Fluorescence Behavior of β-Naphthol-Labeled Polycarboxylic Acids: A New Approach to the Characterization of Chain Flexibility[1]

Yongcai Wang, Jiří Labský,[2] and Herbert Morawetz*

Department of Chemistry, Polytechnic University, Brooklyn, New York 11201.

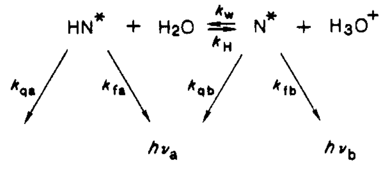
Received February 25, 1987

ABSTRACT: β-Naphthol-labeled poly(acrylic acid), poly(methacrylic acid), poly(acrylylglycine), poly(methacrylylglycine), and poly(methacrylyl-β-alanine) were prepared. Their emission spectra contain a band with a maximum at 360 nm due to the acid form of the label and a band with a maximum at 420 nm due to the unprotonated species which arises from proton transfer to water or to ionized carboxyls. In aqueous solutions of PAA-N and PMA-N, the attachment of the label to the polymer reduces proton transfer to water. Methanol does not accept protons from the excited naphthol, and the intensity of emission from the deprotonated naphthol attached to polycarboxylic acids in methanol solution reflects intramolecular interactions with ionized carboxyls. The data suggest that this does not involve conformational transitions of the chain backbone but is governed by the statistical probability that the interacting groups are in juxtaposition. This reflects the short-range flexibility of the chain and is insensitive to the overall chain expansion. The quantum yield for emission from the acid form of the label decreases with the expansion of the polymer, and it reflects, therefore, the collapse of the PAA-N chain in methanol at higher degrees of ionization.

Introduction

When two groups appended to a polymer chain can interact with one another, the rate of this interaction may be used to characterize the flexibility of the chain. Two cases may be distinguished. If the interaction of the chain substituents leads to a reaction involving a substantial activation energy, the rate of the process will be governed by the statistical probability that the chain assumes a conformation in which the interacting groups are in juxtaposition and the rate will reflect what we might call "the statistical flexibility" of the chain. This case has been studied in this laboratory on polymers carrying reactive and catalytic chain substituents.[3] On the other hand, if the chain substituents interact in a diffusion-controlled process, the rate of this interaction will depend on the velocity of conformational transitions required to produce an encounter and the data obtained in such experiments will characterize "the dynamic flexibility". The theory of this second case has been developed by Wilemski and Fixman,[4] and experimental data have been obtained for polymer chains carrying fluorescent terminal groups which may lead to excimer or exciplex emission if one of these groups is excited and encounters the other terminal group in the appropriate orientation within its excited lifetime.[5]

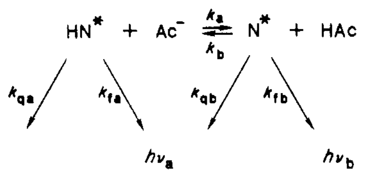
In the present report, we explore a new approach to the study of the kinetics of intramolecular polymer reactions. As first shown by Weller,[6] when β-naphthol is excited in water solution, its pK is reduced from 9.49 to 2.91. Thus, the relative emission from the protonated species HN* and the unprotonated N* is determined by



$$HN^* + H_2O \underset{k_H}{\overset{k_w}{\rightleftharpoons}} N^* + H_3O^+ \qquad (1)$$

where k_{fa} and k_{fb} are rate constants for emission and k_{qa} and k_{qb} rate constants for nonradiative deactivation of the two excited species.

Since the excited β-naphthol is a stronger acid than carboxylic acids, a species such as acetate can also act as a proton acceptor:

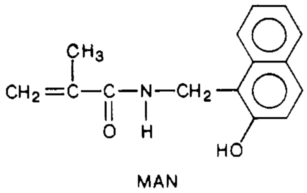


$$HN^* + Ac^- \underset{k_b}{\overset{k_a}{\rightleftharpoons}} N^* + HAc \qquad (2)$$

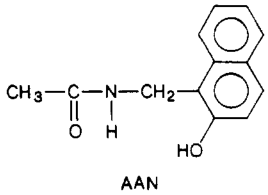
This suggested to us a study of the fluorescence behavior of partially ionized polycarboxylic acids with a small number of side chains carrying β-naphthol residues, so that proton transfer from the excited naphthol groups to the carboxylates would be an intramolecular process. While such a transfer to a specific carboxylate has negligible probability, such a transfer to *any one* of the carboxylates on the polymer chain could easily be studied as a function of the degree of ionization of the carboxyls, the mode of attachment of the carboxyls to the chain backbone, and the nature of the counterions.

