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Study of the Equilibrium and the Kinetics of the Fluorescence Enhancement on Mixing Solutions of Auramine O and Poly(methacrylic acid)

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ABSTRACT: The steady-state fluorescence of aqueous solutions containing poly(methacrylic acid) (PMA) and Auramine O (AO) was studied as a function of pH and the ratio of the PMA normality and the AO molarity (P/D) by viscosity, UV absorption, and emission intensity. The difference spectra of AO in the presence and absence of PMA were shifted by PMA addition at low P/D values but exhibited isosbestic points at high P/D. These difference spectra were interpreted in terms of the PMA–AO association constant K at pH 4.05, 4.98, and 6.02. The shape of these difference spectra was similar to the AO difference spectrum in 50% aqueous dioxane and water. Emission intensities of AO in PMA solutions at low ionic strength increased with pH as long as the PMA remained in its compact conformation but dropped sharply on PMA expansion. At an ionic strength of 0.2 M, the emission intensity decreased with increasing pH even before the polymer expansion. Estimates of K from the dependence of the emission intensity on P/D yielded at pH 4.05 a value similar to that derived from difference absorption spectra, but at pH 4.98 the K obtained from fluorescence data was 4 times smaller. The rise of AO emission intensity on substituting 50% dioxane for water was relatively small, so that the decrease in the polarity of the microenvironment can account for only a small portion of the fluorescence increase when AO is bound to the compact form of PMA. Stopped-flow experiments of the kinetics of fluorescence enhancement when AO solutions are mixed with solutions of PMA yielded rate constants that remained constant or decreased with increasing PMA concentration. This indicates that the fluorescence increase is due to a conformational transition following PMA–AO association. The final approach to equilibrium has the unexpectedly low rate constant of 0.1 s^{-1}.

Introduction

In 1954 Oster discovered[1] that Auramine O, bis(4-(dimethylamino)phenyl)methylideneammonium chloride (AO), which fluoresces very weakly in water solution, has its emission intensity dramatically increased in the presence of DNA. Four years later, he reported[2] a similar effect in the presence of poly(methacrylic acid) (PMA). He suspected that the phenomenon was due to the local rigidity of the medium which would prevent the quenching of the excited molecule by internal rotation and showed that the emission intensity of AO increased, in fact, with the viscosity of its solutions.[3]

The change in the fluorescence intensity of AO when associated with PMA is of special interest because this polymeric acid exhibits a cooperative transition from a highly contracted to an expanded state at a critical density of anionic charges along the chain molecule.[4] Anufrieva et al.[5] showed that the enhancement of the AO fluorescence is associated with the contracted form of PMA—thus, the effect disappears when this form is destabilized by a high degree of ionization, α, of the PMA or when addition of methanol to the aqueous solution eliminates the hydrophobic bonds opposing chain expansion. Anufrieva et al. believed that only the contracted form of PMA binds AO and that the fluorescence intensity of the dye is proportional to its amount complexed with the polymer.

An extensive and careful study in Mandel's laboratory[6] showed that the situation is, in fact, much more complex. Comparing the fluorescence data with the results of dialysis equilibria of AO and PMA at varying degrees of ionization, they concluded that the binding of AO increases monotonously with the PMA charge density, even though the fluorescence intensity may drop precipitously in the range of α corresponding to the transition from the compact to the expanded state of the polymer. This drop of emission intensity was very pronounced when the ratio of the polymer normality to the molarity of the dye, P/D, was very high, while for $P/D \leq 2$ the fluorescence varied only slightly with α, with the maximum shifting to high α values. Thus, the fluorescence was shown to depend not only on the amount of the dye complexed with the polymer but also on the expansion of the polymer chain and the fraction of the PMA residues associated with the dye. Another striking observation, based on titration and viscosity behavior, was the stabilization of the compact PMA form by minute amounts of AO.

