Macromolecules **1990,** *23,* 3124–3129

(23) Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.* **1986,** *32,* 6299.

(24) Moore, D. R.; Mathias, L. J. *Polym. Compos.* **1988,** *9,* 144.

(25) Vandenberg, E. J.; Diveley, W. R.; Filar, L. J.; Patel, S. R.; Barth, H. G. *Polym. Mater. Sci. Eng.* **1987,** *57,* 139.

(26) Salamone, J. C.; Krauser, S. F.; Richard, R. E.; Clough, S. B.; Waterson, A. C.; Vandenburg, E. J.; Dively, W. R.; Filar, L. J. *Polym. Mater. Sci. Eng.* **1987,** *57,* 144.

(27) Salamone, J. C.; Li, C. K.; Clough, S. B.; Bennett, S. L.; Watterson, A. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988,** *29,* 273.

(28) Takayangi, M. *Pure Appl. Chem.* **1983,** *55,* 819.

(29) March, J. *Advanced Organic Chemistry,* 3rd ed.; Wiley: New York, 1985; p 324.

(30) Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1987,** 621.

Water-Soluble Copolymers. 35. Photophysical and Rheological Studies of the Copolymer of Methacrylic Acid with 2-(1-Naphthylacetyl)ethyl Acrylate

C. L. McCormick,* C. E. Hoyle, and M. D. Clark

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

Received October 2, 1989; Revised Manuscript Received January 22, 1990

ABSTRACT: Fluorescence and dilute solution viscosity behavior of a 20:80 mol % copolymer of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) and methacrylic acid (MAA), respectively, have been studied. The fluorescence spectra of this copolymer showed an almost 4-fold increase in excimer emission relative to monomer emission (I_E/I_M) upon increasing from pH 5 to 9. Similarly, as the pH of the medium increases, reduced viscosity increases, indicating a transition from a compact coil to a more expanded coil at pH 7.5. This behavior is unlike that previously reported presumably due to the extent of naphthyl group substitution, the hydrophobic character of both the naphthyl groups and the pendant methyl groups of MAA, and effective decoupling of the chromophore from the polymer backbone by a spacer group. The effects of urea, a water-structure breaker, and of polymer concentration indicate that, at high pH, NAEA–MAA forms an intramolecular "hypercoil". High quenching efficiencies of both monomer and excimer fluorescence by copper(II) ions result from ionic binding of the quencher ions with the copolymer.

Introduction

Recently, polyelectrolytes containing pendant aromatic chromophores such as naphthalene or phenanthrene have attracted a great deal of attention, particularly as models for artificial photosynthetic systems.[1–4] These polymers have been reported to exist in dilute aqueous solution as "hypercoils", which are characterized by hydrophobic aromatic groups clustered toward the center of the coil and hydrophilic ionic groups located in the aqueous boundary.[5–7] The microenvironment produced by the polyelectrolytes to which the hydrophobic chromophores are covalently attached often dramatically affects both the photophysical and photochemical properties of the chromophore. Most investigations to date have primarily been conducted on solutions of polymers in the electrolyte form. To date few comprehensive studies directed toward understanding the effect of pH on the conformation, and consequently the photophysical and rheological properties, of these "pseudomicellar" polymers have been conducted.

In this paper, we report the results of both fluorescence emission and viscosity studies of a polymer of methacrylic acid containing 20 mol % of 2-(1-naphthylacetyl)ethyl acrylate. Data suggest that the observed behavior relates, at least in part, to hydrophobic naphthyl group associations along the polymer chain.

Experimental Section

Materials. The synthesis of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) has been outlined elsewhere.[8] Poly[2-(1-naphthylacetyl)ethyl acrylate-*co*-methacrylic acid) (NAEA–MAA) was prepared by 2,2′-azobis(isobutyronitrile) (AIBN) (1.0 mol %) initiated radical polymerization of NAEA (20 mol %) and MAA (80 mol %) in degassed *N,N*-dimethylformamide (DMF) solution at 65. After 6 h, the sample was precipitated into diethyl ether, redissolved into DMF, and reprecipitated into diethyl ether. A dialysis/HPLC technique indicated <0.1 mol % residual NAEA in the copolymer. The composition of the polymer was determined from both elemental analysis (MHW Laboratories, Phoenix, AZ) and the UV absorption spectrum of NAEA–MAA in DMF (ϵ = 6745 M^{-1} cm^{-1} at 280 nm). The polymer consists of 20.5 mol % NAEA and 79.5 mol % MAA.

Urea (Aldrich, 99+%) was recrystallized three times from methanol. Copper nitrate (Aldrich 99.99%) was used as received.

The polymer solutions were prepared in deionized water. Due to the inherent hydrolytic instability of NAEA,[9] solutions were discarded after 48 h and fresh solutions prepared for subsequent studies.