Experimental Section

Materials. Acetic acid was refluxed with acetic anhydride in the presence of 0.2% β-naphthalenesulfonic acid and fractionally distilled. Spectroscopic grade methanol and dioxane were used. *N*-Acrylylglycine (AGly, mp 130–132 °C), *N*-methacrylylglycine (MGly, mp 117–118 °C), and *N*-methacrylyl-β-alanine (MAla, mp 74–76 °C) were prepared by Schotten–Baumann acylation of the corresponding amino acids. The 1-[(methacrylylamino)methyl]-2-naphthol (MAN, mp 160–162 °C) and its analogue, 1-[(acetylamino)methyl-2-naphthol (AAN, mp 159–160 °C) were prepared as described for the latter.[7] Labeled and unlabeled



MAN



AAN

polymers were prepared by solution polymerization initiated by 0.1% AIBN at 60 °C. Poly(acrylic acid) (PAA) and copolymers of acrylic and methacrylic acid with MAN (PAA-N and PMA-N) were prepared in methanol solution. The MAN copolymers of AGly, MGly, and MAla (PAGly-N, PMGly-N, and PMAla-N) were prepared in dioxane; they precipitated as formed and were purified by four precipitations from methanol into anhydrous ether. Table I lists the intrinsic viscosities of the polymers and their content

0024-9297/87/2220-2128$01.50/0

Table I
Polymer Characterization

sample designation	[η], dL/g	naphthol content, mol %
PAA	0.456[a]	
PAA-N1	0.52[a]	0.67
PAA-N2	0.58[a]	2.0
PMA	0.315[b]	
PMA-N1	0.805[c]	1.42
PMA-N2	1.23[c]	0.46
PMGly-N	0.28[d]	2.12
PAGly-N	0.51[d]	1.6
PMAla-N	1.14[e]	1.1

[a] In dioxane at 30 °C. [b] In aqueous 0.002 N HCl at 30 °C. [c] In methanol at 26 °C. [d] In aqueous 1 N NaOH at 26 °C. [e] In aqueous NaOH at 20.3 °C.

Table II
Fluorescence Lifetimes of AAN

solvent	temp, °C	τ_a, ns	τ_b, ns
methanol	20	5.10	
	25		5.66
	30	4.82	
	40	4.67	
20% methanol/80% dioxane	25	5.31	6.92
98% water/2% methanol	25	5.87	8.13

of naphthol residues which was obtained from the absorption at 278 nm using the extinction coefficient 5400 M^{-1} cm^{-1} for AAN. Concentrations of polymeric acids, determined by potentiometric titration, were specified in terms of the normality, N, of the carboxyl groups.

Fluorescence Measurements. Fluorescence spectra were recorded at room temperature on a Perkin-Elmer MPF 448 fluorescence spectrometer over a range of 300–540 nm using excitation at 278 nm. Emission intensities I_a and I_b at the maxima of 357 and 420 nm, characteristic of the acidic and basic forms of the β-naphthol residue, respectively, were related to the corresponding emission intensities I_a^0 and I_b^0 in solutions in which the chromophore was completely in the acidic or basic form. For the basic emission, the ratio I_b/I_b^0 was corrected for the overlap of the acidic and basic emission spectra using $F_b = I_b/I_b^0 - 0.075I_a/I_a^0$; no such correction was required for the acid emission so that $F_a = I_a/I_a^0$. All fluorescence spectra were taken for solutions in equilibrium with atmospheric oxygen. The excited lifetimes of AAN in various solvents were measured by Dr. Z. Grauer in Professor N. C. Turro's laboratory at Columbia University.

Results and Discussion

Fluorescence of AAN in Solutions Containing Acetate, PAA, and PMA. Before exploring the behavior of naphthol-labeled polymers, we looked at the fluorescence of the low molecular weight analogue AAN. Its excited lifetimes, $\tau_a = 1/k_{fa}$ and $\tau_b = 1/k_{fb}$, in various solvents are listed in Table II. Figure 1 contains plots of F_a and F_b for AAN in water containing 2% methanol with various concentrations of sodium acetate obtained by a 90% neutralization of acetic acid so as to keep a constant pH of 5.72. According to Weller,[6] if the probability of finding an acetate acceptor within the diffusion volume of the excited chromophore is negligible, if the reaction of the excited naphtholate with hydrogen ion or with acetic acid is unimportant, and if k_{qa}/k_{fa} and k_{qb}/k_{fb} are independent of the fraction of the excited naphthol which is deprotonated, then

$$F_a = \frac{1}{1 + [k_w + k_b(\mathrm{Ac}^-)]\tau_a} \tag{3a}$$

$$F_b = \frac{[k_w + k_b(\mathrm{Ac}^-)]\tau_a}{1 + [k_w + k_b(\mathrm{Ac}^-)]\tau_a} \tag{3b}$$

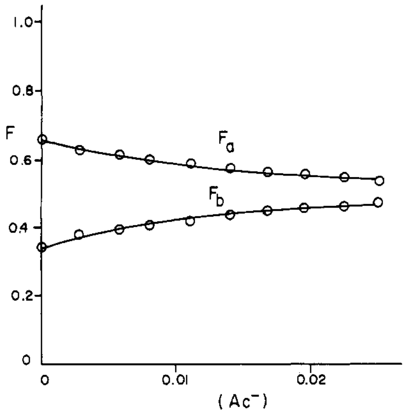


Figure 1. Relative fluorescence intensities of AAN (2 × 10^{-4} M) in water containing 2% methanol as a function of sodium acetate concentration. The pH was kept constant by keeping the molar ratio of acetate/acetic acid at 9:1.

