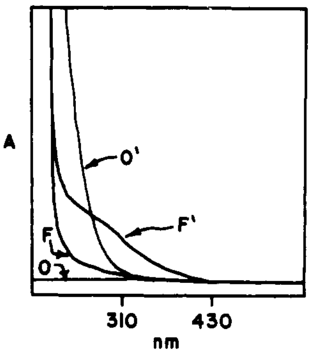
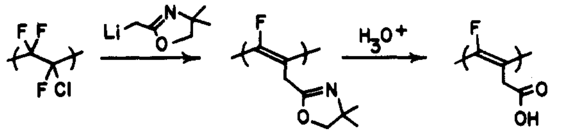


Figure 4. UV–vis spectra of PCTFE oil (O), PCTFE oil after reaction (0.5 equiv) with methyllithium (O′), PCTFE film (F), and PCTFE film after reaction (5 min) with methyllithium (F′).

The surface modification reaction appears to be less surface selective than the two-phase dehydrofluorination of poly(vinylidene fluoride):[3] it does not, however, exhibit autocatalysis and pitting. If the stoichiometry in eq 2 is assumed, the mass losses at 2-, 10-, and 20-min reaction times correlate with average reaction depths of 45, 136, and 285 Å, respectively. The contact angle data further suggest that the reaction is not surface selective: changes within the sampling depth (several angstroms) of this technique are occurring after an average of many tens of angstroms of material have reacted.

Work in progress concerns extending this chemistry to introduce surface polar functional groups (alcohols, aldehydes, and carboxylic acids). The strategy involves protecting-group chemistry. Carboxylic acids have been introduced by using the chemistry in eq 3.



(3)

Acknowledgment. We are indebted to Dr. Ralph G. Nuzzo and AT&T Bell Laboratories for assistance in obtaining ESCA spectra and the Office of Naval Research for financial support.

Registry No. PCTFE, 9002-83-9; phenyllithium, 591-51-5; methyllithium, 917-54-4.

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Fluorescence Study of Factors Affecting the Complexation of Poly(acrylic acid) with Poly(oxyethylene)

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ABSTRACT: Complex formation between poly(acrylic acid) (PAA) and poly(oxyethylene) (POE) was studied by following changes in the emission of dansyl-labeled PAA (Dan-PAA). Addition of POE with a molecular weight of 24 000 (POE-24) to Dan-PAA produced an up to eightfold increase of fluorescence with a blue shift of the maximum. Addition of much higher molecular weight POE led to a relatively small increase of fluorescence, and the emission maximum was *red-shifted*, suggesting increased exposure of the dansyl label to water. This was interpreted as indicating that Dan-PAA stretched out and was in contact with POE only at widely separated regions. The model was supported by the observation that addition of POE-24 to the Dan-PAA complex with high molecular weight POE leads to emission changes similar to those seen when POE-24 is added to Dan-PAA alone. Also, displacement of Dan-PAA from POE complexes by unlabeled PAA leads first to a sharp drop but later to an increase of fluorescence, indicating that Dan-PAA is first liberated in a stretched state before contracting to its equilibrium extension. An acrylic acid copolymer with 9 mol % acrylamide forms POE complexes similar to those of PAA although polyacrylamide does not complex with POE. This suggests than an uninterrupted sequence of interacting groups is not important in the formation of PAA–POE complexes.

Introduction

It has been known for a long time that poly(acrylic acid) (PAA) forms an association complex with poly(oxyethylene) (POE).[3] This phenomenon has been studied in great detail by Kabanov and his associates, who concluded early, on the basis of solution viscosity data and pH shifts accompanying the complex formation, that the process is highly cooperative and that the complex contains stoi-

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Table I
Characterization of Polymers Used in This Study

	[η], mL g^{-1}			
polymer designation	in benzene	in water	$\bar{M}_v \times 10^{-5}$	dansyl content, mol %
Dan-PAA		192	2.86[a]	1.8
POE-14	30	30	0.16[b]	
POE-24	40	34	0.24[b]	
POE-100	74	68	0.58[b]	
POE-300	242	247	3.13[b]	
POE-4000	953	913	24.3[b]	
Dan-PAAm		79	0.44[c]	1.4
Dan-P[AA/AAm]		214	3.36[a]	1.9

[a] Reference 10. [b] Reference 9. [c] Reference 11.

chiometrically equivalent carboxyls of PAA and ether groups of POE.[4] Calorimetry established later[5] that the enthalpy and entropy of complexation are both positive in water solution, suggesting that, while complexation involves hydrogen bonding between carboxyl and ether groups, hydrophobic bonding is the main driving force to association.

