the other evidence that the line broadening is inhomogeneous.

This combination of relaxation studies, the field dependence of the line width, and the hole-burning experiment provides convincing evidence that in cross-linked poly(sodium acrylate) the NMR lines are inhomogeneously broad. The cross-linking creates a distribution at different chemical environments, which is reflected in the distribution of chemical shifts.

Acknowledgment. We are indebted to the Natural Science and Engineering Research council of Canada for financial support of this research and to Bruker Spectrospin (Canada) Ltd. for the use of the AM400, AM300, and AC200 spectrometers located in their Milton (Ontario) laboratories.

Registry No. (Sodium acrylate)(*N*,*N*′-methylenebis(acrylamide)) (copolymer), 25359-44-8.

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Photophysics of Nominally Alternating Copolymers of 2-Isopropenylnaphthalene and Maleic Acid in Aqueous Solution

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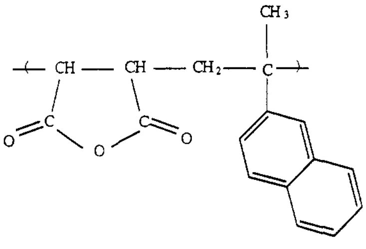
ABSTRACT: A copolymer of maleic anhydride (MAn) and 2-isopropenylnaphthalene (2IPN) has been prepared and found to be water soluble over a wide pH range. The copolymer composition has been determined to be dependent upon the monomer feed ratio in a manner suggesting a 1:1 alternating sequence distribution. The fluorescence spectrum exhibits monomer and excimer emissions at high pH and shifts dramatically over the pH range 5–3 to a nearly pure excimer spectrum. At high pH, the excimer emission is ascribed to nearest-neighbor naphthalene–naphthalene diads which are present in small quantities as "defects". Excitation spectra and 77 K fluorescence spectra demonstrate that this static excimer component persists for all pHs, and dynamic excimer component arises upon acidification. This is attributed to the collapse of the coil structure as the acid groups are neutralized. Experiments utilizing an environmentally sensitive optical probe (1,8-anilinonaphthalene sulfonate) supported this picture as did anthracene sensitization and copper(II) quenching studies. It is proposed that electronic energy transport between chromophores is efficient, especially at low pH. Dynamic light scattering studies gave evidence for polymer aggregation at high concentration.

Introduction

Studies on polymer-bound chromophore systems have shown that the details of photoprocesses are highly dependent upon the microenvironments of the chromophores. Of particular interest are aqueous solutions of amphiphilic polyelectrolytes incorporating various levels of hydrophobic aromatic groups.[1-4] For low loadings, intramolecular chromophore interaction is avoided, but as the chromophore content is increased, such interaction becomes significant. The solution behavior of these systems is not fully understood, but possibly they can be viewed as organized assemblies similar to micelles or vesicles.

An interesting class of amphiphilic copolymers is alternating copolymers, which in some cases represent the upper limit of hydrophobic character with continued water solubility. Relatively few photophysical studies have been conducted on these systems, and the results are ambiguous. In 1974, Fox et al. reported no excimer fluorescence for alternating copolymers of 2-vinylnaphthalene and styrene with methyl methacrylate.[5] Mikawa and co-workers[6] likewise found no evidence of excimer formation in *N*-vinylcarbazole alternating copolymers in organic solution. Webber et al. found exclusively monomer emission in an alternating copolymer of methyl methacrylate and 4-vinylbiphenyl in THF.[1b] In 1975, however, Wang and Morawetz[7] reported prominent excimer emission for an alternating acenaphthalene–maleic acid system. In recent studies, excimer fluorescence has been observed for aqueous solutions of alternating copolymers of 2-vinylnaphthalene with methacrylic acid and maleic acid. Very recent results from this laboratory and Morishima et al. indicate that, for these polymers, excimer formation is critically depedent upon the precise monomer sequence distribution.[8] Thus, it is possible that a comparison of different "alternating" copolymers is misleading. It is expected that factors such as hydrophilic spacer group, molecular weight, coil conformation, and sequence defects will all influence the manner in which chromophores communicate via energy migration and/or excimer formation. The present paper focuses on the photophysical behavior of a previously unstudied nominally alternating copolymer of maleic anhydride and 2-isopropenylnaphthalene. This polymer also represents an interesting comparison to 2-vinylnaphthalene maleic acid copolymers because of the additional methyl groups on the α-carbon of the vinylnaphthalene moiety (**1**).