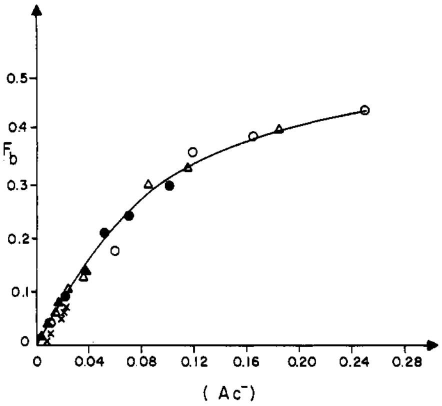


Figure 2. Relative emission intensity from the basic form of AAN as a function of acetate concentration in methanol solutions containing different degrees of ionization of added acetic acid: (▲) 0.1; (●) 0.3; (△) 0.5; (○) 0.7. Data for N-acetylglycine (×) are given for comparison.

The predicted linear dependence of F_b/F_a on (Ac^-) was observed up to (Ac^-) = 0.017, leading to $k_w = 9.2 \pm 0.1 \times 10^7$ s^{-1} and $k_b = 2.52 \pm 0.05 \times 10^9$ M^{-1} s^{-1} using the τ_a values from Table II. These AAN values are close to $k_w = 7.3 \times 10^7$ s^{-1} and $k_b = 2.9 \times 10^9$ M^{-1} s^{-1} obtained by Weller[6a] for β-naphthol.

Absolute methanol has no tendency to accept a proton from the excited AAN so that emission from its basic form is entirely due to proton transfer to ionized carboxyls. Figure 2 shows a plot of F_b as a function of acetate concentration in solutions containing a range of stoichiometric acetic acid concentrations neutralized to various degrees, α, with lithium methoxide. All the data could be fitted by $F_b = k_b(\mathrm{Ac}^-)\tau_a/[1 + k_b(\mathrm{Ac}^-)\tau_a]$ with $k_b = 8.5 \times 10^8$ M^{-1} s^{-1}. Also, the data yielded $F_a + F_b = 1$, as required by relation 3. The temperature dependence for the proton transfer from 2 × 10^{-4} M AAN to 0.05 M acetate was obtained from $F_b = 0.20$ at 23.5 °C and $F_b = 0.26$ at 41.8 °C. Using the τ_a values in Table II, we estimated $\tau_a = 5.0$ and 4.6 ns at these two temperatures, leading to $k_b = 1.0 \times 10^9$ and 1.5×10^9 M^{-1} s^{-1}, respectively. This small temperature dependence is similar to that corresponding to Weller's value[6] of 4.4 kcal/mol for the activation energy for proton transfer from β-naphthol to acetate in water solution, confirming his conclusion that "the reaction is largely, though not entirely, diffusion controlled".

When AAN was added to a solution of 0.019 N PAA in absolute methanol, no emission from the basic species was detected up to a degree of carboxyl neutralization of α = 0.75. Comparison with Figure 2 shows that a corre-

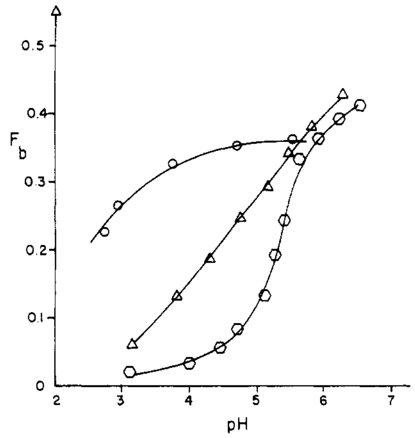


Figure 3. Comparison of the emission intensity from the basic forms of 2×10^{-4} M AAN (○), 0.019 N PAA-N (△), and 0.019 N PMA (○) in water as a function of pH.

sponding carboxylate concentration in acetate solution would lead to a small but significant F_b; the possibly slightly smaller rate constant for proton transfer to carboxylates attached to PAA may be due to a partial exclusion of the AAN (less polar than the methanol solvent) from the polymer domain. In methanol–0.017 N PMA solution, very different behavior was observed, with some emission of the basic species characterizing solutions in which α exceeded 0.25. This result is a consequence of the higher basicity of partially ionized PMA in methanol so that, as we demonstrated previously[8] by UV spectroscopy, β-naphthol is deprotonated in the ground state.