In earlier communications[6-8] we employed PAA labeled with the fluorescent dansyl group (Dan-PAA) to study equilibria and kinetics of this polymer association. The method was based on the high sensitivity of the emission characteristics of the dansyl group to its microenvironment, the fluorescence being about an order of magnitude more intense in organic solvents than in water. Thus, the complexation of Dan-PAA with hydrogen-bond acceptor polymers led to a displacement of water molecules from the neighborhood of the label, resulting in a sharp increase in emission intensity. However, while for the complexation of Dan-PAA with poly(*N*-vinylpyrrolidone) the data were consistent with the assumption that the complex contains an equivalent concentration of hydrogen-bond donor and acceptor groups, results obtained when Dan-PAA and POE solutions were mixed were unexpected, with the emission intensity continuing to increase up to a 25-fold excess of POE and no indication that a limit was approached even at that point.[6]

Since these previous studies employed only POE samples up to a molecular weight of 24 000, it seemed desirable to study Dan-PAA complexation with larger POE chains. Such a study revealed a strikingly different pattern of behavior, which carries important implications concerning the structure of the complex. In a second approach to the principles governing complex formation, the effect on complex stability of a substitution of an acrylic acid copolymer for PAA was determined.

Experimental Section

Materials. Acrylic acid (AA) was distilled and acrylamide (AAm) was recrystallized before use. *N*-[2-(Dansylamino)-ethyl]acrylamide (Dan-AAm, mp 104–105 °C) was prepared as previously described.[6] Dansyl-labeled poly(acrylic acid) (Dan-PAA), polyacrylamide (Dan-PAAm), and acrylic acid–acrylamide copolymer (Dan-P[AA/AAm]) were prepared by copolymerization in methanol solution initiated by AIBN and carried to low conversion. After dialysis and freeze-drying, the content of the dansyl label was determined by spectral absorption in water at pH 7 or in methanol. The composition of Dan-P[AA/AAm] was obtained from the N/C ratio. Samples of POE were designated by molecular weights specified by the supplier (Polysciences) as 1.4 × 10^4, 10^5, 3 × 10^5, and 4 × 10^6 (POE-14, POE-100, POE-300, and POE-4000); POE-24 (J. T. Baker Chemical Co.) was the sample used in our previous study.[6] These polymers were dissolved in chloroform and reprecipitated into hexane. Table I lists the characteristics of all the polymers employed. The viscosity-average molecular weights of POE,[9] Dan-PAA (and Dan-P[AA/AAm], which was assumed to behave similarly),[10] and Dan-PAAm[11] were calculated from [η]-$\bar{M}$ relations in the literature.