A few years ago, Chen and Thomas[7] showed that the emission intensity from a solution containing PMA and pyrene changes sharply when the polymer expands and they used a stopped-flow apparatus with fluorescence

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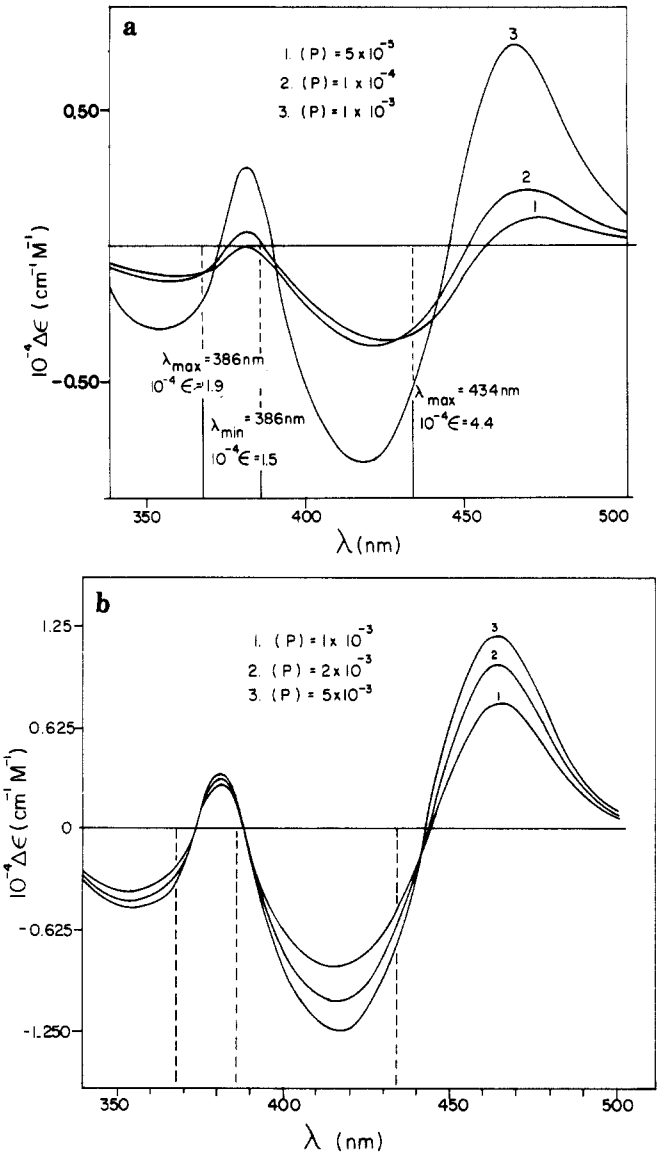

Figure 1. Difference absorption spectra of AO (10^{-5} M) in the presence and absence of PMA. (pH 4.98, ionic strength 0.02 M). (a) Comparison of $\Delta\epsilon$ at low and high P/D. (b) $\Delta\epsilon$ at various high P/D. The locations and magnitudes of the maxima and minima of the AO spectrum in the absence of PMA are also indicated.

detection to monitor the kinetics of this process. We have used an apparatus of this kind and polymers with covalently attached medium-sensitive fluorescent labels to study the kinetics of polymer complex formation[8] and the conformational transition of PMA after a pH jump.[9] The present investigation was designed to supplement spectroscopic equilibrium data on the PMA–AO complexation by kinetic data using this stopped-flow apparatus.

Results and Discussion

In the classical study of AO interaction with PMA by Stork et al.[6] the fluorescence intensity was measured in solutions in which the charge of the PMA was varied by partial neutralization in the absence of any other buffer. Since the PMA concentration in these experiments was only 2.3×10^{-3} N, the low buffering capacity of the system might have introduced some uncertainty concerning the presumed ionization of the polymeric acid. We chose, therefore, to conduct our experiments in solutions to which higher concentrations of conventional buffers had been added.

Absorption Spectra. Stork et al.[6] reported difference spectra between AO in the presence and absence of PMA

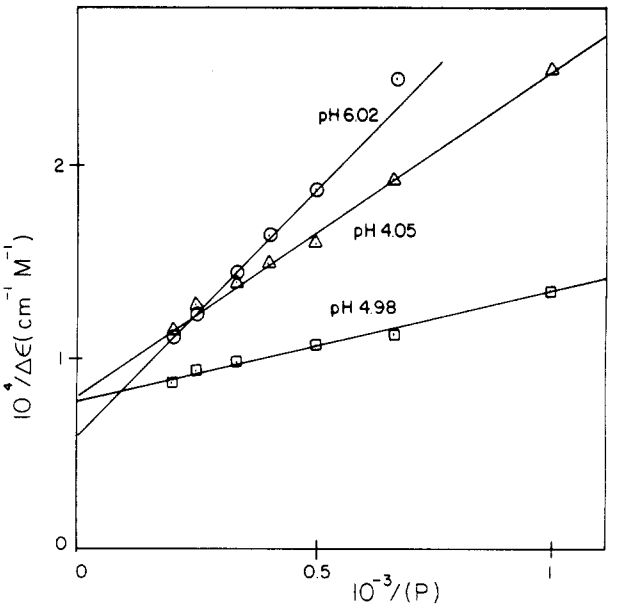

Figure 2. Dependence of $1/\Delta\epsilon$ on $1/(P)$ at three pH values. (AO) = 1×10^{-5}; $\Delta\epsilon$ at 462 nm.