Methods. Polymer Characterization. UV absorbance measurements (Perkin-Elmer Lambda 6B) and elemental analysis (MHW Laboratories, Phoenix, AZ) were used to determine the composition of the copolymer. The copolymer contained 20.5 mol % NAEA and 79.5 mol % MAA. The number average molecular weight, M_n, of the copolymer was estimated to be 140 000, based on osmotic pressure measurements (Knauer Osmometer with 600W membrane, Arro Laboratories, Inc.) in *N,N*-dimethylacetamide.

Fluorescence Spectroscopy. The concentration of polymer in solution was ca. 0.01 g/dL (unless otherwise noted) such that the concentration of naphthyl moieties in solution was always $<10^{-4}$. Sample solutions were degassed with N_2 for 15 min prior to emission measurements. Steady-state fluorescence spectra were measured on a Perkin-Elmer 650-10B spectrophotometer;

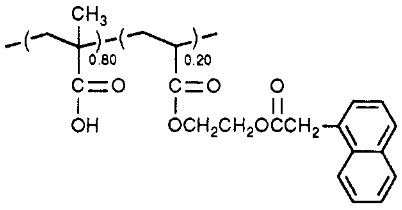
0024-9297/90/2223-3124$02.50/0

spectra were not corrected for photomultiplier response. All samples were excited at 280 nm, and monomer and excimer intensities were measured at 330 and 420 nm, respectively. Fluorescence decays were measured with a PRA single-photon-counting system with an H_2-filled PRA 510B flashlamp (fwhm ca. 2.5 ns). The nonlinear iterative deconvolution technique was used to fit the decay curves.[10]

Viscosity Measurements. Polymer concentrations of approximately 0.10 g/dL were used for rheological studies. Solution viscosities were measured at 25 °C with a Contraves LS-30 low-shear rheometer at a shear rate of 6.0 s^{-1}.

Results and Discussion

The copolymer of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) and methacrylic acid (MAA) was prepared by free-radical polymerization in *N,N*-dimethylformamide. Elemental and UV compositional analyses indicate a 20:80 mol % copolymer of NAEA and MAA, respectively. Copolymer microstructural data as determined by monomer *Q* and *e* values[11] indicate that NAEA units (mean sequence length = 1.06) are essentially isolated from one another by relatively long sequences of MAA monomers (mean sequence length = 15.1).



structure of the NAEA–MAA copolymer

Effect of pH. The fluorescence emission spectra (normalized at the monomer emission maximum) of the NAEA–MAA copolymer over a broad range of pH are shown in Figure 1. The emission spectra consist of two bands: a structured band at shorter wavelength (λ_{max} = 340 nm) assigned to monomer emission and a broad, structureless emission (λ_{max} = 392 nm) ascribed to excimer fluorescence.

The intensity of excimer emission relative to monomer emission for the NAEA–MAA copolymer exhibits a considerable dependence on the pH of the aqueous solution. The maximum value of the excimer (420 nm) to monomer (330 nm) intensity ratio (I_E/I_M) is observed under alkaline conditions (pH 9.0) while the minimum occurs at a pH of 5.0 (Figure 2). A sharp transition occurs at pH 7.5. However, in *N,N*-dimethylformamide (DMF), a good solvent for the copolymer and more specifically the hydrophobic NAEA units, the degree of excimer formed is negligible (Figure 1), indicating a distinctly different conformation of the copolymer in DMF. We feel that this observation, when compared with copolymer microstructural data, indicates that the formation of excimer in aqueous solutions is largely due to non-nearest-neighbor interactions. The increase in I_E/I_M is accompanied by a concordant pH-induced increase in the reduced viscosity (η_{sp}/c) of the polymer solution, a general indicator of the polymer hydrodynamic size (Figure 2). This behavior is rather unusual for a labeled polyelectrolyte as an increase in hydrodynamic size is more often associated with a decrease in excimer formation as chromophore density within the polymer coil is decreased.