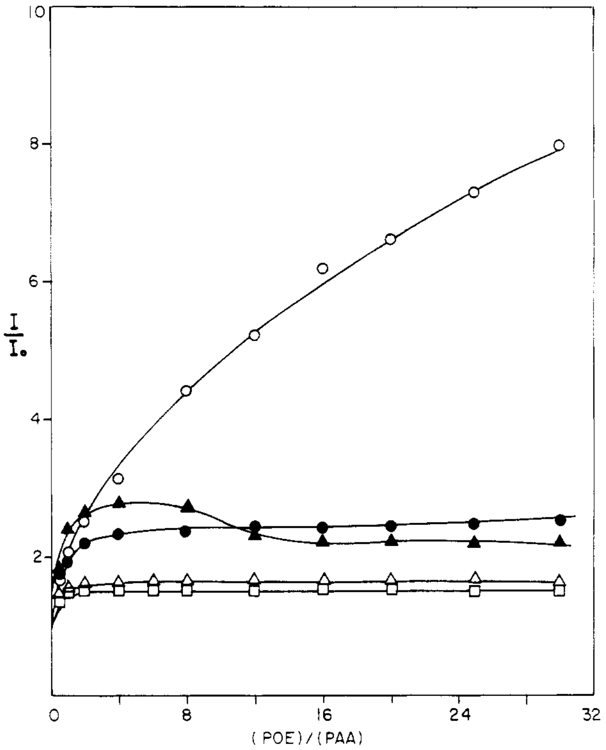


Figure 1. Enhancement of fluorescence intensity of Dan-PAA (6.35 × 10^{-3} N) on complexation with POE: (●) POE-14; (○) POE-24; (▲) POE-100; (△) POE-300; (□) POE-4000.

Fluorimetry. Reflectance fluorescence spectra[6] of solutions containing unneutralized Dan-PAA or Dan-P[AA/AAm] with or without POE were recorded on a Perkin-Elmer MPF 44B spectrofluorimeter using an excitation wavelength of 340 nm. Mixtures of donor and acceptor polymer solutions were prepared at least 24 h before fluorescence measurement. The relative fluorescence intensities of dansyl-labeled donor polymers and their mixtures with POE (I/I_0), as well as shifts in the emission maximum, were found to be identical with polymers carrying 0.8 and 1.8 mol % of the dansyl label; the higher label concentration was used in later studies. Unless otherwise stated, data were collected at 25 °C.

Results

Fluorescence Study of PAA–POE Complex Formation. Figure 1 contains plots of the enhancement of the fluorescence intensity at the maximum of the emission spectrum on addition of POE solutions to solutions of Dan-PAA. The excitation wavelength of 340 nm was close to the absorption maximum of the basic form of the chromophore (330 nm) while the absorption of the protonated form is negligible.[12] The I/I_0 rose steadily with an increasing POE/PAA ratio, reaching a value of 8 at a POE/PAA base molar ratio of 30 with no indication of leveling off. Surprisingly, the behavior of POE samples of higher molecular weight was very different. Addition of POE-100 solutions first increased I/I_0 to a maximum of 2.8, to drop off at higher POE/PAA ratios to 2.2. POE samples of still higher molecular weight produced even smaller enhancements in fluorescence intensity.

Even more unexpected were the shifts observed in the wavelength of the emission maximum produced by POE addition. Figure 2 shows that addition of POE-14 solution leads to a blue shift in the emission maximum, and this is much more pronounced with POE-24. However, with POE-100 the wavelength of the emission maximum increases after an initial drop, and very large POE molecules (POE-300 and POE-4000) cause a *red shift* from the onset

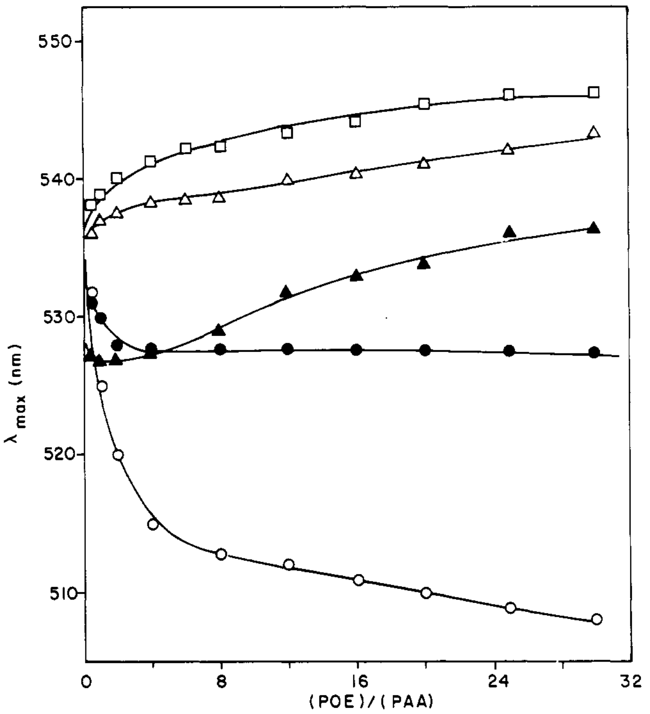


Figure 2. Shift in the wavelength of the emission maximum accompanying the complexation of Dan-PAA with POE. Significance of symbols as in Figure 1.