at various degrees of neutralization of the polymer. We have expanded such a study, varying not only the pH but also the P/D. Typical results, obtained at pH 4.98, are presented in Figure 1. They show that two effects have to be differentiated: (1) At low P/D, the location of the maxima and minima of the difference extinction coefficients are seen to shift. This phenomenon may possibly be caused by the interaction between the complexed AO molecules at low P/D, in analogy with the behavior of complexes of acridine orange with PMA.[10] (2) At a high P/D, the difference extinction coefficients recorded at different P/D ratios pass through well-defined isosbestic points, and the intensity of the difference spectrum may, therefore, be assumed to be proportional to the amount of the dye bound to the polymer. Thus, with an equilibrium constant K characterizing the process $P + D \rightleftarrows PD$ and $(PD)/(D) = (\Delta\epsilon/\Delta\epsilon_{max} - \Delta\epsilon)$, where $\Delta\epsilon$ is the difference extinction coefficient observed at a polymer normality (P) while $\Delta\epsilon_{max}$ is that corresponding to the complete complexation of AO, we obtain

$$(\Delta\epsilon_{max}/\Delta\epsilon) - 1 = 1/K(P) \quad (1)$$

Figure 2 shows plots of $1/\Delta\epsilon$ against $1/(P)$ that lead to estimates of K of 340, 1450, and 220 M^{-1} at pH 4.05, 4.98, and 6.02, respectively. Thus, the affinity of the dye to PMA increases as long as the charge of the polymeric acid does not disrupt its compact conformation but drops sharply when the pH is raised beyond the point of the PMA transition to the expanded state. Our data are thus in sharp disagreement with those of Stork et al.,[6] whose dialysis results (none too accurate by their admission) indicated for high P/D ratios a continuous increase of AO binding with an increasing PMA charge. They used buffer with an ionic strength of only 10^{-3} M. Under such conditions the electrostatic interaction between the AO and the PMA would have been larger than in our experiments but the low buffer capacity would have introduced some uncertainty concerning the polymer charge. We believe, therefore, that the spectroscopic determination of the dependence of AO complexation on pH and P/D yields more reliable data.

Since the difference spectrum reflects presumably a change in the microenvironment of the bound dye, it seemed of interest to record difference spectra of AO in

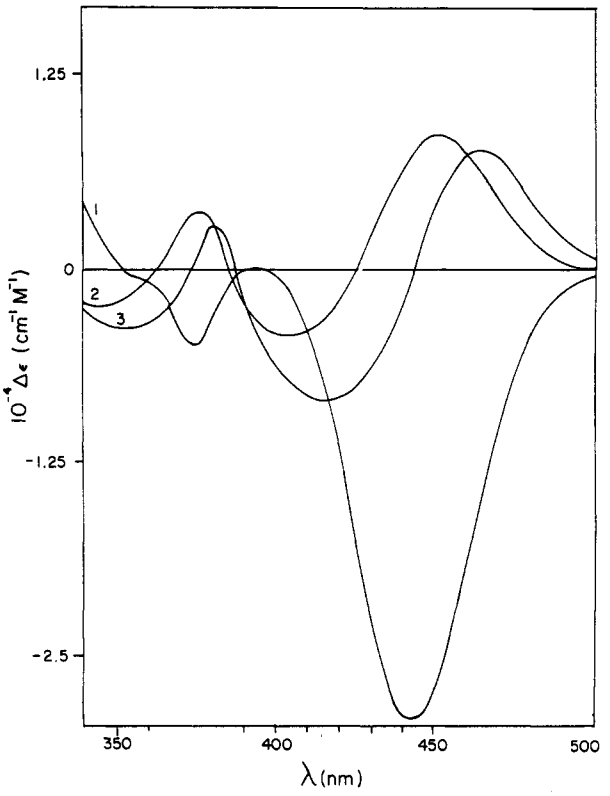

Figure 3. Comparison of the difference spectra of AO in dioxane (1), in 50% aqueous dioxane (2), and in 10^{-3} N PMA (pH 4.98, ionic strength 0.02 M) against water solutions of AO. (AO) = 2×10^{-5} M in (1) and (2); (AO) = 1×10^{-5} M in (3).