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Experimental Section

Materials. 2-Isopropenylnaphthalene (2IPN) was kindly supplied by Dr. Rolf C. Schulz of the Institute for Organic Chemistry of the University of Mainz. It was recrystallized twice from methanol, vacuum dried, and stored over $CaCl_2$. Maleic anhydride (MAn) briquettes from Aldrich were recrystallized twice from chloroform, vacuum dried, and stored over $CaCl_2$. Tetrahydrofuran (THF) used for polymerization and workup was distilled over $LiAlH_4$. Diazomethane used for esterification was prepared by codistillation of an ethereal solution of Diazald (Aldrich) in strong base using an apparatus with no ground-glass joints.[9] Water used for fluorescence measurements was deionized and distilled. The pH of aqueous solutions was adjusted with aqueous sodium hydroxide and hydrochloric acid and determined by using a Beckman Model 3500 pH meter. 1,8-Anilinonaphthalene sulfonate (ANS) (Molecular Probes) was recrystallized twice from aqueous magnesium chloride. 9-Anthraceneethanol was supplied by Dr. Phil Britt, The University of Texas at Austin. 2,2′-Azobis(isobutyronitrile) (AIBN; Kodak) was recrystallized twice from methanol. Anthracene (99%, Aldrich) and cupric sulfate (Fisher Scientific) were used as received.

Polymer Preparation. Copolymerizations of 2IPN and MAn were performed as follows: a solution containing known amounts of the two monomers (ca. 10 wt % total in THF) and 0.05 mol % (on the basis of total monomers) AIBN was outgassed in a glass ampule by 6 freeze–pump–thaw cycles and then sealed. The ampule was typically heated to 60 °C for 24 h. The solution was concentrated by evaporation and the polymer precipitated into excess cold benzene. The polymer was collected by centrifugation and reprecipitated twice from THF into benzene. Copolymerizations were carried out with various mole fractions of 2IPN in the feed. In all cases, monomer conversion was kept under 25%.

The copolymer was hydrolyzed by treating a highly concentrated THF solution with 0.25 M sodium hydroxide. Typically, ca. 0.5 g of polymer was mixed with 100 mL of sodium hydroxide solution and heated at 50 °C for 30 min whereupon the solution turned clear. The solution was allowed to stir at room temperature overnight. Next, the solution was dialyzed against pure distilled water for several days, changing the water frequently, and finally lyophilized to yield an off-white fluffy solid.

Esterification of the polymer for characterization and organic solvent studies was carried out as follows. An aqueous solution of the hydrolyzed polymer was acidified with concentrated HCl and the precipitated polymer dried and suspended in ca. 50 mL of benzene. A large excess of freshly prepared diazomethane in ether was added to the mixture and stirred at room temperature for ca. 12 h, with almost immediate dissolution of the polymer. This esterified polymer was purified by repeated precipitation from benzene into ether, and finally the benzene solution was freeze-dried. It is assumed that methyl esterification was 100% complete.

Anthracene-tagged polymers were prepared by reacting the initially formed anhydride polymers with 9-anthraceneethanol (9EA). Sixteen milligrams of freshly prepared polymer and 1.1 mg of 9EA were dissolved in 30 mL of THF and refluxed in the dark for 6 h. The solution was then concentrated by evaporation and hydrolyzed as above. We note that attempts to esterify 9EA with the polyacid were not successful.

Polymer Characterization. In order to determine the copolymer composition, UV absorption spectra were recorded on an HP8451A diode array spectrophotometer in THF using 2-ethylnaphthalene as a standard. As an additional check, elemental analyses of the methyl ester derivatives were used to calculate C/H ratios.

Qualitative molecular weight estimates were made from gel permeation chromatography (GPC) measurements calculated on a Waters system employing a bank of 500-, 10^3-, 10^4-, and 10^5-Å μ-Styragel columns and a different refractometer in series with a Perkin-Elmer LS-1 fluorescence detector. Monodisperse polystyrene standards (Scientific Polymer Products) were used to establish a calibration curve, such that all GPC M_w's quoted later refer to the equivalent polystyrene molecular volume.