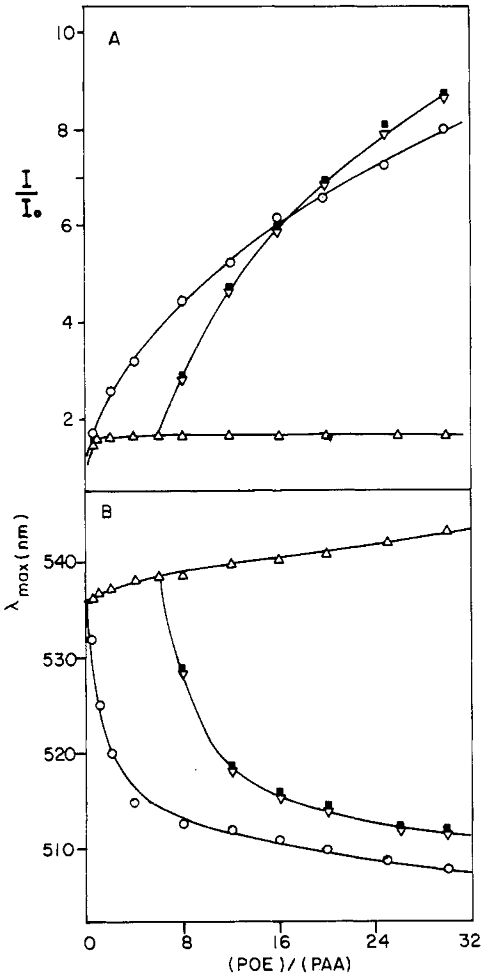


Figure 3. Enhancement of the fluorescence intensity and shift in the wavelength of the emission maximum on addition of POE-24 to solutions containing Dan-PAA and POE-300 or Dan-PAA and POE-4000: (▽) POE-300 + POE-24; (■) POE-4000 + POE-24. Significance of other symbols as in Figure 1.

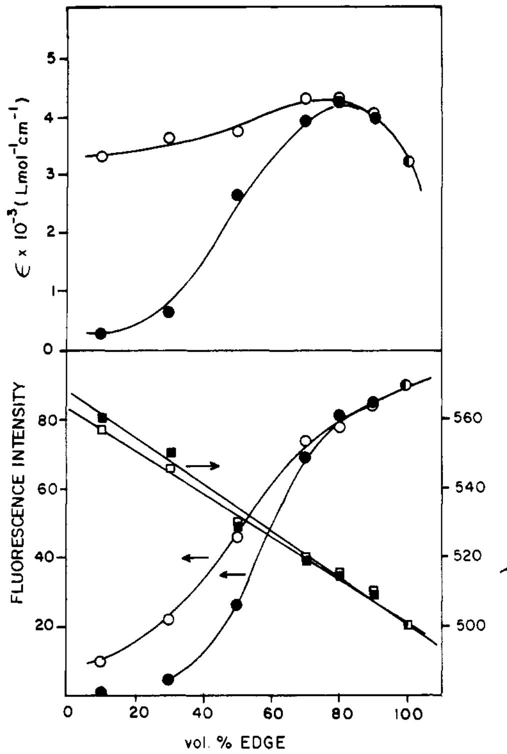


Figure 4. Extinction coefficient (ϵ) of Dan-PAA at 340 nm, the emission intensity and wavelength of the emission maximum when excited at this wavelength. Dependence on the composition of mixtures of EGDE with water in solutions buffered at pH 6 (open points) and in solutions containing 0.01 N HCl (filled points).

of their addition. This suggests that the dansyl label is in even more intimate contact with water after addition of these very high molecular weight POE than in the solution containing only Dan-PAA.

Further information was obtained from experiments in which POE-24 solutions were mixed with solutions containing both Dan-PAA and POE-300 or POE-4000. As shown in Figure 3, the addition of this relatively low molecular weight POE results in a sharp increase in fluorescence intensity similar to that produced by POE-24 on Dan-PAA in the absence of high molecular weight POE. The emission maxima now also exhibit the expected blue shift. These results were shown to be independent of the order in which the three polymers were mixed, so that we may assume that they reflect the properties of equilibrium states. Also, the fluorescence readings were found to be stable over several days.