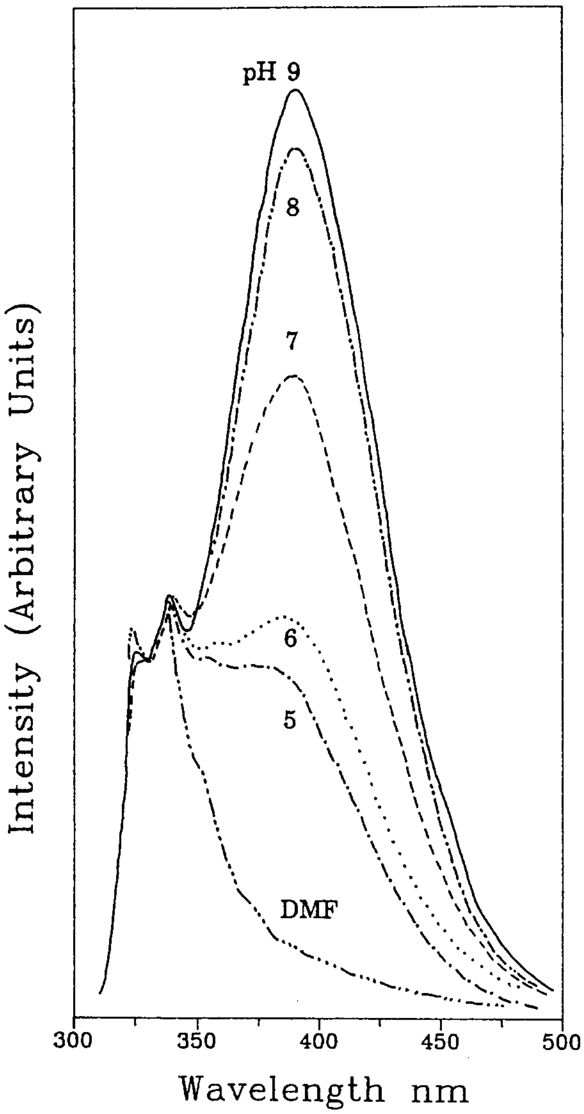


Figure 1. Steady-state fluorescence spectra (λ_{ex} = 280 nm) of NAEA–MAA (C_p = 0.01 g/dL) in aqueous solution at several different values of pH and in *N,N*-dimethylformamide.

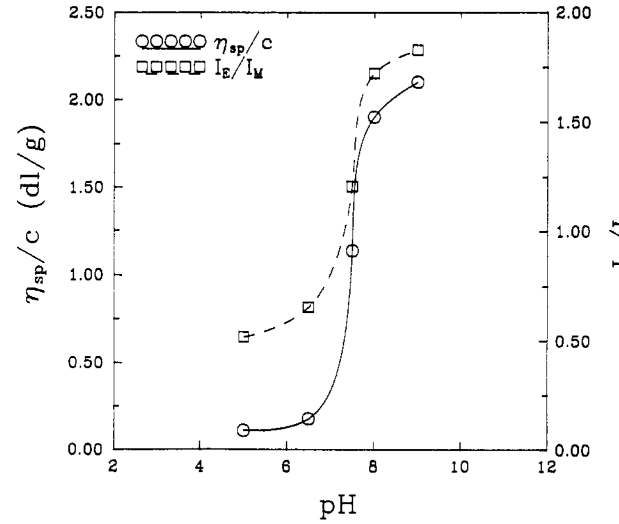


Figure 2. Dependence of the relative efficiency of excimer formation (I_E/I_M) and solution reduced viscosity (η_{sp}/c) on solution pH. $C_p(I_E/I_M)$ = 0.01 g/dL. $C_p(\eta_{sp}/c)$ = 0.10 g/dL.

In general, methacrylic acid polymers in aqueous solution at low pH have been reported to adopt a very tightly coiled structure due to hydrophobic interactions between pendant methyl groups along the polymer chain.[12-14] As the pH is increased, the polymer coil expands due to electrostatic repulsions, giving rise to a large increase in the hydrodynamic size of the polymer. In our system, at low pH the hydrophobic character within the NAEA–MAA polymer coil is provided by both the methyl groups on

Table I
Monomer and Excimer Emission Decays for NAEA–MAA in Aqueous Solution[a]

pH	λ_{EM}, nm	a_1	τ_1,[b] ns	a_2	τ_2,[b] ns	a_3	τ_3,[b] ns	$[\tau]$,[b] ns
9.0	330	0.30	2.62	0.24	14.83	0.14	39.77	27.73
	420	−0.15	3.42	0.44	52.74			53.90
8.0	330	0.22	3.20	0.17	17.49	0.07	45.92	29.87
	420	−0.14	2.89	0.41	55.63			56.58
7.5	330	0.26	3.08	0.19	18.17	0.08	52.04	33.61
	420	−0.13	3.31	0.30	60.14			61.33
6.5	330	0.13	5.46	0.20	28.23	0.17	59.77	46.47
	420	−0.07	6.03	0.22	78.64			80.42
6.0	330	0.11	5.77	0.22	33.09	0.11	70.29	49.90
	420	−0.09	6.35	0.36	78.78			80.30
5.0	330	0.10	6.41	0.19	32.77	0.07	72.10	48.18
	420	−0.07	5.58	0.26	76.44			77.94

[a] λ_{ex} = 280 nm for all samples. [b] See eq 1 in the text for fitting function. [c] Average lifetime defined by eq 2.

the MAA repeat units and the naphthyl chromophores. There is no driving force for exclusive hydrophobic association of NAEA units. The naphthyl chromophores (20%) may be envisioned as being "diluted" within the hydrophobic portion of the coil by the presence of the protonated methacrylic acid groups (80%).