Viscosity measurements were carried out in aqueous solution at 30 °C using Cannon-Fenske viscometers.

Dynamic light scattering or photon correlation spectroscopy (PCS) studies were conducted by using a Brookhaven Model BI-200 with a polarized argon ion laser operating at 488 nm. The sample chamber was in a thermostated index matching bath (xylene), and a Brookhaven Model BI-2030 autocorrelator (64 real time channels) and associated software were used to process signals. All data presented are for a 90–deg scattering angle at 20 °C.

Much care must be taken during aqueous sample preparation in order to remove all traces of dust. This was done by using distilled, deionized, filtered water for initial preparation under a positive pressure cleanbox and filtering the solutions in-line for several hours using Millipore 0.22-μm pore size cellulose nitrate filters. Contaminated samples were easily identified by their nonreproducible and erratic scattering signals.

Fluorescence Spectroscopy. Steady-state fluorescence spectra were recorded on either of two instruments. The first was a Spex Fluorolog 2 employing a 450-W xenon lamp for excitation and a Hamamatsu R508 photomultiplier tube for emission detection. The Fluorolog 2 uses double monochromators at the entrance and exit, allowing a scan of 180–900 nm with a ±0.4-nm accuracy. A Spex Datamate controls instrumentation and processes data.

The other instrument used was also a Spex Fluorolog with a double monochromator for excitation using a 150-W xenon lamp and a single monochromator spectrograph for projection of the spectrum onto a 512-channel diode array which was controlled by a Tracor Northern 6500 system. This system allowed a spectrum to be recorded in as little as 5 ms. The spectral resolution of the former system was better than the latter, and all spectra are uncorrected for PMT/diode array response. Solutions were typically deaerated by N_2 bubbling.

Fluorescence lifetime measurements were conducted either by using a Photochemical Research Associates single-photon-counting instrument in our laboratory or by using CFKR (The Center for Fast Kinetics Research, The University of Texas at Austin) facilities.

A cooled Hamamatsu IP21 photomultiplier tube was used for the PRA system, which utilizes a PRA Model 510 pulsed lamp air filled to 380 Torr and discharged at 5 kV. Lamp width at half-height was typically 2–3 ns. Excitation and emission wavelengths were selected by using PRA monochromators. Naphthalene was excited by using the 316-nm line of nitrogen.

Two instruments were used for CFKR lifetime measurements. The single-photon-counting apparatus was similar to the above system except for the excitation source, which was a synchronously pumped, cavity-dumped dye laser pumped by a frequency-doubled Nd:YAG laser mode locked at 81.66 MHz. The dye laser is cavity dumped at 800 kHz and gives an instrument response function of ca. 400 ps at 295 nm. Band pass (340-nm) or cutoff (400-nm) filters were used to select the emission region of interest. A Tracor Northern TN-7200 optical multichannel analyzer was used, operating at speeds up to 2.5 ps/point.

A different electronics arrangement was used when exciting at 266 nm with a Nd:YAG (Quantel YG402, fwhm = 30 ps) operating at the fourth harmonic with the energy attenuated by a dispersion lens and neutral density filters. A Hamamatsu R306 phototube was used to capture fluorescence and input to a Tektronix R7912 transient digitizer with subsequent processing by a DEC PDP 11/70 computer.

Fluorescence decay data were analyzed by the commonly used reconvolution technique.[10] The real fluorescence decay function $I(t)$ is related to $I_{obs}(t)$ through the instrument response function $R(t)$ by $I_{obs}(t) = \int I(t-t')\,R(t')\,dt'$. $I(t)$ is assumed to be described

Table I
Compositional Analysis Data for P(2IPN-*a*-MAA) Copolymer

	% 2IPN polymer				
% 2IPN feed	EA[a]	UV[b]	av	F_{11}[c]	F_{22}[d]
20.8	42	51	47	0.01	0.05
32.4	45	53	49	0.02	0.03
54.8	48	55	52	0.05	0.01
67.8	52	60	56	0.09	0.005
82.9	55	64	59	0.18	0.002

[a] From elemental analysis of C/H ratios for methyl-esterified polymer. [b] From ultraviolet absorption using 2-ethylnaphthalene as standard. [c] Fraction of naphthalene–naphthalene diads. [d] Fraction of maleic anhydride–maleic anhydride diads.