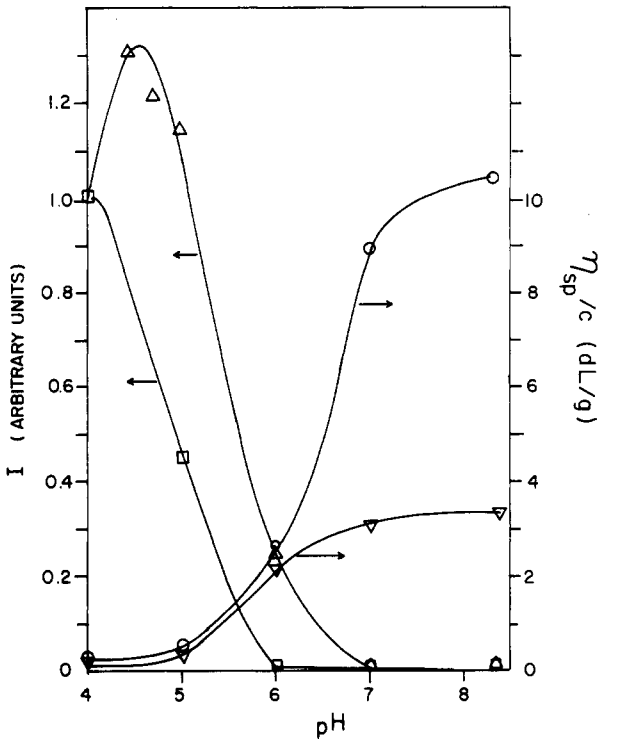

Figure 4. The pH dependence of the fluorescence intensity at the emission maximum and the reduced viscosity in solutions containing (AO) = 1×10^{-5} M, (P) = 5×10^{-3} N at an ionic strength of 0.02 M [(△), (○)] and 0.2 [(□), (▽)].

water and in less polar media in the absence of polymer. Figure 3 shows that such a difference spectrum in 50% aqueous dioxane has a shape quite similar to that of PMA-bound AO, with the maxima at 377 and 454 nm and the minimum at 406 nm slightly blue-shifted from their locations at 382 and 462 nm and 417 nm, observed in the polymer-bound dye. Surprisingly, the difference spectrum of AO in pure dioxane was entirely different. It has been suggested[11] that for aniline and phenol an increasing polarizability of the solvent reduces the excitation energy while hydrogen bonding acts in the opposite direction. It appears then that the first effect is dominant in 50% dioxane, whereas the elimination of hydrogen bonding in pure dioxane accounts for the spectral shift observed in that case.

Emission Spectra. The pH dependence of the fluorescence intensity at the emission maximum of solutions containing 10^{-5} M AO and 5×10^{-3} N PMA is compared in Figure 4 with the pH dependence of the reduced viscosity of PMA solutions. At an ionic strength of 0.02 M, the fluorescence first increases as the pH is raised above 4, and this can be understood as due to an increase of the anionic charge of the polymer, leading to an increasing binding of the cationic dye. Above pH 5 the fluorescence intensity drops sharply and the increasing solution viscosity reflects the expansion of the PMA. Surprisingly, at the higher ionic strength of 0.2 M, the fluorescence intensity drops by about half between pH 4 and 5, although PMA remains in the contracted form in this pH range.

Although Stork et al.[6] claimed that at constant pH the emission intensity of AO increases on PMA addition "without important alterations of the spectrum", our data revealed a more complicated behavior (Figure 5). In the absence of PMA the emission spectrum of AO exhibits a broad peak with a maximum at 500 nm and a sharp peak at 543 nm. The latter peak is probably due to a dimer or a higher aggregate of the dye; it was seen at a dye concentration of 4.17×10^{-5} M but not at a concentration of 1×10^{-5} M. It remained prominent on addition of PMA at pH 6.02 but disappeared on PMA addition at lower pH values. The position of the broad peak shifted slightly on PMA addition to 508 nm at pH 4.05 and remained constant at pH 6.02. At pH 4.98 the behavior was more complex, with the emission maximum first moving on PMA addition to 525 nm and then shifting in the opposite direction to 510 nm.