As the pH is increased, the MAA groups in the polymer chain become increasingly hydrated, forming a charged shell around the hydrophobic core of NAEA units, consistent with the hypercoil model proposed by Guillet[5,7] and others. In this highly hydrated environment, association of the naphthyl groups occurs providing the minimum separation (ca. 4 Å) necessary to permit excimer formation. We speculate that the relatively long spacer group between the naphthyl moiety and the polymer backbone tends to "decouple" the chromophore from the backbone aiding excimer formation while the remainder of the coil is allowed to expand due to increased electrostatic repulsions.

Alternatively, one might imagine that at low pH the higher polymer density, and consequently the lower mobility, within the tightly collapsed coil could interfere with the ability of two chromophores to orient in a manner favorable for the formation of an excimer. Morishima and Webber[6] have proposed such interactions in studies on similar polyelectrolyte systems. As pH is increased, the expansion of the coil decreases the polymer density within the coil. Increased mobility of the chromophores allows orientation in the preferred coplanar or sandwich arrangement, while hydrophobic interactions among the chromophores maintain their proximity to one another, yielding the observed increase in I_E/I_M.

In addition to changes in the I_E/I_M ratio, a significant change in the fluorescence decay of both monomer (330 nm) and excimer (420 nm) fluorescence was observed upon altering the pH of the solution. Neither the monomer nor the excimer decay profiles could be fit satisfactorily to a single exponential. Instead, using the general equation

$$I(t) = \sum a_i \exp(-t/\tau_i) \qquad (1)$$

the monomer decays were fit to a triple-exponential function while the excimer decays were fit to a double exponential. The values of the preexponential factor, a_i, and the lifetime, τ_i, are listed in Table I together with the average lifetimes[15] as defined by

$$[\tau] = \sum a_i \tau_i^2 / \sum a_i \tau_i \qquad (2)$$

Both the values of monomer and of excimer average lifetimes, $[\tau]_M$ and $[\tau]_E$, respectively, exhibit a marked decrease with increasing pH of the solution (Figure 3). Interestingly, the lifetime of a model compound of NAEA in solutions of DMF, 50/50 DMF/water, and water was found to decrease from 49.4 to 41.0 to 30.3 ns, respectively. The conclusion: expansion of the polymer coil with increasing pH allows the chromophores to experience a much more hydrated/hydrophilic environment. Since the fluorescence lifetime of the model compound depends, at least in part, on the polarity of the medium, the decrease in both $[\tau]_M$ and $[\tau]_E$ with increasing pH is apparently due to a change in the microenvironment experienced by the probe.

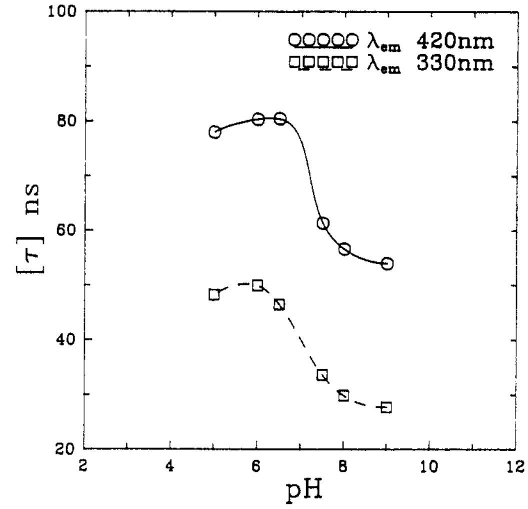
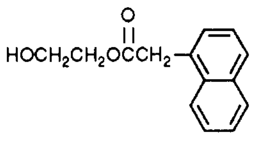


Figure 3. Dependence of the average lifetime $[\tau]$ (see eq 2 in text) for both monomer (λ_{em} = 330 nm) and excimer (λ_{em} = 420 nm) fluorescence on solution pH.



model compound for NAEA

Effect of Urea. The structuring of water molecules around a hydrophobic molecule, though entropically unfavorable, has been reported to be necessary for solubilization of the material.[16,17] The driving force for hydrophobic association in aqueous systems is partially attributed to the need for the hydrophobic material to minimize its surface area and consequently minimize the amount of water that must be "structured" in order to solubilize it. This phenomena has been termed the "hydrophobic effect". The addition of urea to aqueous solutions of surfactants disrupts the structuring ability of water around the hydrophobic groups, thereby disrupting hydrophobic interactions within the solution.[18,19] We have thus

