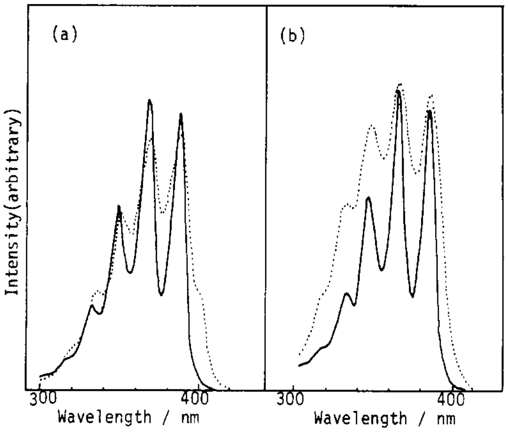


**Figure 4.** Absorption (——) and fluorescence excitation spectra at the monitoring emission of 500 nm (···) of PIA-6 (a) and DIA (b) in methanol. [PIA-6] = 5.9 × $10^{-5}$ mol/dm$^3$, and [DIA] = 5.7 × $10^{-5}$ mol/dm$^3$.

The results of absorption and emission spectroscopy show that the chromophore interactions of PIA-6 and DIA are stronger than those of PE(A-8) in the excimer state, although the separation between anthryl groups is even larger than that in PE(A-8). If the excimer-like emission is in part due to excitation of ground-state dimer or the aggregate detectable by absorption spectroscopy, the fluorescence excitation spectra should be dependent on the monitoring emission wavelength.

**Fluorescence Excitation Spectra of the Ionenes.** The results are presented in Figures 3 and 4 and are summarized in Table III. Comparing the results for PIA-6

Table III
Absorption, Fluorescence, and Excitation Profiles of the Ionenes in Water and Methanol

| | | peak/valley ratio of the spectrum | | | | |
|---|---|---|---|---|---|---|
| | | | excitation[a] | | | |
| ionene | concn, mol/dm$^3$ | absorption ($OD_{370}/OD_{380}$) | $\lambda_{em} \simeq$ 417 nm | $\lambda_{em} =$ 500 nm | excimer intensity ($I_{500}/I_{417}$) | shoulder at 400 nm in the excitation spectra ($\lambda_{em}$ = 500 nm) |
| | | A. Profiles in Water | | | | |
| PIA-6 | $1.0 \times 10^{-5}$ | 1.88 | 2.12 | 1.62 | 0.27 | not observed |
| | $5.4 \times 10^{-5}$ | 2.02 | 1.93 | 1.59 | 0.43 | not observed |
| DIA | $5.0 \times 10^{-5}$ | 2.36 | 1.70 | 1.50 | 0.10 | not observed |
| MIA | $5.0 \times 10^{-5}$ | 2.44 | 2.17 | 1.61 | 0.03 | observed |
| | | B. Profiles in Methanol | | | | |
| PIA-6 | $5.0 \times 10^{-5}$ | 3.14 | 2.05 | 1.46 | 0.02 | observed |
| DIA | $5.7 \times 10^{-5}$ | 3.22 | 1.45 | 1.43 | 0.03 | not observed |
| MIA | $4.6 \times 10^{-5}$ | 3.24 | 2.35 | 1.57 | 0.03 | observed |

[a] $I_{370}/I_{380}$.

and MIA yields the following observations. (i) The excitation spectra of both PIA-6 and MIA are sharper when the monomer emission peak at 417 nm is monitored in comparison with excitation spectra monitoring at 500 nm. (ii) There is no dramatic solvent effect on the excitation spectra. (iii) A small but clear shoulder is observed at 400 nm in the excitation spectra monitored at 500 nm when the excimer intensity is very low, regardless of solvents and samples. (iv) The main difference between PIA-6 and MIA is the broadness of the excitation spectra either in water or in methanol. Without exception, the excitation spectra for PIA-6 are broader than those for MIA, provided that the conditions of measurement are identical.