as a sum of exponentials: $I(t) = \sum a_i \exp(-t/\tau_i)$, with three components usually being adequate to fit the curve. The coefficients a_i and lifetime τ_i are varied in order to minimize the weighted residuals χ^2 defined as $\chi^2 = \sum |I_{obs}(t_i) - \int R_{obs}(\tau) F(t_i - \tau)\, d\tau|^2 \omega(t_i)$ where $I_{obs}(t_i)$ is the experimental fluorescence intensity at t_i, $R_{obs}(\tau)$ is the instrument response function, and $F(t)$ is the fitting function. The weighing factor $\omega(t_i)$ is equal to $1/I_{obs}(t)$ for $I_{obs}(t)$ not equal to zero.

Results

Polymer Characterization. Maleic anhydride is well-known to form copolymers with an alternating sequence distribution when polymerized with a number of different vinyl monomers in a free-radical reaction.[11] It is thought that the mechanism for this process involves homopolymerization of a charge-transfer (CT) complex formed between the two monomers.[12] Indeed, when colorless 2IPN and MAn were mixed in THF, the solution appeared yellowish presumably indicating the formation of a CT complex.

In order to determine whether the copolymer propagates via an alternating sequence distribution, it was necessary to analyze the polymer composition when different monomer ratios are used in the feed. The UV absorption and elemental analysis results showed that the copolymer tended toward a 1:1 composition over the intermediate range of monomer feed ratios as summarized in Figure 1. The results from UV and elemental analysis are presented in Table I. The UV results could contain a systematic error if there is a difference in extinction coefficient for the polymeric naphthalene and the model, 2-ethylnaphthalene. It is possible that the elemental analysis results underestimate the naphthalene content because the assumption has been made that the polymer is 100% methyl esterified. The monomer reactivity ratios were determined from a least-squares fit of the feed and composition data to the Fineman–Ross equation.[13] The calculated values were r_1(2IPN) = 0.093 ± 0.02 and r_2(MAn) = 0.025 ± 0.009. The consecutive diad fractions for M_1M_1 and M_2M_2 can be calculated from the reactivity ratios, and the potential effect of such diads upon the photophysics will be discussed later.

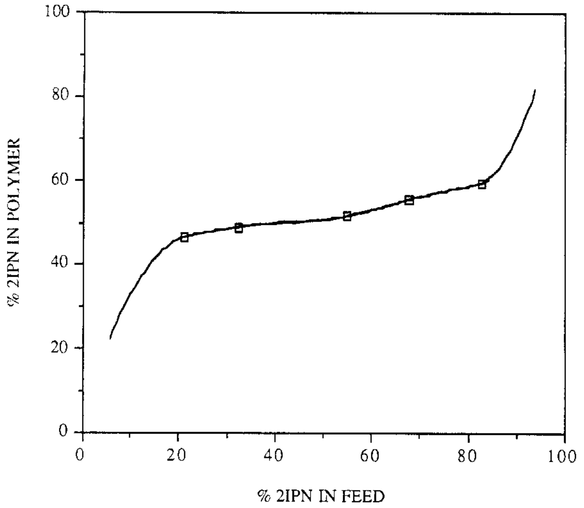

Figure 1. Compositional analysis curve for the copolymerization of 2IPN and MAn initiated by AIBN at 60 °C in THF. Shown are the averages of elemental analysis and ultraviolet absorption data.

Gel permeation chromatography results indicated that the copolymer, hereafter referred to as P(2IPN-*a*-MAA), tended to be of low molecular weight. Initial polymerizations were in benzene, but the macromolecular species precipitated with a M_w of ca. 6000. Copolymerization carried out in THF did not yield a precipitate and produced polymers with a molecular weight up to 18 000. All polymers gave similar unimodel elution curves. One explanation for low molecular weights could be monomer depletion by a competing Diels–Alder reaction. Although we made no attempt to isolate this adduct, Schulz and Engel have reported the competition between copolymerization and Diels–Alder addition to be temperature dependent.[14] The polymer for which all photophysical data will be presented was from a 38 mol % 2IPN in feed run and was found by GPC to have M_w = 11.2 × 10^3 with a polydispersity of ca. 1.5. This corresponds to a degree of polymerization of ca. 35 2IPN–MAn pairs. It must be emphasized that the solution behavior of this class of amphiphilic copolymers is not well-known, and molecular weight comparisons with polystyrene must not be taken too seriously.