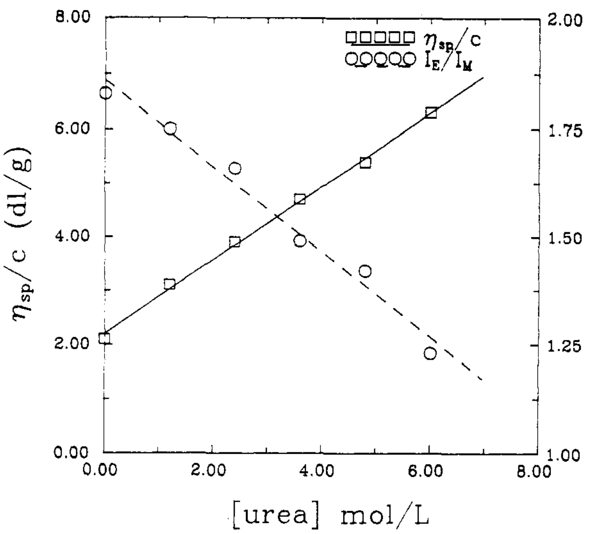


Figure 4. Dependence of the relative efficiency of excimer formation (I_E/I_M) and solution reduced viscosity (η_{sp}/c) at pH 8.0 on the concentration of added urea in the solution. $C_p(I_E/I_M) = 0.01$ g/dL. $C_p(\eta_{sp}/c) = 0.10$ g/dL.

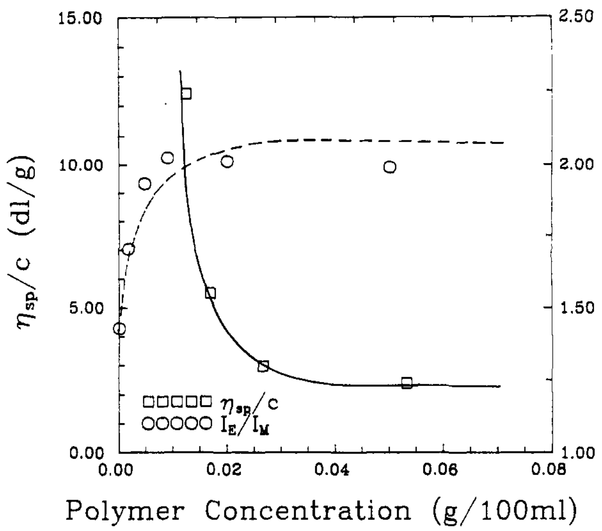


Figure 5. Dependence of the relative efficiency of excimer formation (I_E/I_M) and solution reduced viscosity (η_{sp}/c) at pH 8.0 on polymer concentration.

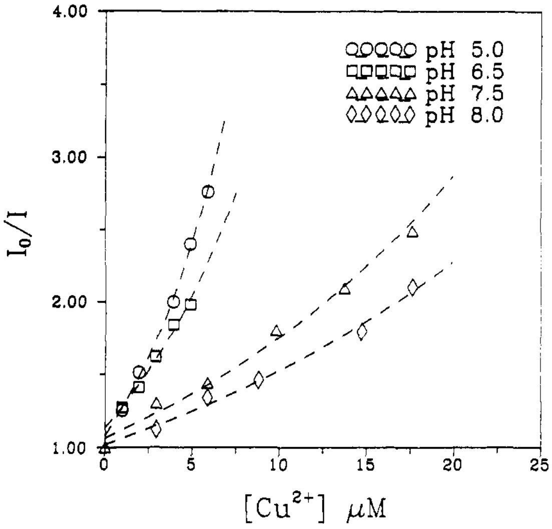


Figure 6. Stern–Volmer plot of the ratio of monomer (λ_{em} = 330 nm) fluorescence intensities (I_0/I) in the absence (I_0) and presence (I) of quencher versus concentration of copper(II) ions in the solution at several different values of pH.

employed urea to determine the role of hydrophobic association of pendant NAEA units at high pH.

At pH 8.0, a significant decrease in I_E/I_M is observed with the addition of urea to the polymer solution (Figure 4). Since urea was found not to quench the fluorescence of the NAEA model compound, this decrease in I_E/I_M is attributed to the effective solubilization of the hydrophobic core of naphthyl groups by the urea. As these hydrophobic interactions are disrupted, the polymer coil begins to expand due to electrostatic repulsions. With increased coil expansion, the chromophores can no longer maintain the minimum separation necessary for excimer formation to occur, such that excimer intensity, and therefore I_E/I_M, is decreased. One might expect that upon disruption of specific NAEA interactions, the overall hydrodynamic size of the polymer would increase: Figure 4 indicates that this is indeed the case. An increase in the reduced viscosity of the polymer solution is observed with an increase in urea concentration.