First of all, it is evident that the broad emission around 500 nm is not true excimer. By definition, excimer is an excited-state complex formed between two like molecules when one molecule is excited. In other words, no complex formation is expected in the ground state and, consequently, distinction between monomer and excimer is not possible by absorption spectroscopy. Excitation spectra for monomer and excimer should be therefore the same. The finding that the shape of the excitation spectrum depends upon the monitoring wavelength is a definitive indication for the presence of more than two emitting species besides monomeric emission from anthracene. One is true excimer which is formed after excitation of the monomeric anthryl group and the other may be the stable dimer and/or aggregate reported by Chandross.[11] A small shoulder at 400 nm in the excitation spectra is observable only when the emission intensity at 500 nm is very small and may be in support of the presence of such ground-state complexes. Such absorbing species having an absorption around 400 nm are, however, not detected by absorption spectroscopy. If the quantum yield of excimer-like emission is higher when the molecular aggregates are excited, the excitation spectrum monitored at 500 nm should be the sum of the absorption by monomeric and aggregated anthryl groups, the contribution of the latter being more than that expected from the absorption spectrum. Consequently, band broadening is more prominent for the excitation spectrum monitored at 500 nm. Although MIA is an isolated chromophore and excimer formation under high-dilution conditions is not expected, detailed fluorescence spectroscopy indicates that the tailing part of the long-wavelength limit of the emission consists of the emission from molecular aggregates. We have already shown the aggregation of an anthracene-containing surfactant at $1.2 \times 10^{-5}$ M, which is much below CMC.[7] MIA would behave in a similar manner as the surfactant.

Apparent discrepancy between absorption and excitation spectra even when the monomeric emission is monitored at 417 nm will be attributed to the difference between the line width of scanning excitation wavelength and the resolution of the absorption spectrometer, the latter being narrower. Consequently, excitation spectra do not seem to follow absorption spectra quantitatively, in particular, when absorption spectra are very sharp as in methanol. In addition, the concentration region given in Table III is too high to obtain true excitation spectra[12] and the absorbance of each sample is different. Discussion should therefore be confined to monitoring wavelength effects in the individual case. Cross discussion between absorption and excitation spectra is not possible. Also comparison between different samples is permitted only for samples of comparable absorbance.

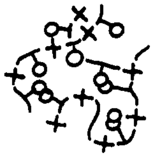
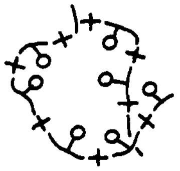
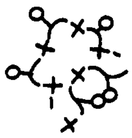
The excitation profile of DIA is different from those of MIA and PIA-6. Both in water and in methanol, the profile is broad and not much affected by monitoring wavelength whereas the emission intensity at 500 nm is between those of MIA and PIA-6. This might be related to efficient photodimerization of DIA, twice as fast as that of PIA-6.[2] If the majority of excited species are quenched by photodimerization and those of unfavorable chain conformation for photodimerization are allowed to fluoresce either excimer or monomer emission, the present results would be understandable.

**Environmental Effects on Fluorescence Spectra of PIA-6.** Since the conformation of a polyelectrolyte in solution is sensitive to the nature of the solvent, dependence of fluorescence from PIA-6 on solvents would provide insight into polymer conformation as reflected in the degree of interaction between anthryl groups. Particular interests with PIA-6 are to control Coulombic and hydrophobic interactions by changing solvents and additives.

Upon addition of urea, known to be a destructive agent for hydrophobic interaction,[13] excimer emission by PIA-6 nearly disappears as shown in Figure 5. Destruction of hydrophobic interaction is, however, not directly related to polymer chain expansion, as determined by viscosity measurements. At a urea concentration of 1 M, which is sufficient to suppress excimer emission, the viscosity of the PIA-6 solution is nearly identical with that in water whereas the viscosity is doubled in the presence of 1.5 M urea. Consequently, excimer formation would correspond to more microscopic environmental changes which do not directly change the dimensions of the whole molecules.

Contrary to the urea effect, the excimer intensity of PIA-6 is enhanced by addition of potassium chloride whereas that of DIA is unaffected or even reduced as shown in Figure 6. Since the polyionene shrinks with increasing ionic strength, the increase in chromophore interaction would be a natural consequence of enhanced

Table IV
Sketches and Summary of Results for PIA-6 in Different Environments

| | environments | | | | |
|---|---|---|---|---|---|
| | in aqueous KCl[a] | in water | in aqueous methanol[b] | in methanol | information |
| polymer chain conformation[c] |  |  |  |  | |
| reduced viscosity[d] | 0.042 | 0.25 | 0.82 | 0.49 | a measure of polymer chain expansion |
| dimerization rate[e] | 0.58 | 0.88 | | 0.22 | efficiency of head-to-tail encounters |
| excimer emission[e] intensity[f] | 0.68 | 0.32 | 0.02 | 0.02 | efficiency of all face-to-face encounters which do not lead to photodimerization |