Viscosity determinations were done in order to get an initial indication of aqueous solution behavior. The reduced viscosities of 0.15 mg/mL solutions at pH 9.6 and 2.8 were found to be 63 and 29 cm^3/g, respectively. These results are what would be expected for a polyelectrolyte that undergoes coil expansion upon deprotonation. The overall viscosity increase over pure solvent (η_{rel}) was low due to the low molecular weight.

The pH dependence of the coil diffusion coefficient was examined by dynamic light scattering for a wide range of polymer concentrations with no added electrolyte. Under basic conditions, the diffusion coefficient was found to be independent of concentration. For dilute solutions (<2 mg/mL), the total scattering intensity increases upon protonation, but surprisingly there is not change in the diffusion constant. The Stokes–Einstein relation is usually assumed, $D = kT/(3\pi d_h \eta)$, such that these results imply a constant hydrodynamic diameter (d_h). Similar observations were obtained for a 1 mg/mL solution of poly(methacrylic acid). Above 2 mg/mL, the diameter increases dramatically at low pH, indicating polymer aggregation. It should be noted that the fluorescence properties were constant over the range of concentrations studied by light scattering. Further studies in this laboratory are under way to correlate light-scattering and fluorescence data for polyelectrolyte systems.

Steady-State Fluorescence. Polymer-pendant naphthalene is well-known to exhibit both monomeric and excimer fluorescence in a number of systems.[15] Naphthalene monomer emission is usually centered at 340 nm, while the excimer maximum is ca. 390 nm. An alternating copolymer of MAn and 2-vinylnaphthalene (P(2VN-*a*-MAn)), which differs from P(2IPN-*a*-MAn) only by the absence of the α-methyl group attached to the backbone, has recently been studied in this laboratory and in Osaka by Morishima et al.[1g] For the hydrolyzed polymer, P(2VN-*a*-MAA) in

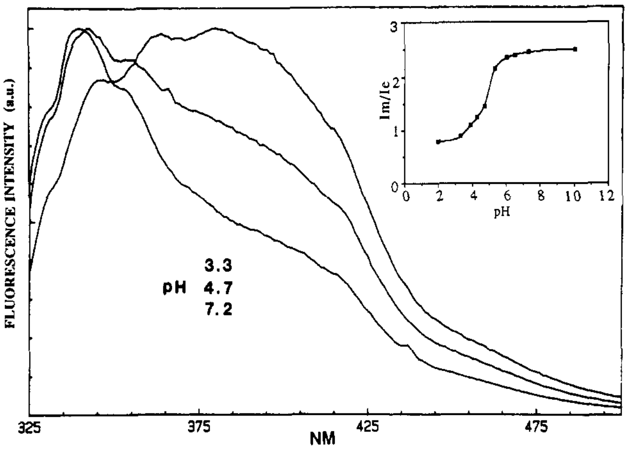

Figure 2. Steady-state fluorescence spectra of an aqueous solution of P(2IPN-*a*-MAA) as a function of pH (all spectra normalized). Polymer concentration: 1.9 mg/mL. Inset shows pH dependence of relative intensities of monomer (340-nm) to excimer (400-nm) emission. Excitation wavelength: 300 nm.

aqueous solution, the excimer component dominates over the monomer emission for a wide pH range.

P(2IPN-*a*-MAA) was expected to give similar aqueous solution spectra but in fact proved to be quite different. As is seen in Figure 2, monomer emission is predominate at high pH. As the solution is acidified, the I_m/I_e ratio decreases sharply over the pH range 5.5–3.5. It has been shown that alternating copolymers of maleic acid/styrene[16] and maleic acid/alkyl vinyl ethers[17] undergo conformational transitions from an expanded to contracted coil upon protonation. As the ionic character of the macromolecule decreases, polymer–polymer interactions begin to be favored over polymer–solvent interactions and the coil collapses. It is believed that hydrophobic bonding between the aryl or alkyl groups stabilizes these compact structures at low pH. It is reasonable to expect that protonation would enhance excimer emission in P(2IPN-*a*-MAn) by one or more of three mechanisms:

(a) A shrinking of coil dimensions could lead to the formation of ground-state naphthalene–naphthalene dimers, which could be directly excited. Such associations would not necessarily be detectable in the absorption spectrum but should contribute to the excitation spectrum.