Effect of Polymer Concentration. In order to determine whether the associations among naphthyl groups at high pH are predominantly inter- or intramolecular in nature, the effect of polymer concentration on I_E/I_M was investigated. At pH 8.0, while both monomer and excimer intensities increase with increasing polymer concentration, there is no change within experimental error of the I_E/I_M ratio above 7 mg/100 mL (Figure 5). Below 7 mg/100 mL, however, I_E/I_M decreases precipitously. The latter can be attributed to an increase in Coulombic repulsions often associated with polyelectrolytes in extremely dilute solution, i.e., the "polyelectrolyte effect".[20] Thus, the absence of any appreciable change in I_E/I_M above a limiting polymer concentration indicates that the hydrophobic associations are intramolecular in nature. Further confirmation of the absence of intermolecular interactions can be found from a study of the reduced viscosity of the polymer solutions as a function of polymer concentration. If the associations were intermolecular in nature, the reduced viscosity would be expected to increase steadily with increasing polymer concentration above a concentration of 7 mg/100 mL. In contrast, intrapolymer interactions should have very little effect on the reduced viscosity of the polymer solution.[21,22] Figure 5 (curve b) shows a plot of the reduced viscosity as a function of concentration. The initial rapid drop of the reduced viscosity at lower concentrations corresponds to the polyelectrolyte effect arising from ion diffusion and chain expansion due to charge repulsion. After this initial drop, the reduced viscosity of the polymer solution changes very little over the range of 25–150 mg of polymer/100 mL. Therefore, over this concentration range, it can be concluded from both steady-state fluorescence and viscosity measurements that the NAEA-MAA copolymer exhibits pseudomicellar, intrapolymer associations among naphthyl groups at high pH; these associations are greatly affected by the polyelectrolyte effect at low polymer concentrations.

Fluorescence Quenching with Copper(II) Ions. Both monomer (330 nm) and excimer (420 nm) fluorescence quenching by Cu^{2+} were investigated over a broad pH range. The solution basicity was limited to pH 8 due to possible complications from the formation of cupric hydroxide gels and chromophore hydrolysis. The Stern–Volmer plots of monomer (Figure 6) and excimer (Figure 7) fluorescence intensities in the absence and the presence of Cu^{2+} are shown as a function of solution pH. At each pH, Cu^{2+} displayed a high quenching efficiency for both monomer and excimer fluorescence as well as a marked upward curvature with increasing quencher concentration since copper(II) quencher ions are bound pref-

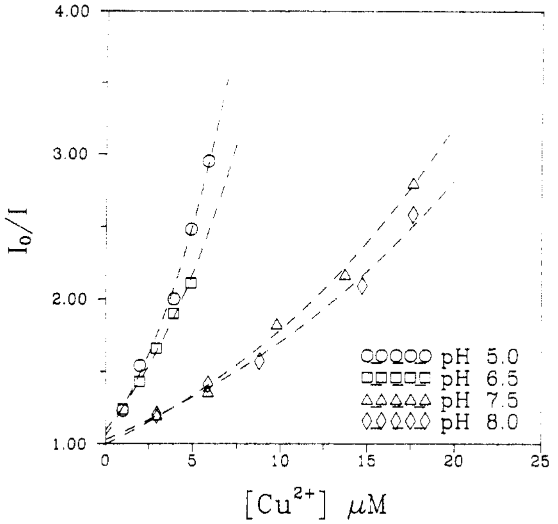


Figure 7. Stern–Volmer plot of the ratio of excimer (λ_{em} = 420 nm) fluorescence intensities (I_0/I) in the absence (I_0) and presence (I) of quencher versus concentration of copper(II) ions in the solution at several different values of pH.

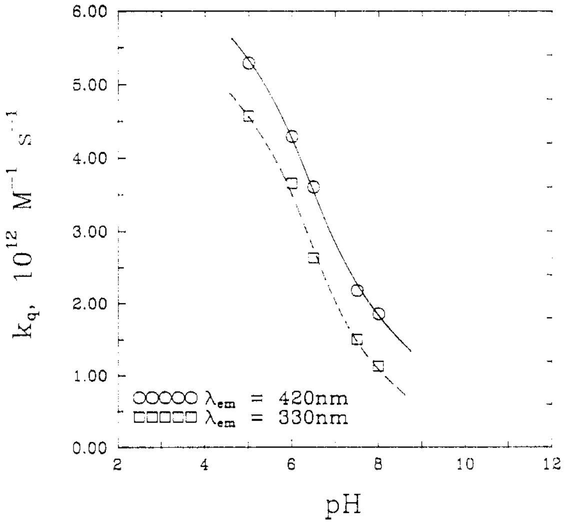


Figure 8. Dependence of apparent rate quenching constant of copper(II) ions $(k_q)_{app}$ for both monomer (λ_{em} = 330 nm) and excimer (λ_{em} = 420 nm) fluorescence on solution pH.

erentially to the negatively charged polymer at low pH as well as high pH. In order to compare at least semiquantitatively the quenching efficiency of Cu^{2+} at the different pH values, an apparent Stern–Volmer constant, $(K_{SV})_{app}$, was estimated from the initial slope of the plots of I_0/I vs quencher concentration. From $(K_{SV})_{app}$ and the average lifetimes, apparent second-order quenching rate constants, $(k_q)_{app}$, of both monomer and excimer fluorescence were calculated.