[a] Measured in 0.1 N aqueous KCl solution. [b] Measured in 80% aqueous methanol solution. [c] + and ɓ denote quaternary ammonium salt and pendant anthryl group, respectively. [d] Polymer concentration is 0.24 g/100 cm$^3$. [e] [PIA-6] = 5.0 × 10$^{-4}$ mol/dm$^3$; dimension is 10$^6$ mol dm$^{-3}$ count$^{-1}$. [f] [PIA-6] = (2.8–2.9) × 10$^{-4}$ mol/dm$^3$.

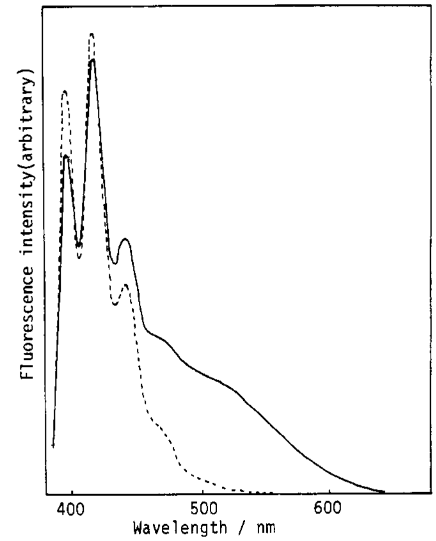


**Figure 5.** Urea effect on the fluorescence spectra of PIA-6: (——) in water; (---) in 1 M aqueous solution.

local chromophore concentration; i.e., chain conformation as a determining factor for chromophore encounter would be important for DIA whereas the average local concentration rather than the specific chain conformation would determine the ease of excimer formation for PIA-6.

It is worth noting that the neutral salt effects on photodimerization of PIA-6 and DIA are the reverse of those reported in the previous article.[2] The initial rate in 0.1 N KCl solution was 0.6 times that in water for PIA-6 whereas the rate of DIA in the salt solution was 1.3 times that in water. It is well-known that a number of 9-substituted anthracenes yield exclusively head-to-tail photodimer.[14] This generality results from steric effects on the substituents. When the polymer chain of PIA-6 shrinks with increasing ionic strength, the head-to-head overlaps between pendant anthryl groups would increase in salt solution relative to the head-to-tail encountering, since the latter overlap is restricted by steric hindrance imposed by the polyionene chain or other pendant anthryl groups. Consequently, the photodimerization reaction of PIA-6 diminished in salt solution. On the other hand, the DIA molecule will not be influenced much by steric effects because the molecule consists of a long ionene chain and terminal anthryl groups. Construction of a molecular model of DIA shows that both head-to-tail and head-to-head encounters between anthryl groups are intramolecularly possible. However, it is difficult for PIA-6 to take the intramolecular head-to-tail conformation under conditions of a constrained polymer chain. Consequently, the photodimerization for DIA is enhanced in salt solution. These interpretations of the salt effects on the photodimerization rate for PIA-6 and DIA are not in conflict with the salt effects on the excimer intensity. Since the photodimerization reaction of the anthracenes proceeds via the excimer state,[15] a decrease in the dimerization rate is considered to result in an increase in the excimer intensity and vice versa if other kinetic conditions are constant. As expected, when the dimerization rate for PIA-6 was diminished in salt solution, an enhancement of the excimer intensity was observed in the salt solution as shown in Figure 6. This trend for DIA was reverse of that of PIA-6.

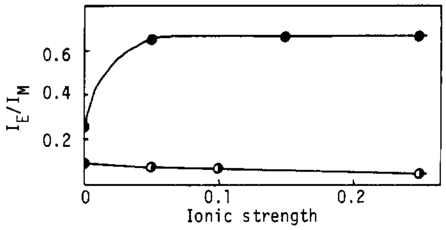


**Figure 6.** Effect of ionic strength on excimer emission of PIA-6 (●) and DIA (◑). Ionic strength is controlled by KCl; $I_E$ = 500 nm, $I_M \simeq$ 417 nm, [PIA-6] = 2.8 × 10$^{-4}$ mol/dm$^3$, and [DIA] = 1.4 × 10$^{-4}$ mol/dm$^3$.