Changes in the Absorption Spectrum of the Dansyl Label. The formation of the PAA–POE complex leads to two changes that affect the emission of the label: The dansyl group is transferred to a medium of lower polarity, and its degree of protonation is reduced. According to Strauss and Vesnaver[12] the protonation equilibrium of the dansyl group is characterized by $pK_a \sim 4$, so that this group is essentially fully protonated at pH 1 and deprotonated at pH 6. When Dan-PAA was dissolved in a mixture of water with ethylene glycol dimethyl ether (EGDE, a low molecular weight analogue of POE) containing 0.01 N HCl or a pH 6 buffer, the absorption at 340 nm and the emission on excitation at this wavelength changed as shown on Figure 4. We see (Figure 4a) that the absorption of the basic form depends relatively little on the medium, while in the presence of 0.01 N HCl the absorption is very sensitive to it. In water, the protonated form of the dansyl group has a very low absorption, but in EGDE-rich media the dansyl absorption is that char-

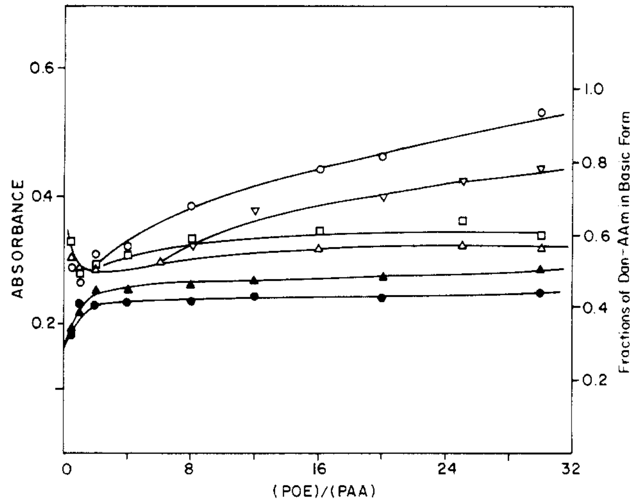


Figure 5. Change in the protonation of the dansyl label on complexation of Dan-PAA with POE. Significance of symbols as in Figure 1.

acteristic of its basic form. This shows that even in this strongly acid solution the dansyl remains unprotonated in a nonpolar environment.

Figure 4b shows that the location of the emission maximum is virtually independent of the state of ionization of the dansyl group and depends essentially only on the polarity of the medium. The emission intensities are influenced by both factors, the latter being dominant. Thus, the emission intensity increases sharply, both in 0.01 N HCl and in solutions buffered at pH 6, with an increasing EGDE content over the entire range of composition, in spite of the decreasing absorption observed in solutions containing more than 80 vol % EGDE.

Using data in the model systems depicted in Figure 4a, we have interpreted changes in absorption of Dan-PAA on addition of POE in terms of a change in the fraction of the dansyl label present in the deprotonated form. The results are shown in Figure 5, and they have features similar to those of emission intensity data on Figure 1: On addition of POE-24 the unprotonated dansyl fraction increases continuously even with a large excess of POE; with POE-300 or POE-4000, an initial small decrease is reversed at higher POE concentrations, leveling off at values only slightly different from those observed for Dan-PAA before POE addition.

Association of POE with an Acrylic Acid–Acrylamide Copolymer. Mixing of Dan-PAAm solutions with solutions of POE led to no change in emission intensity, so that the acrylamide residues do not seem to associate with the POE ether groups. In comparing the interaction of Dan-PAA and Dan-P[AA/AAm] with POE (Figure 6) we see that the complexation appears to be somewhat more efficient with the homopolymer at low ratios of OE/AA of the ethylene oxide and acrylic acid residues, but for high values of OE/AA the copolymer, containing 9 mol % of acrylamide residues, seems to participate in complex formation quite as efficiently as the acrylic acid homopolymer.

