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EFFECTS OF MACROMOLECULAR ASSOCIATION ON FLUORESCENCE AND PHOTODIMERIZATION BEHAVIORS OF POLYMERIC ANTHRACENE CHROMOPHORE IN AN AQUEOUS SOLUTION

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Anthracene chromophore attached to the chain end of poly(ethylene glycol)(PEG-Ant) was found to exhibit excimer fluorescence down to 10^{-7} M in an aqueous solution. Macromolecular association of PEG-Ant with poly(methacrylic acid)(PMAA) increased excimer emission intensity by a factor of 10 as well as the rate of photodimerization.

A number of investigators have found that intramolecular excimers can form in various polymeric systems such as polystyrene,$^{1)}$ polyvinylnaphthalene,$^{1-2)}$ poly(N-vinylcarbazole),$^{3)}$ poly(N,N-dibenzylacrylamide),$^{4)}$ and polyesters having pendant anthryl groups.$^{5)}$ The excimer formation in these systems ocurrs by the encounter of the nearest neighboring chromophores in the repeating units. This article concerns with the effects of macromolecular association on the fluorescence and photodimerization behaviors of anthracene chromophore anchored to the chain end of polymer in the water solution(Figure 1).

Poly(ethylene glycol) 9-anthroate was obtained by refluxing benzene solution of purified poly(ethylene glycol)(PEG) with a mol. wt. of 20,000 and anthracene-9-carboxylic acid(Ant-9CA) chloride in the presence of triethylamine. It was found that 49.6% of total alcoholic end group of PEG was substituted by Ant-9CA from

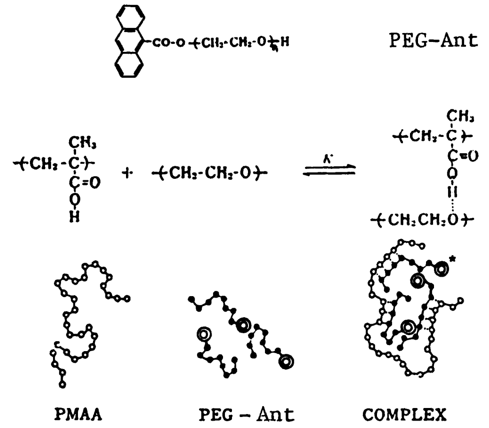


Fig.1 Schematic representation of the complexation between poly(methacrylic acid)(PMAA) and poly(ehtylene glycol)9-anthroate(PEG-Ant)

a spectrophotometric measurement.

Fluorescence emission spectra were obtained with a Shimadzu RF-500 spectrophotometer. No attempt was made to eliminate atmospheric oxygen during fluorescence measurements. The ratio of the quantum yields of monomer and excimer fluorescence was estimated from the integrated emission spectra. Kinetic of photodimerization was carried out by measuring 255 nm absorption change on irradiation with a 6 W UV lamp.

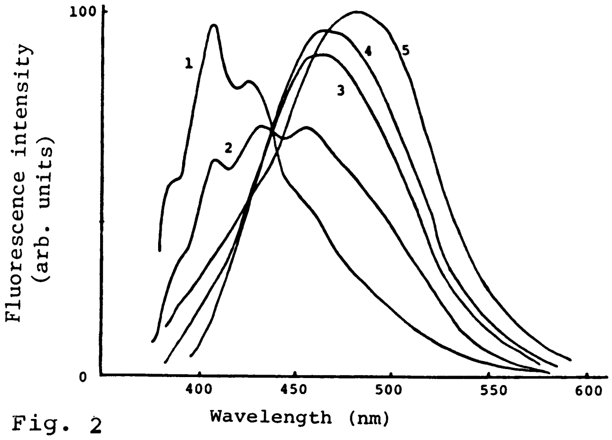


Fig. 2

Typical emission spectra of anthracene-9-carboxylic acid(Ant-9CA) (1-3) and poly(ethylene glycol)9-anthroate(PEG-Ant) (4-5)
(1)10^{-6}in methanol, (2)10^{-5}in methanol, (3)10^{-4}in methanol
(4)10^{-7}in methanol, (5)10^{-7}in water (mol/l)

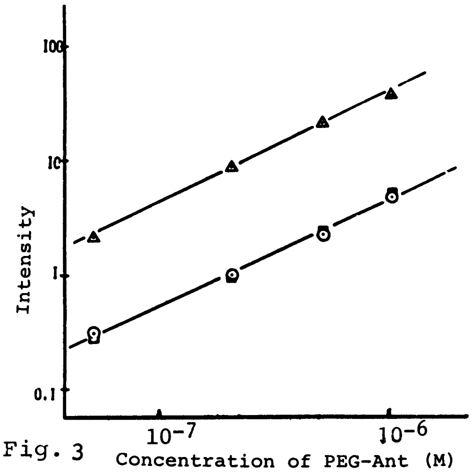


Fig. 3

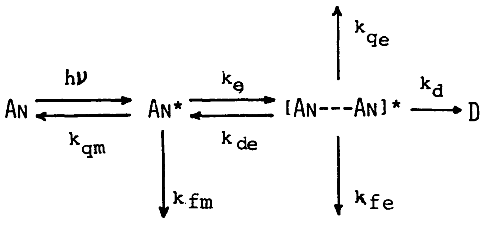
Effect of polymer-complexation on excimer emission intensity
(△)PEG-Ant and PMAA, (⊙)PEG-Ant
(⊡)PEG-Ant and PAA,
[PEG-Ant] = [PMAA] = [PAA]

Fig. 2 shows the typical emission spectra of Ant-9CA and PEG-Ant in methanol or water solution excited at 365 nm. It is seen that the spectra of Ant-9CA contains a structureless excimer band with a maximum at 465 nm in addition to the normal structured emission at 409 nm, and the ratio of the excimer fluorescence to monomer fluorescence intensity is strongly dependent on the Ant-9CA concentration.