Fluorescence Behavior of Naphthol-Labeled PAA and PMA. The attachment of a naphthol label to a partially ionized polycarboxylic acid in water solution may affect the fluorescence of the label for two reasons. (a) The label may be partially shielded from the solvent, reducing the extent of proton transfer to water. (b) Collision of the excited naphthol residues with ionized carboxyls attached to the polymer chain will lead to proton transfer. A priori, it was unclear which of these effects, working in opposite directions, will be dominant. Figure 3, where we compare F_b values over a range of pH for AAN, PAA-N, and PMA-N, demonstrates that up to pH 5.5 less of the naphthol residues is deprotonated in the excited state when attached to the polymers. As might have been expected, the label is protected from contact with water much more effectively when attached to the "supercontracted state" of PMA[9] than when attached to PAA.

Data obtained for solutions of PAA-N in absolute methanol are easier to interpret, since protons are not transferred from the excited naphthol residues to the solvent. The results with partially ionized PAA-N were found to be different when lithium and sodium methoxide were used to neutralize the polymeric acid. Klooster et al.[10] pointed out that the titration behavior and the solution viscosity of PAA in methanol are markedly different with different counterions. Figure 4 demonstrates this difference in the viscosity behavior. At low degrees of ionization, α, the polymer expands, but this expansion is followed at higher α by a sudden collapse which we have attributed[8] to ion pair interaction. This collapse occurs earlier and more sharply with sodium counterions.

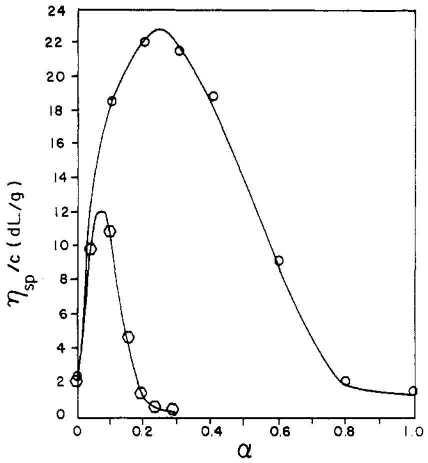


Figure 4. Reduced viscosities of 0.018 N PAA-N1 in methanol as a function of the degree of neutralization with lithium (○) and sodium (○) methoxide.

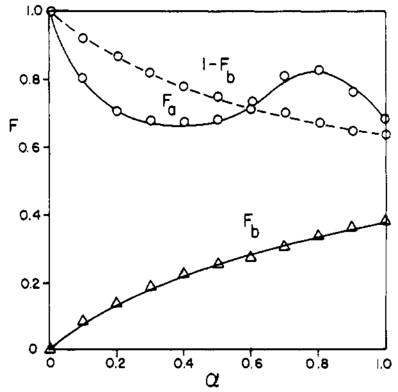


Figure 5. Relative emission intensity of 0.018 N PAA-N1 in methanol solution neutralized with lithium methoxide.

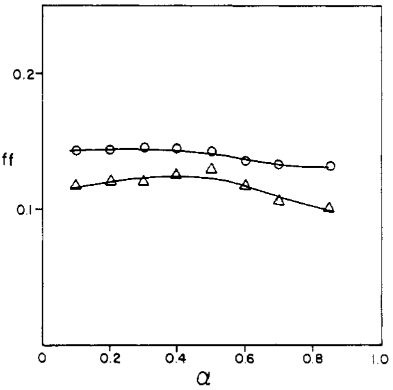


Figure 6. Dependence of c_{eff} for encounters of the naphthol label with carboxyls on the chain backbone on α for PAA-N1: (○) 0.018 PAA-N1; (△) 0.0035 N PAA-N1.

The fluorescence behavior of partially ionized PAA-N with lithium counterions in methanol is shown in Figure 5. Here F_b is seen to increase smoothly with α, showing no effect of the polymer chain collapse. It may also be noted that we found the results to be independent of the concentration of the naphthol label on the polymer. We may analyze these results by defining the quantity c_{eff}[3] as the concentration of carboxyl groups uniformly distributed in the solution which would produce the same number of encounters with the excited naphthol residues as the intramolecular encounters in PAA-N. We have then, in analogy with (3b),

$$F_b = \frac{k_b c_{eff} \alpha \tau_a}{1 + k_b c_{eff} \alpha \tau_a} \tag{4}$$

Assuming that τ_a in PAA-N is the same as in the analogue AAN and if the value observed for AAN is used for k_b of the MAN residues in the copolymer, c_{eff} values were derived which are plotted as a function of α for two con-

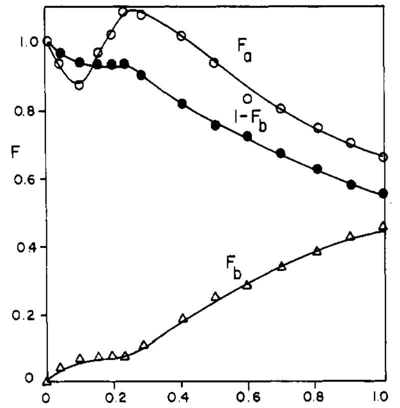


Figure 7. Relative emission intensity of 0.018 N PAA-N1 in methanol solution neutralized with sodium methoxide.