A plot of apparent $(k_q)_{app}$ vs pH for the NAEA-MAA copolymer (Figure 8) indicates that electrostatic interactions between the Cu^{2+} quencher and the polymer do in fact play an important role in the quenching process. The values for $(k_q)_{app}$ range from approximately 1.0 to 5.5 × 10^{12}, some 2 orders of magnitude greater than typical diffusion-controlled processes. Also, a sharp decrease in $(k_q)_{app}$ for both monomer and excimer fluorescence is observed with increasing pH. Morishima and Webber[6] have postulated that such a decrease could be explained in terms of an effective concentration of quencher within the polymer coil. As viscosity data indicate (Figure 2), the NAEA–MAA copolymer assumes a more compact conformation at pH 5 than at pH 8. However, even at pH 5, a significant fraction of carboxyl groups (approximately 60%) are still ionized, allowing essentially all of the quencher cations to be effectively bound. Therefore, the effective concentration of quencher within the polymer coil at pH 5 is higher than that at pH 8 where the polymer hydrodynamic volume is greater.

Perhaps $(k_q)_{app}$ is also influenced by "hypercoiling" of the polymer at high pH. As the pH of the solution is increased, the negatively charged shell of carboxylate groups which surrounds the hydrophobic core of NAEA units can effectively "screen" the naphthalene chromophores from interaction with the cationic Cu^{2+} quenchers.

Conclusions

Photophysical and rheological data presented above indicate that the conformation adopted by the NAEA–MAA copolymer in aqueous solution is dependent upon the pH of the solution as well as hydrophobic interactions inherent within the polymer. At high pH, the polymer apparently assumes a pseudomicellar conformation, with the naphthyl groups forming a hydrophobic core which is surrounded by a charged shell of methacrylic acid units. The behavior, both photophysical and rheological, observed with changes in polymer concentration and the addition of the water-structure breaker urea indicates that these hydrophobic interactions are largely intramolecular in nature. As the pH is lowered, we speculate that a "dilution" of NAEA units within the hydrophobic portion of the coil and/or nonfavorable chromophore orientation due to decreased mobility are responsible for the observed decrease in excimer formation.

Acknowledgment. The financial support of the United States Department of Energy and the Office of Naval Research is gratefully acknowledged. We also acknowledge the Experimental Program to Stimulate Competitive Research (EPSCoR), Research Initiation and Improvement Division, for partial support. Thanks are extended to Stephen Ezzell for synthesis of the model compound and to Teresa Schott for her work as an undergraduate assistant.

References and Notes

(1) Guillet, J. E.; Wang, J.; Gu, L. *Macromolecules* **1986**, *19*, 2793.
(2) Itoh, Y.; Morishima, Y.; Nozakura, S. *Photochem. Photobiol.* **1984**, *39*, 451.
(3) Itoh, Y.; Morishima, Y.; Nozakura, S. *Photochem. Photobiol.* **1984**, *39*, 603.
(4) Morishima, Y.; Kobayashi, T.; Furui, T.; Nozakura, S. *Macromolecules* **1987**, *20*, 1707.
(5) Guillet, J. E.; Rendall, W. A. *Macromolecules* **1986**, *19*, 224.
(6) Morishima, Y.; Kobayashi, T.; Nozakura, S.; Webber, S. E. *Macromolecules* **1987**, *20*, 807.
(7) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11.
(8) McCormick, C. L.; Kim, K. *J. Macromol. Sci., Chem.* **1988**, *A25*, 285.
(9) McCormick, C. L.; Kim, K. *J. Macromol. Sci., Chem.* **1988**, *A25*, 307.
(10) Ware, W. R.; Doemeny, L. J.; Nemzek, T. L. *J. Phys. Chem.* **1973**, *77*, 2038.
(11) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981.
(12) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1984**, *17*, 2142.
(13) Olea, A. F.; Thomas, J. K. *Macromolecules* **1989**, *22*, 1165.
(14) Ghiggino, K. P.; Tan, K. L. *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: New York, 1985.
(15) Bai, F.; Chang, C.-H.; Webber, S. E. *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987.
(16) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley and Sons: New York, 1973.
(17) Shinoda, K. *J. Phys. Chem.* **1977**, *81*, 1300.
(18) Mukerjee, P.; Ray, A. *J. Phys. Chem.* **1963**, *67*, 190.