Discussion

The results of this study show that the nature of the complexation of PAA with POE is fundamentally different for POE-24 and for POE samples of higher molecular weight. On association with POE-24, the dansyl label of Dan-PAA seems to be effectively removed from contact with water molecules if a sufficient excess of POE is used; both the enhancement of emission intensity and the shift of the emission maximum to shorter wavelengths are very similar to those observed for a dansyl label in a mixture of 10 vol % water and 90 vol % of low molecular weight POE.[6]

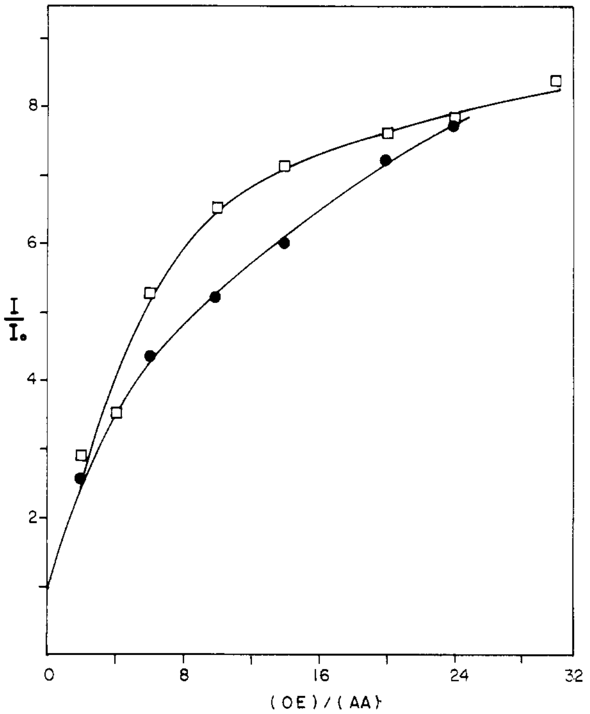


Figure 6. Change in emission intensity on complexation of POE with Dan-PAA and Dan-P[AA/AAm].

In view of the striking differences between the behavior of POE-24 and the high molecular weight POE, the possibility was considered that POE-24 might have contained some contaminant residues. However, no difference could be detected between the IR spectra of the various POE samples. Another possibility which was considered was that the behavior of POE-24 is related to micelle formation. Polik and Burchard[13] found anomalies in the Zimm plots of POE solutions, which were tentatively interpreted as arising from crystalline spherulites stable below 60 °C. Brown,[14] who studied aqueous POE solutions by dynamic light scattering, concluded that aggregates formed from POE with an average molecular weight of 2.5×10^4 but not from POE with molecular weights exceeding 4×10^4. Because of these reports, we compared the effect of POE-24 addition on the fluorescence of Dan-PAA at 25 °C and at 65 °C. The results, shown in Figure 7, indicate only a minor temperature effect on fluorescence intensity; there is a red shift in the emission maximum when the temperature is raised, but its magnitude remains unchanged as POE-24 is added to the Dan-PAA. We have, therefore, no evidence for the assumption that the emission behavior of the Dan-PAA complex with POE-24 is related to anomalies in the solution behavior of POE in this range of chain lengths.

On complexation of Dan-PAA with POE samples of high molecular weight, only relatively small increases in fluorescence intensity were observed and the emission maximum shifted to *longer* wavelengths. Since an intensification of the fluorescence of the dansyl label has previously always been observed to be associated with a blue shift of the emission maximum, this unusual behavior can only be understood as the superposition of two effects. We propose that the Dan-PAA chain is in contact with the POE only at widely separated regions along its contour and that the chain is stretched out between these contact points. Thus, some of the dansyl labels are removed from