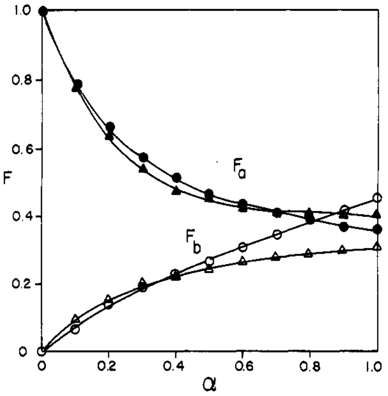


Figure 8. Relative emission intensity of 0.018 N PAA-N1 (○, ●) and 0.015 N PMA-N2 (△,▲) in methanol containing 30% water neutralized with lithium methoxide.

centrations of PAA-N in Figure 6. Two points may be noted. (a) The c_{eff} values vary little with α. This suggests that the expansion and collapse of PAA chains reflect long-range interactions while local conformations, which control proton transfer from the excited naphthol label to carboxylates, remain relatively unaffected. Such an insensitivity of local conformations to the ionization of PAA was demonstrated by X-ray scattering data by Muroga et al.[11] (b) With the intrinsic viscosity of PAA-N in methanol, $[\eta] = 1.85$ dL/g, the critical concentration for chain overlap may be estimated as $1/[\eta] = 0.54$ g/dL, whereas the concentrations of PAA-N for which c_{eff} were plotted in Figure 6 were only 0.02 and 0.1 g/dL. It is true that the value for the critical concentration was estimated for the unionized polymer, but since c_{eff} exhibited no tendency to increase with chain expansion, it is hard to see why its values should have been found to be significantly dependent on the polymer concentration.

A striking feature of Figure 5 is the pronounced deviation of F_a from $1 - F_b$. Up to $\alpha = 0.6$, the emission intensity of the protonated naphthol residues is lower than expected, while at higher α, $F_a > 1 - F_b$. It seems that the quantum efficiency of emission from the acid form of the naphthol label decreases with the expansion of the polymer chain. Thus, the efficiency decreases during the initial stages of the ionization but rises sharply when the polymer chains collapse. Significantly, the crossover from $F_a < 1 - F_b$ to $F_a > 1 - F_b$ occurs already at $\alpha = 0.14$ when PAA-N is titrated with sodium methoxide (Figure 7), and this correlates with the low α at which a collapse of PAA is observed when the counterions are sodium (Figure 4). This effect cannot be ascribed to a changing polarity of the microenvironment, since the τ_a values in Table II show only a small enhancement when dioxane is substituted for methanol as the solvent for AAN. We suggest that the increased emission intensity of the protonated label when attached to a compact polymer chain is due to the high local rigidity which reduces internal quenching of the excited state by rotation around the bond connecting the hydroxyl to the naphthol residue. A similar effect of local rigidity on internal quenching leads to an increased fluorescence intensity of Auramine O when this dye is bound to the contracted form of PMA.[12]

We must now address the crucial question whether the extent of intramolecular proton transfer from the excited naphthol label to an ionized carboxyl attached to the polymer backbone is governed by the statistical or dynamic flexibility of the polymer chain. This point may be illuminated by a comparison between the behavior of PAA-N and PMA-N. However, absolute methanol is not a suitable solvent medium for such a comparison since, as pointed out before, the higher basicity of partially ionized PMA leads to significant deprotonation of the naphthol label in the ground state. Fortunately, this difficulty could be overcome by using for the solvent methanol containing 30% water. In this medium, no proton transfer to the solvent was observed, and UV absorption spectra indicated no deprotonation of the naphthol label up to $\alpha = 0.6$.

We have seen that the extent of proton transfer from the naphthol label to a carboxyl on the chain backbone was governed by the *local* chain flexibility, being insensitive to the overall chain expansion. Therefore, if the proton-transfer efficiency is governed by the statistical flexibility of the chain, it should correlate with the relative chain extension in a Θ-solvent. In fact, this extension is changed very little when the α hydrogens of polyacrylates are substituted by methyl groups. The Mark–Houwink relations between the intrinsic viscosity and the molecular weight, $[\eta] = KM^{1/2}$, in Θ-solvents yield $K = 48 \times 10^{-3}$ for poly(methyl methacrylate)[13] and $K = 68 \times 10^{-3}$ for poly(methyl acrylate),[14] leading to a ratio of 0.96 for an equal contour length of these two polymers.[15] On the other hand, Anufrieva and Gotlib[16] studied the dynamic flexibility of these two polymers by the anisotropy of fluorescence of anthracene residues built into their chain backbones and estimated that conformational transitions are at least 6 times slower in the polymethacrylate chain, as might be expected from the very crowded transition state in their hindered rotations. Since the F_b data plotted in Figure 8 for PAA-N and PMA-N are practically identical up to $\alpha = 0.5$, the approach of the naphthol labels to ionized carboxyls cannot be governed by the rate of conformational transitions of the chain backbone, although a greater dynamic flexibility of the PAA-N chain seems to make a minor contribution to the rate of proton transfer at higher degrees of ionization. It should also be noted that in methanol containing 30% water, $F_a < 1 - F_b$ over the entire range of ionization, as would be expected, since the polymeric acids do not collapse at high α values in this medium.