(19) Schick, M. J. *J. Phys. Chem.* **1964**, *68*, 3585.
(20) Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley and Sons: New York, 1961.
(21) Strauss, U. P.; Gershfeld, N. L. *J. Phys. Chem.* **1954**, *65*, 747.
(22) McCormick, C. L.; Blackmon, K. P.; Elliot, D. L. *Angew. Makromol. Chem.* **1986**, *144*, 87.

Conformational and Motional Characteristics of *trans*-1,4-Diene Polymers Confined to Channels

A. E. Tonelli

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received November 10, 1989; Revised Manuscript Received January 17, 1990

ABSTRACT: Prompted by the studies of Sozzani and co-workers, who have polymerized diene monomers complexed with perhydrotriphenylene (PHTP) to form inclusion compounds, we have investigated the conformations and mobilities of the resulting isolated *trans*-1,4-diene polymer chains confined to the channels of their inclusion compounds with PHTP. This was achieved by a two-step procedure: (i) from all the possible conformations available to the free polymer chains, those conformations which fit into the channels of their inclusion compounds with PHTP were defined; (ii) a test was performed to determine whether or not it was possible to interconvert between these channel conformations while the *trans*-1,4-diene polymers remained inside their channels. This procedure was applied to *trans*-1,4-polybutadiene, *trans*-1,4-polyisoprene, and isotactic *trans*-1,4-poly(penta-1,3-diene) chains confined to the channels of their inclusion compounds with PHTP. We found the channel conformers of the butadiene and pentadiene polymers able to interconvert while inside their channels. By contrast, the isoprene polymer was not able to interconvert between its channel conformers without significant expansion of its confining PHTP channel (ca. 30% increase in channel diameter, compared to the 0–5% increase observed for interconverting butadiene and pentadiene chains). These results are consistent with the solid-state ^{13}C and ^{2}H NMR studies performed by Sozzani et al. to elucidate the conformations and mobilities of the same *trans*-1,4-diene polymers when restricted by the channels formed in their PHTP inclusion compounds.

Introduction

When the crystals of perhydrotriphenylene (PHTP) are exposed to small molecule liquids or gases, crystalline inclusion compounds are formed. Farina and co-workers[1] have studied many PHTP inclusion complexes, including those with polymers such as polyethylene. Generally the physical properties of both the PHTP matrix and the entrained molecules of the inclusion compound are markedly different from their separate pure phases. As an example, the melting temperature of the complex formed between the PHTP matrix and the included molecule is significantly elevated over the melting points of their pure phases.

Many polymers are easily prepared[1,2] in the channels of PHTP inclusion compounds. After diffusion of gaseous or liquid monomer into the PHTP crystals, the confined monomers of the inclusion compound are polymerized by irradiation of the complex. The polymerization propagates inside the PHTP crystal, linking together monomers to form high molecular weight polymers. No amorphous polymer is produced because polymerization cannot occur outside the crystal. The constraints imposed by the PHTP channels lead to a reduction in the side reactions that would introduce polymer defects;[3] thus the polymers produced in PHTP crystals have highly regular structures.

The polymerization of 1,3-butadiene in PHTP channels has been studied by X-ray crystallography[4] and ESR spectroscopy.[3b,5] During the polymerization, which proceeds through a living radical mechanism,[3b] the PHTP crystal structure is not destroyed. Instead the inclusion complex of PHTP with monomer is transformed to a crystalline complex with the polymer, resulting in significant changes in the crystalline lattice parameters. The X-ray diffraction pattern after polymerization does not reveal the presence of the *trans*-1,4-polybutadiene (TPBD) molecules in the PHTP channels. Similar results were observed for TPBD polymerized in urea channels.[6]

It was suggested that either the TPBD repeat distance, when confined by the channel, was identical with the PHTP matrix repeat (4.78 Å) or the polymer was disordered and only produced diffuse scattering. Freely rotating TPBD chains in the PHTP channels would explain this observation, but the X-ray data could not distinguish between time-averaged or space-averaged conformational disorder. Sozzani and co-workers[7,8] have subsequently employed solid-state ^{13}C and ^{2}H NMR spectroscopy in an attempt to resolve the question of disorder among the TPBD chains in their PHTP channels. They have found the TPBD chains to be mobile, probably as a consequence of intrachannel conformational transitions. The motions and conformations of TPBD chains included in the complex with PHTP were found[7,8] to be very similar to those experienced[9,10] by pure TPBD above 60 °C in their form II crystals. Unlike pure TPBD, which transforms[11] to rigid form I crystals below 60 °C, TPBD chains in the PHTP complex remain mobile down to very low temperature (−160 °C).

Sozzani and co-workers[12,13] have also synthesized and investigated the PHTP channel polymerization of isoprene and 1,3-pentadiene to yield *trans*-1,4-polyisoprene (TPIP) and isotactic *trans*-1,4-poly(penta-1,3-di-

0024-9297/90/2223-3129$02.50/0