Erny and Muller[12] assumed that the fluorescence quantum yield of AO in the presence of varying concentrations of PMA at constant α is linear in the fraction of the dye bound to the polymer. Since the nature of the emission spectrum changes at some pH values with P/D, we felt that this assumption should be restricted to high P/D ratios, where the location of the emission maximum is constant. A treatment analogous to that applied to the difference extinction coefficients then leads to

$$I_0/I = (I_0/I_{max})[K^{-1}(P)^{-1} + 1] \quad (2)$$

where I, I_0, and I_{max} refer to emission intensities at a given P/D, at (P) = 0, and at a complete complexation of the dye. Figure 6 shows a plot of I_0/I against 1/(P) from which K values of 300 and 360 M^{-1} are obtained at pH 4.05 and 4.98, respectively. The data obtained at pH 6.02 extrapolate to close to zero for 1/(P) = 0, so that they cannot be interpreted by eq 2. The K value obtained in this manner at pH 4.05 is in reasonable agreement with the estimate obtained from the difference spectra. However, the K value obtained from fluorescence at pH 4.98 is only a quarter of the estimate based on eq 1. We feel that K values derived from difference spectra are more likely to be reliable since the emission intensity depends on two independent factors, the polarity and the rigidity of the medium.

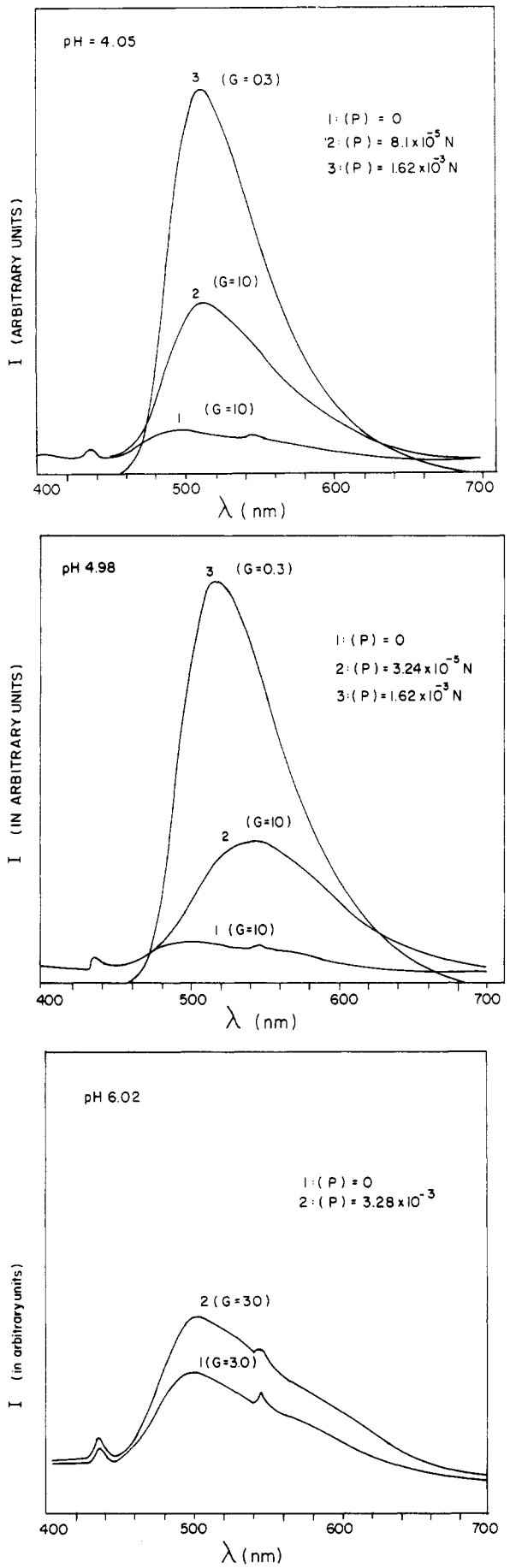

Figure 5. Emission spectra of AO at different pH and PMA concentrations. The G values are the relative sensitivities of the fluorimeter employed in recording the spectra. (AO) = 4.2×10^{-5} M, ionic strength 0.02 M.