Even more striking results are represented in Figure 9. Here we compare the emission spectra of PAA-N at $\alpha = 0.6$ (lithium counterions) in methanol and when incorporated in a poly(*N*-vinylpyrrolidone) (PVP) film. If no proton transfer could occur in the rigid medium, the ratio of emission intensities at 420 and 360 nm would be 0.075. In fact, $I_{420}/I_{360} = 0.33$ in the PVP film, only slightly lower than $I_{420}/I_{360} = 0.48$ observed in methanol solution. We conclude that little motion is required for a significant portion of the proton transfer from the naphthol label to the ionized carboxyls on the chain backbone.

Fluorescence of PAGly-N, PMGly-N, and PMAla-N in Methanol Solution. We also studied the dependence

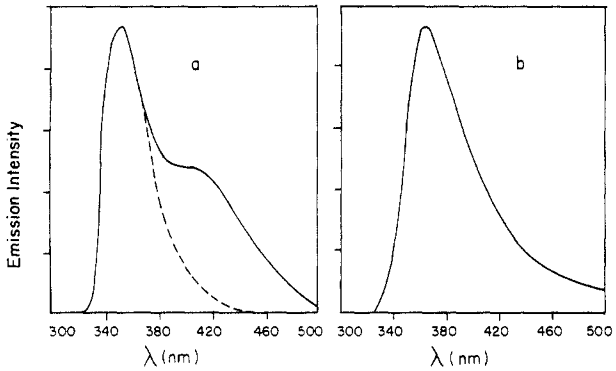


Figure 9. Emission spectra of PAA-N1, 60% neutralized with lithium methoxide (a) in methanol solution and (b) incorporated in a PVP film. The dashed curve in (a) shows the emission in acid solution in which the naphthol label is fully protonated.

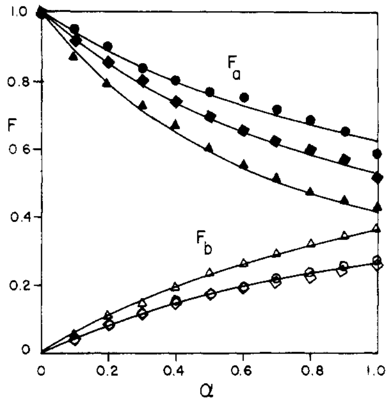


Figure 10. Relative emission intensities of 0.013 N PAGly-N (○,●), 0.014 N PMGly-N (◇,◆), and 0.013 N PMAla-N (△,▲) in methanol with 2% water (lithium counterions).

of the proton transfer from the excited naphthol labels on the spacing of the carboxylate acceptors from the chain backbone. In the case of the naphthol-labeled polymers of acrylyl- and methacrylylglycine, the acidity of the carboxyls would be expected to be substantially higher than in PAA and PMA, since for *N*-acetylglycine the pK = 3.60[17] is 1.24 units higher than for acetic acid. However, the corresponding lower basicity of *N*-acetylglycinate did not affect noticeably the rate of proton transfer from the excited AAN (Figure 2), and this factor may then presumably be disregarded in interpreting the behavior of PAGly-N and PMGly-N. Results obtained with these two polymers are shown in Figure 10. Again, the F_b values are the same for the polymers with the polyacrylic and polymethacrylic backbones. They increase when the spacing of the carboxylates from the chain backbone is increased in PMAla-N. For all three polymers, $F_a < 1 - F_b$ over the entire range of ionization, since no collapse of the chains at high α is observed.

Concluding Remarks

Results of this study show that the extent of proton transfer from an excited naphthol label to carboxylates of a polycarboxylic acid involves no conformational transitions in the chain backbone but depends on the probability of conformations in which the interacting groups are within a reaction radius. The emission intensity from the deprotonated naphthol residues is proportional to the extent of proton transfer, whereas the emission intensity of the acid form of these residues decreases with the overall chain expansion, presumably because the quantum efficiency is enhanced by the rigidity of the microenvironment. This interpretation is supported by Figure 11, which shows that the fluorescence intensity of PAA-N increases 45% when the polycarboxylic acid forms a complex with PVP by cooperative hydrogen bonding.[18]

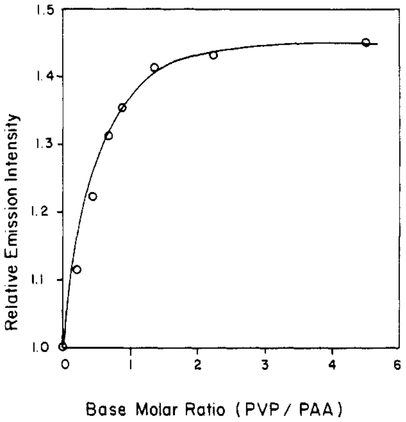


Figure 11. Relative change in the emission intensity of PAA-N1 (4.45×10^{-4} N) in methanol solution on addition of poly(*N*-vinylpyrrolidone) as a function of the ratio of their monomer residue concentrations.