It is of interest that no monomer fluorescence spectrum is seen in the case of PEG-Ant even at the concentration as low as 10^{-7} M both in methanol and water solution. On the contrary, concentration dependency was found for PEG-Ant neither in alcohol nor water solution. It should be mentioned that this concentration of excimer formation is extremely low in comparison with other condensed aromatic hydrocarbons. The reason of the preferential excimer formation of PEG-Ant at such low concentration in water is not understood at present, and we have no convincing interpretation for this hyperchromic effect. However, inter- and intramoleculer encounter of PEG-Ant which follow the excitation of one of the chromophores leading to the formation of the excimer should involve undoubtely a conformational transition of polymer chain which is required to bring the two anthracene groups in their proper steric relationship.

An interesting feature here is that the excimer fluorescence intensity of PEG-Ant increases ca. tenfold by the addition of PMAA and this increased excimer emission intensity does not depend on the concentration of constituent polymers(Figure 3). On the other hand, no monomer fluorescence intensity is increased for Ant-9CA of the same concentration by addition of PMAA in water (contains 1% of DMSO for solubilization of Ant-9CA).

It is well established[6-8] that polycarboxylic acids such as PMAA and poly(acrylic acid)(PAA) undergo intermacromolecular association with PEG through cooperative hydrogen bonding, and form a polymer-polymer complex with an equimolar composition in water as schematically illustrated in Fig. 1. The PEG-PMAA complexation is known to result in a drastic conformational shrinkage of constituent polymer chains, and therefore, the chromophores anchored to the polymer are considered to be concentrated in the complex domain, where the polarity and hydrophobicity are quite different from the bulk solution, and apparently lead to increase in excimer emission intensity.



Schematic representation of fluorescence emission and dimerization of anthracene derivative

k_{qm} : monomer internal quenching
k_{fm} : monomer fluorescence
k_e : excimer formation
k_{de} : excimer dissociation
k_{fe} : excimer fluorescence
k_{qe} : excimer quenching
k_d : dimerization

Fig. 4

It should be noted that PAA which forms the complex in the similar manner as PMAA, but is more loosely bound with PEG,[7] no increase in the excimer fluorescence intensity was observed(Figure 3). Described effect of PMAA strongly suggests that the chain conformation of PEG realized by the polymer complexation allows the increased excimer formation and this conformation(excimer forming state) exists prior to chromophore electronic excitation in the complex domain. This fact is rather interesting, because a significant part of the polymer chains of PEG is bound with PMAA[8)] and the mobility and the interconversion of chain conformation which is necessary for the excimer formation is considered to be appreciably depressed. The obtained result of increased excimer intensity indicates that the complexed PEG-PMAA chains can keep the mobility enough to have configurational encounter between two chromophores. The increased hydrophobicity in PEG-PMAA domain should certainly favor the excimer formation since no excimer increase in emission intensity was observed in PEG-PAA complex.

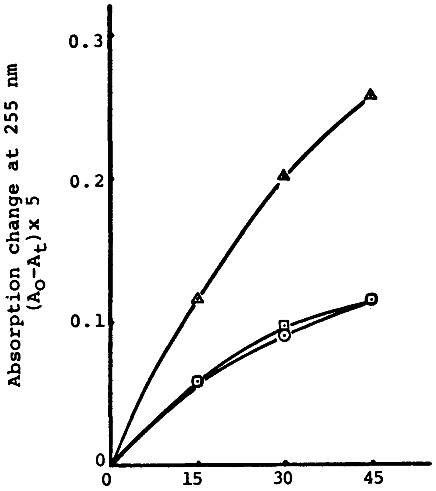


Fig.5

Effect of poly(methacrylic acid)(PMAA)(△) and poly(acrylic acid)(PAA)(□) on the rate of photodimerization of poly(ethylene glycol) 9-anthroate(PEG-Ant) [PEG]=[PMAA]=[PAA]=1.3×10^{-6} M, (⊙): no polymer was added.

The increased excimer formation and the assembly of chromophores in the complex domain led us to the kinetic study of photodimerization of polymeric anthracene. Photodimerization of anthracene derivatives on irradiating UV is well studied[9)], and is believed to proceed through excimer formation(Figure 4). Fig. 5 shows the absorption change of PEG-Ant in the presence and absence of PMAA or PAA. It is evident that the addition of equimolar amount of PMAA accelerates the photodimerization, whereas no increase in the rate of dimerization was obtained by the addition of PAA. These results may be correlated with the effects of polymer complex on the excimer formation behaved as "microreactor".

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