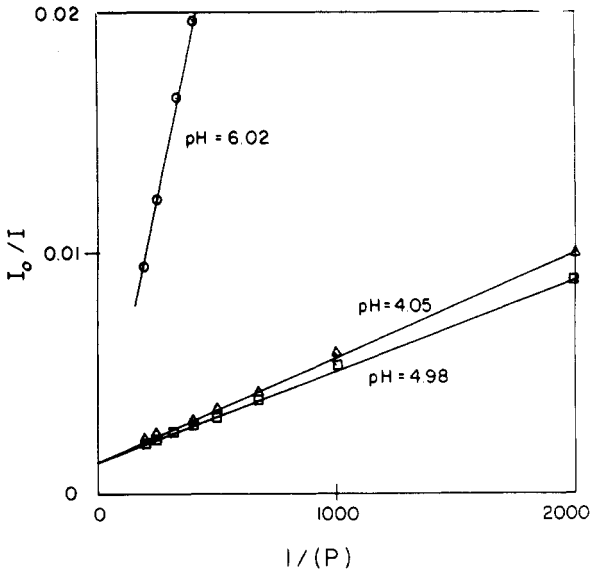

Figure 6. Dependence of the ratio of the emission intensity in the absence and the presence of PMA on 1/(P). Ionic strength 0.02 M.

The effect of PMA on the fluorescence of AO is similar to that of other poly(carboxylic acids) which undergo cooperative transitions from a compact to an expanded state.[13,14] Oster[2] believed that the "rigidity" of the microenvironment of the bound dye, which would restrict quenching by internal rotation and thus increase the fluorescence quantum yield, is responsible for the observed effect. This interpretation became less convincing when it was shown that binding to the extended PMA produces only a small increase in fluorescence intensity. Mandel and Stork[15] argued that the unfolding of PMA "makes new degrees of freedom available to the bound dye and increases the possibility of quenching the excited dye through interaction with the solvent", but an alternative interpretation is suggested by the existence of a number of dyes which fluoresce strongly in organic solvents but whose emission is quenched by contact with water molecules.[16] Erny and Muller[12] proposed, therefore, that the strong fluorescence of AO bound to compact PMA molecules is due to the fact that "the environment has a more organic character".

To illuminate this problem, we recorded the fluorescence of AO in water, water–dioxane mixtures, and pure dioxane. We found that the emission intensity at its 500-nm maximum was enhanced by a factor of 3.6 when 50% dioxane was substituted for water as the solvent medium. In pure dioxane, the maximum emission intensity was increased tenfold, but the location of the maximum was blue-shifted to 470 nm. No corresponding shift was ever found for AO bound to PMA. We must conclude that a change in local polarity can account only for a small fraction of the large increase in the emission intensity of AO complexed with the compact form of PMA. This leads us to believe that interference with the internal rotation of the excited dye is indeed, as surmised by Oster, the cause of the strong emission under these conditions. The low affinity of the dye to the expanded PMA, as evidenced by our data on the P/D dependence of the difference spectra, must be the cause of the low fluorescence intensity of AO in PMA solutions at high pH.

Kinetics Studies. When equal volumes of buffered AO and PMA solutions were mixed, the rise in fluorescence could be followed in a stopped-flow apparatus. Table I lists the results obtained. Here I_∞, I^*, and I_0 are the intensity of fluorescence observed when equilibrium had

Table I
Kinetics of Fluorescence Increase after Mixing of AO with PMA at 21 °C at an Ionic Strength of 0.02 M

PMA						
mol wt	milliequiv/L	pH	$(I_\infty - I_0)/(I_\infty - I^*)$	k_1, s^{-1}	k_2, s^{-1}	q
1.5×10^5	1	4.05	0.86	4.25	0.102	0.67
	2	4.05	0.86	4.17	0.100	0.66
	4	4.05	0.86	4.08	0.099	0.66
	6	4.05	0.85	4.10	0.093	0.66
	10	4.05	0.85	4.22	0.094	0.66
2.3×10^5	1	4.05	0.85	4.47	0.104	0.67
	2		0.86	4.32	0.100	0.67
	4		0.86	4.05	0.099	0.67
	6		0.85	3.97	0.098	0.67
	10		0.84	4.36	0.101	0.67
5.5×10^5	1		0.87	4.41	0.100	0.67
	2		0.84	4.20	0.101	0.67
	4		0.85	4.19	0.103	0.67
	6		0.85	4.28	0.100	0.67
	10		0.85	4.25	0.101	0.68
1.5×10^5	1	5.16	0.59	9.82	0.111	0.79
	4	5.16	0.63	8.34	0.110	0.77
	6	5.16	0.64	8.07	0.111	0.75
	10		0.66	6.91	0.109	0.74
2.3×10^5	1		0.58	9.60	0.116	0.79
	4		0.59	8.07	0.111	0.75
	6		0.60	7.53	0.108	0.74
	10		0.62	6.96	0.105	0.73
5.5×10^5	1	5.16	0.62	9.13	0.111	0.78
	4	5.16	0.64	8.17	0.112	0.75
	6	5.16	0.65	7.41	0.109	0.74
	10	5.16	0.65	6.80	0.101	0.72