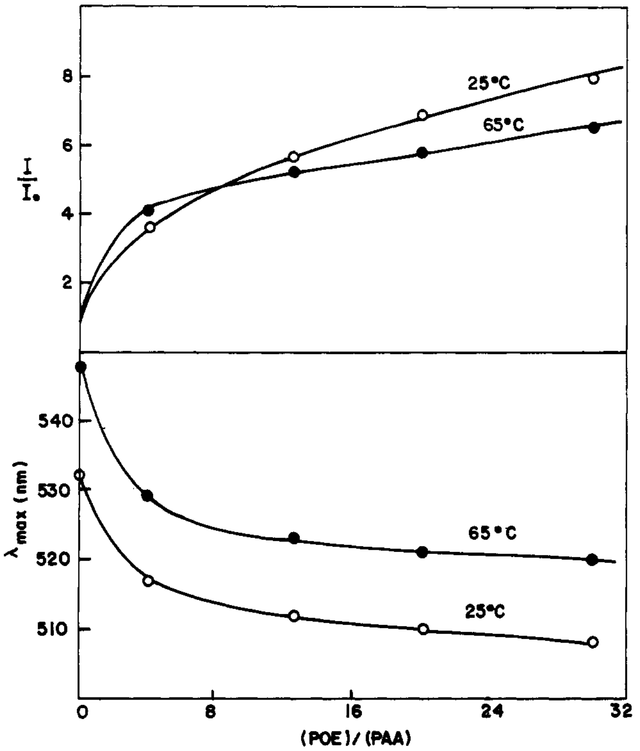
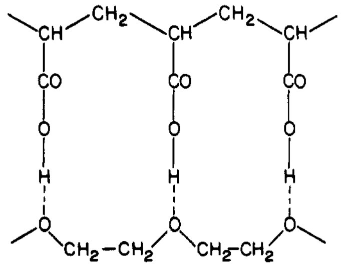


Figure 7. Effect of temperature on the fluorescence changes accompanying the complexation of Dan-PAA with POE-24.

the aqueous environment while others are in an even more intimate contact with water than in unassociated Dan-PAA chains. Two pieces of evidence support this model: (1) Addition of a solution of POE-24 to a solution of a complex of Dan-PAA and high molecular weight POE leads to fluorescence changes, suggesting the association of POE-24 with free stretches of Dan-PAA. (2) When a large excess of unlabeled PAA was mixed with the complex of Dan-PAA with a high molecular weight POE in a stopped-flow apparatus,[15] the fluorescence intensity first decreased sharply, but later increased somewhat (Figure 8). This was interpreted as indicating that the Dan-PAA displaced from the complex is first liberated in a stretched state which later contracts so that the exposure of the dansyl label to water is reduced.

Our results disagree with the conclusions of Baranovsky et al.,[16] according to which there exist "uninterrupted sequences of bonds in polycomplexes of simple synthetic macromolecules". According to this view, PAA–POE complexation would be represented by the structure



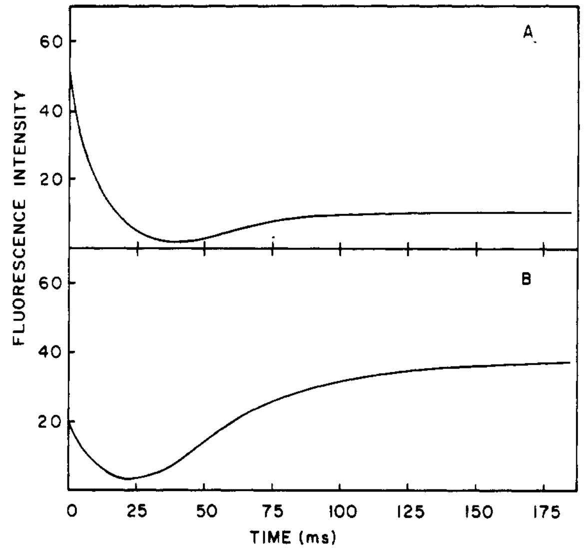


Figure 8. Change in fluorescence intensity after addition of 7×10^{-2} N PAA to a solution containing 7×10^{-3} N POE and 7×10^{-4} N Dan-PAA: (A) POE-300; (B) POE-4000.

that is, by a long sequence of 11-membered condensed rings. The well-known improbability of such rings (apart from the steric irregularity of the PAA chain) makes it most difficult to assume a structure of this kind. If "uninterrupted sequences" were important in polymer association, the introduction into PAA of 9 mol % comonomer residues that do not participate in complex formation with POE also should have affected profoundly the association equilibrium—an effect that was not observed.

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Registry No. PAA, 9003-01-4; POE, 25322-68-3; P[AA/AAm], 9003-06-9.

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