It is known that steric constraints hinder the formation of rings containing 8–14 atoms, and we may assume that the hydroxyl of the naphthol label can only approach a carboxylate on the chain backbone within a reaction radius if these two groups are separated by at least three monomer residues. With a larger number of monomer residues separating the interacting groups, the probability of cyclic conformations decreases rapidly, so that the probability of interaction between groups at a large distance along the polymer chain in negligible. Thus, the results of experiments such as described in this study sample the short-range conformational properties.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this investigation by Grant DMR 85-00712, Polymers Program.

Registry No. (MAN)(AA) (copolymer), 109687-02-7; (MAN)(MA) (copolymer), 109687-03-8; (MAN)(AGly) (copolymer), 109687-04-9; (MAN)(MGly) (copolymer), 109687-05-0; (MAN)(MAla) (copolymer), 109687-06-1.

References and Notes

(1) Abstracted from a Ph.D. thesis to be submitted by Y. Wang to the Graduate School of Polytechnic University, June 1987.
(2) On leave of absence from the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.
(3) Goodman, N.; Morawetz, H. (a) *J. Polym. Sci., Part C.* **1970**, *31*, 177; (b) *J. Polym. Sci., Part A-2* **1971**, *9*, 1657.
(4) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1974**, *60*, 866.
(5) (a) Cuniberti, C.; Perico, A. *Eur. Polym. J.* **1977**, *13*, 369. (b) Perico, A.; Cuniberti, C. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1435. (c) Winnik, M. A.; Redpath, A. E. C.; Richards, D. H. *Macromolecules* **1980**, *13*, 328. (d) Winnik, M. A. In *Photophysical and Photochemical Tools in Polymer Science*; Winnik, M. A., Ed.; NATO ASI Series C; D. Reidel: Dordrecht, 1986; Vol. 182; pp 293–324.
(6) Weller, A. (a) *Z. Phys. Chem.* (*Frankfurt*) **1958**, *17*, 224; (b) *Discuss. Faraday Soc.* **1959**, *27*, 28; (c) *Progr. Reaction Kinetics*; Porter, G., Ed.; Wiley: New York, 1961, Vol. 1, Chapter 7.
(7) Böhme, H.; Broese, R.; Dirk, A.; Eiden, F.; Schunemann, D. *Chem. Ber.* **1959**, *92*, 1603.
(8) Wang, Y.; Morawetz, H. *Macromolecules* **1987**, *20*, 194.
(9) Leyte, J. C.; Mandel, M. *J. Polym. Sci., Part A* **1964**, *2*, 1873. Crescenzi, V.; Quadrifoglio, F.; Delben, F. *J. Polym. Sci., Part A-2* **1972**, *10*, 357.
(10) Klooster, N. T. M.; van der Touw, F.; Mandel, M. *Macromolecules* **1984**, *17*, 2070.
(11) Muroga, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1576.
(12) Wang, Y.; Morawetz, H. *Macromolecules* **1986**, *19*, 1925.
(13) Fox, T. G. *Polymer* **1962**, *3*, 111.

Macromolecules **1987**, *20*, 2133–2138

(14) Matsuda, H.; Yamano, K.; Inagaki, H. *J. Polym. Sci., Part A-2* **1969**, *7*, 609.
(15) Flory, J. P. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969; Chapter II.
(16) Anufrieva, E. V.; Gotlib, Yu. Ya. *Adv. Polym. Sci.* **1981**, *40*, 1.
(17) Zind, M.; Edsall, J. T. *J. Am. Chem. Soc.* **1937**, *59*, 2247.
(18) Chen, H.-L.; Morawetz, H. *Eur. Polym. J.* **1983**, *19*, 923. Turro, N. J.; Arora, K. S. *Polymer* **1986**, *27*, 783. Studies of the analogous complexation of PMA with PVP have been reported by: Papisov, I. M.; Baranovskii, V. Yu.; Kabanov, V. A. *Vysokomol. Soed.* **1975**, *A16*, 2104; and by Osada, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3485.