been attained (20 s after mixing), the intensity when the AO solution was mixed with a buffer containing no PMA, and the intensity at the first time at which a meaningful reading could be made, i.e., 1 ms. Thus, $(I_\infty - I_0)/(I_\infty - I^*)$ is the fraction of the growth of fluorescence intensity that could be followed kinetically by our experimental technique. This process could be closely fitted expressing the emission intensity I at time t by

$$(I_\infty - I)/(I_\infty - I_0) = q \exp(-k_1 t) + (1 - q) \exp(-k_2 t) \quad (3)$$

It would be expected that the increase in fluorescence involves a continuous distribution of relaxation times and the above expression merely serves as a convenient approximation to the physical reality. Nevertheless, k_2, which describes the final approach to equilibrium, must be considered to have a clearly defined significance.

Table I shows that at pH 4.05 about 85% of the fluorescence change took place after 1 ms. This fraction decreased to ~60% at pH 5.16, still surprisingly high if a diffusion-controlled association of AO with PMA was by itself responsible for the enhancement of the emission intensity. But the most significant feature of the results was the observation that neither k_1 nor k_2 increased with increasing PMA concentration (Figure 7). This could only mean that the major portion of the fluorescence enhancement, the portion which we could follow kinetically, is due to an intramolecular process following the AO complexation with a PMA chain. This is presumably related to the contraction of the molecular coil observed by Stork et al.[6] and confirmed in our solution viscosity measurements. The k_1 data at pH 5.16 have two interesting features: (1) The rate constants *decrease* with an *increasing* PMA concentratin, indicating that the contraction of a chain is slower if a smaller number of AO molecules is bound to it. (2) The constant is, for any given P/D ratio, insensitive to the molecular weight of the PMA, suggesting that the contraction involves only a relatively short stretch of the chain adjoining a complexed AO molecule.

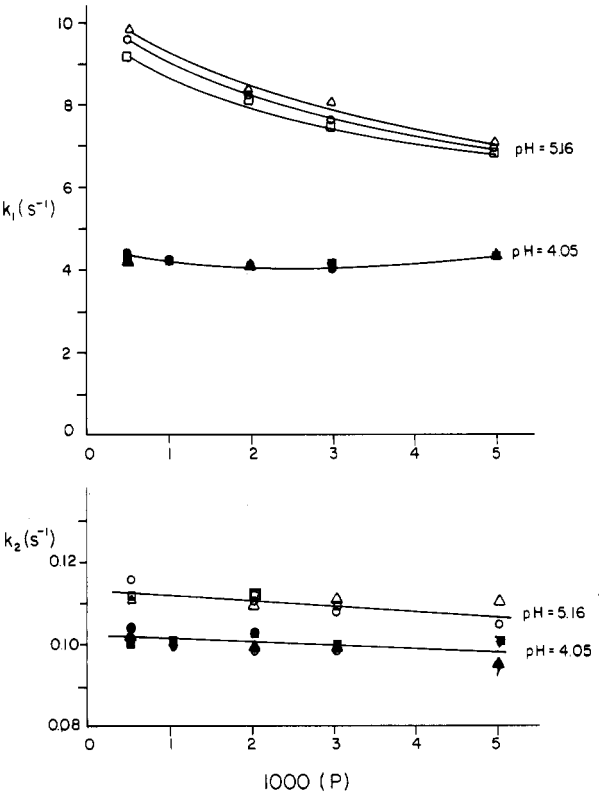

Figure 7. Rate constants for the biphasic increase of emission intensity after mixing AO with PMA: $M_v = 1.6 \times 10^5$ (△, ▲), $M_v = 2.3 \times 10^5$ (○, ●), $M_v = 5.5 \times 10^5$ (□, ■).