The two parameters, hydrophobic interaction and Coulombic repulsion, can be controlled in a different way. The viscosity measurements of PIA-6 in methanol indicated that the expansion of the polymer chain is comparable to that in water. However, the conformation of the polymer chain is expected to be different from that in an aqueous system since the expansion of the polymer chain due to the loss of hydrophobic interaction in methanol would be compensated by a decreased Coulombic repulsion, the overall domain size being kept nearly constant. The loss of hydrophobic interaction results in decreasing methanol content, and excimer intensity decreases steadily and approaches zero in 100% methanol (Figure 7). This fluorescence behavior suggests that the interactions between functional groups bound to a polyionene chain de-

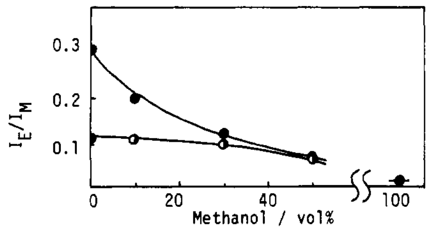


**Figure 7.** Effect of methanol on excimer emission of PIA-6 (●) and DIA (◑). $I_E$ = 500 nm, $I_M \simeq$ 417 nm, [PIA-6] = 2.9 × $10^{-4}$ mol/dm$^3$, and [DIA] = 1.4 × $10^{-4}$ mol/dm$^3$.

pend on the size and conformation of polymer chain.

From the study on the environmental effects on the excimer emission, we have found that the excimer intensity reflects sharply the aggregation nature of the pendant groups. The overall features of PIA-6 molecules in solution can be visualized as shown in Table IV by combining the results of the spectroscopy, photodimerizability, and viscosity studies. In a conclusion, the PIA-6 conformation is very much affected by environment, which is quite different from the case for polyesters bearing anthryl groups in organic solvents in which the chemical structure of the polymer is the dominant factor determining excimer formation and photodimerizability.

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(9) Although excimer formation by ethylenic polymers is often molecular weight independent, excimer as well as exciplex formation by the present series of polyesters increases with the degree of polymerization, indicating nonneighboring group participation.
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# Absorption and Fluorescence Spectra of Vinyl and Methacrylate Polymers Containing Pendant 1,3,5-Triphenyl-2-pyrazoline Chromophores

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ABSTRACT: In order to gain insight into polymer effects on spectroscopic properties of polymers containing polar pendant chromophores, the absorption and emission spectra of vinyl and methacrylate polymers containing pendant 1,3,5-triphenyl-2-pyrazoline (TPP) chromophores were studied in various solvents and compared with those of low-molecular-weight model compounds. The polymers were found to exhibit no excimer fluorescence, emitting only normal fluorescence. The polymer effects on the spectroscopic properties relative to those of low-molecular-weight model compounds were characterized by the following three features: larger Stokes shifts for the fluorescence, decreased quantum yields of the fluorescence, and less sensitivity of the fluorescence band position to the solvent polarity. These characteristic effects of the polymers result from perturbation by neighboring groups and are understood in terms of nearby pendant TPP chromophores in the ground state solvating TPP chromophores in the electronically excited singlet state.

Studies of the absorption and emission spectra of polymers are expected to provide information on the conformation and microenvironment of polymers as well as interactions between chromophores bound to polymers; these will be observed as polymer effects on spectroscopic properties. In addition, an understanding of spectroscopic and photophysical properties of polymers will be of importance for the understanding of the function and in the design of photosensitive functional polymers such as photoconducting polymers.

There have been a few studies comparing the absorption spectra of vinyl aromatic polymers with those of low-molecular-weight analogues, indicating hypochromism in polymers,[1-3] and extensive studies of the emission spectra of vinyl aromatic polymers from the viewpoint of excimer formation[4-15] have been made. Ground-state dimer formation between the pendant chromophores has also been indicated from the absorption and emission spectra of certain vinyl polymers.[16-18] However, there are still some basic questions remaining to be studied concerning polymer effects on spectroscopic properties. For example, except for reports concerning the phosphorescence spectra of a few polymers,[19,20] the question of how the normal emission is affected by the polymeric framework has not been fully studied. Little attention has been paid to the problem of how solvent effects on the absorption and emission spectra of polymers differ from those of low-molecular-weight analogues. Spectroscopic studies on vinyl

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