Photophysical and Photochemical Studies on a Polymeric Intramolecular Micellar System, PA-18K$_2$

Deh-Ying Chu and J. K. Thomas*

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.
Received February 17, 1987

ABSTRACT: A polymeric intramolecular micellar system, PA-18K$_2$ which is a potassium salt of a 1:1 copolymer of maleic anhydride and 1-octadecene, has been investigated via steady-state emission, absorption, time-dependent emission and transient absorption spectroscopy, etc. Pyrene and some of its positively charged derivatives and negatively charged derivatives can be solubilized in the interior of PA-18K$_2$ over the entire pH range. It is observed that there is a significant effect of the polymer main chain surrounding the polymer micelles on the bimolecular quenching kinetics and exciplex formation of guest molecules. Both steady-state and pulsed studies indicate that guest molecules in PA-18K$_2$ experience a larger hydrophobocity than in sodium dodecyl sulfate micelles, but one that is similar to that in sodium cetyl sulfate micelles. Data from Poisson quenching kinetics suggest that one polymer micelle consists of about 25 monomer units; i.e., one PA-18K$_2$ polymer molecule of molecular weight 1×10^4 forms one polymer micelle.

Introduction

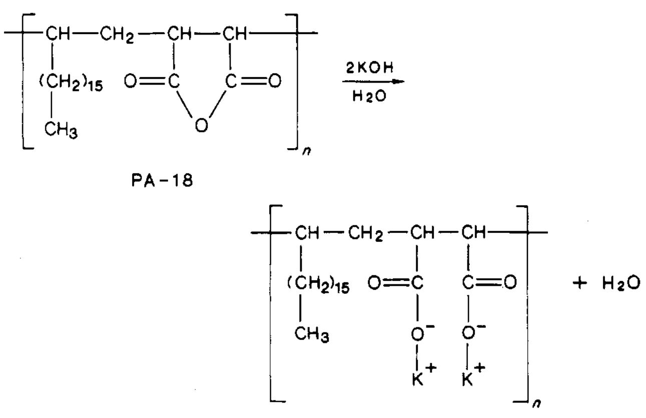
In the last few decades marked progress has been made in photophysical and photochemical studies in organized assemblies, which act as host systems for many hydrophobic molecules. A great variety of experimental data have been reported,[1-4] especially for simple micellar systems, which are aggregated structures formed by the interaction of several surfactant molecules, i.e., intermolecular micelles.

Polyelectrolytes with hydrophobic side chains may exhibit behavior reminiscent of micelles under appropriate conditions. The hydrophobic bonding between the paraffinic side chains in these systems results in stabilization of compact structures, analogous to micelles. Such polymers have been called "polysoaps" or intramolecular micelle-forming polymers. Typical examples are the *n*-dodecyl derivatives of poly(4-vinylpyridine),[5] poly(vinylbenzo-18-crown-6).[6] Synthetic weak polyelectrolytes such as poly(methacrylic acid), PMA,[7] and copolymers of maleic anhydride and *n*-alkylvinyl ethers (n = 4–8)[8] are known to provide hydrophobic microdomains in the low pH range; i.e., compact polymer coils are only formed in strongly acidic solution, while the compact conformation is converted into the extended rod or coil form at high pH. For any practical use of the polymer as a host material for hydrophobic molecules, strongly acidic polymers should be avoided, and a hydrophobic environment is required close to neutral pH. Polyelectrolytes with longer hydrocarbon side chains are expected to behave as hypercoils over the entire pH range. PA-18K$_2$, which is a potassium salt of an alternating copolymer of maleic anhydride and 1-octadecene, offers such an example.

Reports concerning photophysical and photochemical studies in "polysoap" systems are infrequent and mainly focus on steady-state studies.[9,10] In the present paper, PA-18K$_2$ has been investigated by steady-state and pulsed studies. The results are compared to previous studies in PMA systems[11,16] in order to ascertain the effect of long hydrocarbon side chains on the formation of intramolecular micelles.[11c] The comparison of polymer micelle and simple micellar systems was also made in order to study the effect of the polymer main chain on the quenching kinetics of pyrene and pyrene derivatives in these systems. Finally, Poisson quenching kinetics to estimate the mean aggregation number of monomer units and double-exponential kinetics to estimate the equilibrium constant of pyrene between the aqueous phase and polymer micelle are presented.

Experimental Section

Polymer Materials. PA-18, a copolymer derived from 1-octadecene and maleic anhydride, was supplied by Chevron/Gulf Co. The molar ratio of comonomers is referred to as 1:1. PA-18 has a molecular weight of about 1×10^4, measured by HPLC with an ultrastyragel permeation column calibrated with standard samples of polystyrenes. The potassium salt of PA-18, PA-18K$_2$ was prepared by adding 45 g PA-18 (0.1 mol), while stirring, to 50 g of 30% KOH solution (0.24 mol) heated above 85 °C; after all solids dissolved, 150 mL of water was added. The salt PA-18K$_2$ was precipated by addition of a 2-fold excess of methanol to the filtered solution, washed with methanol, reprecipitated from hot water twice, and finally vacuum-dried at 40 °C. IR spectra showed that hydrolysis of the starting material was complete; i.e., the



PA-18K$_2$

0024-9297/87/2220-2133$01.50/0