(b) If preformed excimer sites existed at every pH, then they could serve as energy traps for excitation. As the macromolecule becomes more compact with decreasing pH, singlet energy migration could be enhanced and the probability of populating these preformed sites would increase.

(c) The collapse of the coil brings the pendant chromophores into closer proximity, thus enabling the 3-Å face-to-face geometry required for excimer formation to be attained during the lifetime of the singlet.

In order to distinguish between these schemes, the excitation spectra for fluorescence in the monomer and excimer regions were examined. If the excimer emission derives from dynamically formed excimers or from electronic energy migration to a preformed site, then these spectra should be identical. For each pH, however, the excimer excitation spectrum is red shifted several nanometers from that for the monomer, implying that some of the excimers are statically formed.

To determine whether additional excimer formation was dynamic, the room-temperature fluorescence was compared with that for 77 K. Thin quartz ESR tubes were used so that the solutions could be frozen rapidly. The ice samples are highly scattering but can be used with care.

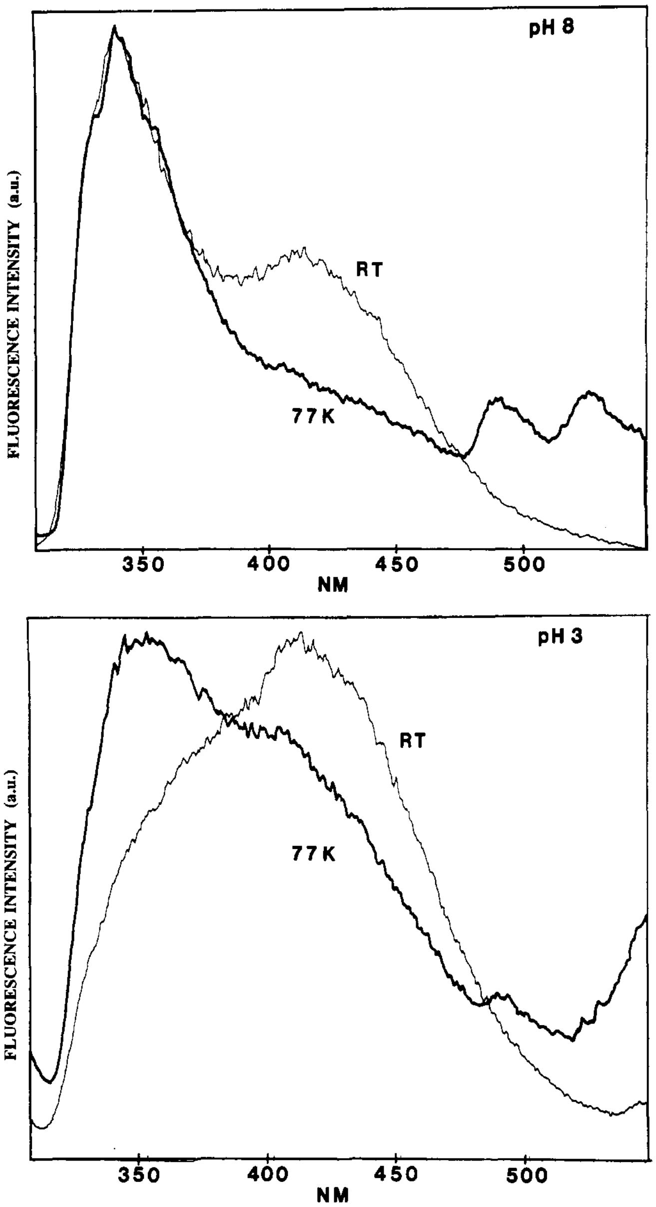

Figure 3. Comparison of room-temperature and 77 K fluorescence spectra for pH 8.0 and 2.9. Note phosphorescence at long wavelengths for the 77 K spectrum.

At this temperature, bond rotations are sufficiently slowed to prohibit excimer formation except by direct excitation or energy transfer to excimer-forming sites. As can be seen in Figure 3, the excimer fluorescence is diminished at 77 K but is not absent. Furthermore, the pH effect on the monomer/excimer ratio persists at 77 K. For most polymers, excimer fluorescence is absent in low-temperature organic glasses (an exception is P2IPN[18]) and the persistence of the excimer component in the present case is undoubtedly the result of the importance of the hydrophilic naphthalene–naphthalene interaction. It is not possible to carry out absorption spectra on these 77 K opaque glasses, so we cannot determine if any appreciable fraction of the excimer fluorescence is due to ground-state dimer excitation.