Finally, we should like to draw attention to the unexpectedly small values of the rate constants, with k_2 of the order of 0.1 s^{-1}. This feature is similar to previous results obtained in this laboratory on the approach to conformational equilibrium of PMA after a pH jump.[9]

Experimental Section

Materials. Poly(methacrylic acid) was prepared by free radical polymerization in 30% methanol solution with AIBN initiator.

The viscosity-average molecular weight was estimated from intrinsic viscosities in 0.002 M HCl solution.[17] Unless otherwise specified, the sample with $\bar{M}_v = 2.3 \times 10^5$ was used. Auramine O was recrystallized from hot methanol and melted at 265–267 °C (lit[18] 267 °C).

Solutions of PMA were prepared with deionized water. The concentration was determined by titration with 0.1 N NaOH in the presence of 0.3 M NaCl. Since AO decomposes slowly, a stock solution was prepared once a week and stored at low temperature in the dark. Potassium phthalate buffers were used for pH 4 and 5, phosphate buffers for pH 6, 7, and 8.

Absorption spectra were recorded on a Cary 2300 UV spectrometer. A Perkin-Elmer MPF-44B fluorescence spectrophotometer was used for static fluorescence measurements. Kinetic fluorescence measurements were carried out on the instrument used in a previous study.[9] Results of at least 10 runs were averaged by the computer to minimize noise rate constants with the best fit to the data were computed.

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Registry No. AO, 2465-27-2; PMA, 25087-26-7.

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Electron Spin Resonance Study of the Photooxidation Mechanism in Poly(*n*-butyl acrylate): Photochemical Processes in Polymeric Systems. 11

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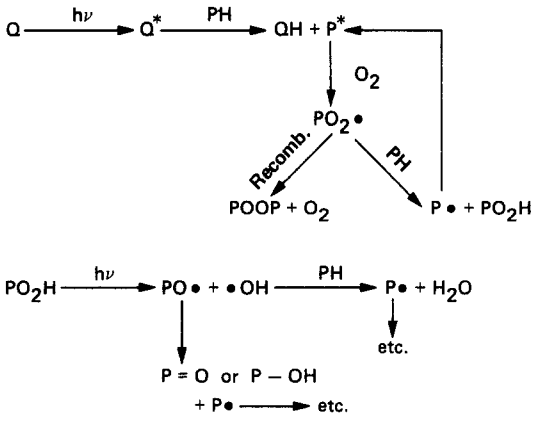
ABSTRACT: Kinetics of the reactions of the principal radical species, the tertiary alkyl and peroxy radicals, generated on photooxidation of poly(*n*-butyl acrylate) (PnBA) were studied at room temperature under different oxygen pressures. A simplified mechanism of photooxidation, similar to that proposed earlier (Liang, R. H.; Tsay, F.-D.; Gupta, A. *Macromolecules* **1982**, *15*, 974), was used to interpret the data. The kinetic rate parameters as well as the radical concentrations developed under steady-state illumination conditions were estimated by a least-squares fit to the observed data by using kinetic equations based on such a mechanism. It was found that at least two different types of tertiary alkyl radicals (i.e., radicals of different reactivities) were being formed during photooxidation of PnBA.

Introduction

Details of the mechanism of photooxidation of polymers are becoming increasingly clearer mainly through the efforts of Scott,[2-4] Guillet,[5,6] and others.[7-9] Generally speaking, this mechanism involves the participation of the polymeric tertiary alkyl radicals and the peroxy radicals formed by reaction of the tertiary alkyl radicals with oxygen as shown in Scheme I. In our earlier study on the photodegradation of PnBA,[1] we showed that the primary radicals formed at initial photolysis underwent a series of abstraction and rearrangement processes until at room temperature the only surviving radical in the system was a polymeric tertiary alkyl radical in the absence of oxygen. Under high oxygen pressures (≥150 torr), the only detectable species was a macromolecular peroxy radical. We therefore planned a brief series of time-resolved UV (broad band, $\lambda \geq 250$ nm) photooxidation studies in order to obtain the yield and kinetics of these radical species. The results reported below show that even in its simplest form the photooxidation mechanism is more complex than is indicated by the simple mechanism shown in Scheme I; in particular, the mechanism is found to involve at least

Scheme I



two different types of metastable tertiary alkyl radicals of significantly different reactivities.

Since its glass transition temperature is 210 K, at room temperature PnBA in the solid state manifests high permeability to oxygen molecules. The resulting photo-

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