Monomer and excimer fluorescence decay curves were obtained for pH 10 and 3 room-temperature solutions. None of the decay profiles could be fit to a single-exponential function. Table II gives the multiexponential fitting parameters together with the average lifetime defined by $\tau = \sum a_i\tau_i$. In general, there is a tendency for both the long and short lifetime components to shorten upon lowering the pH. As the coil collapses, self-quenching

Table II
Fluorescence Decay Parameters for P(2IPN–MAA) Copolymer

	I_m[a]				I_e[b]			
pH	τ[c]	τ_1/A_1	τ_2/A_2	τ_3/A_3	τ	τ_1/A_1	τ_2/A_2	τ_3/A_3
10.3	20.0	6.8/0.47	31.8/0.53	d	14.8	5.7/0.72	25.7/0.21	71.4/0.07
6.9	13.7	2.3/0.56	17.6/0.31	55.1/0.13				
4.0	7.7	2.1/0.62	10.4/0.30	40.8/0.08	8.3	4.9/0.84	21.3/0.14	49.9/0.02
3.6	7.3	1.7/0.55	6.9/0.35	27.3/0.10	8.0	4.5/0.82	18.2/0.14	43.8/0.04
3.2	6.8	2.8/0.28	4.1/0.61	23.0/0.11	7.3	5.2/0.92	31.7/0.08	d

[a] Monomer emission collected at 340 nm. [b] Excimer emission collected at 400 nm. [c] $\tau = \sum a_i \tau_i$. [d] Adequate two-exponential fit.

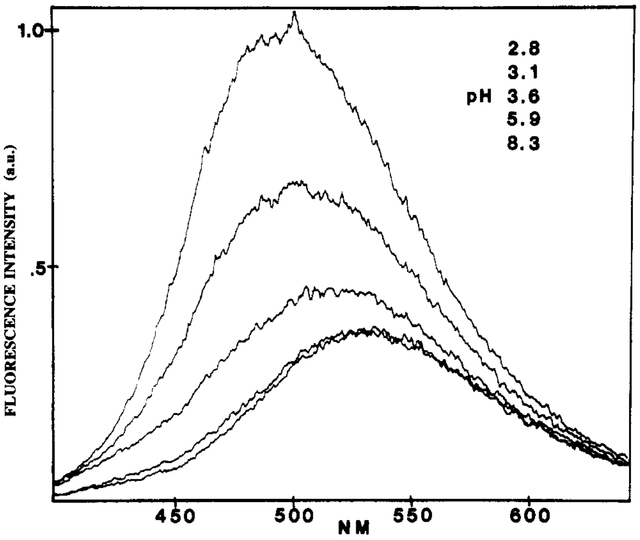

Figure 4. Emission spectra of probe molecule 1,8-anilinonaphthalene sulfonate (ANS) in an aqueous solution of P(2IPN-α-MAA) as a function of pH. Excitation wavelength: 356 nm.

implies a shorter monomer lifetime, but it is not obvious why the excimer lifetime decreases. Emission from preformed defect sites might be expected to be longer lived than dynamically formed excimers having a less stable orientation geometry. In agreement with previous studies on related systems, there was no observed rise component for the naphthalene excimer within the temporal resolution of the instrument.[1g,8]

Fluorescent Probe Study. 1,8-ANS is a well-known fluorescent probe, which is highly wavelength and intensity sensitive to hydrophobicity of the microenvironment.[19] The emission spectrum of 1,8-ANS in water has been found to be pH independent, making it an ideal molecular spy for the present system. Treloar has used ANS to study the conformational transition of poly(methacrylic acid), noting a strong correlation of the degree of ionization with fluorescence intensity.[20] A solution of 0.5 mg/mL of P(2IPN-α-MAA) and 0.06 mM ANS was prepared. This corresponds to ca. one probe molecule per chain (based on polystyrene-based GPC calibration curves). The emission spectrum was recorded with excitation at 356 nm, such that no polymeric naphthalene was excited, and probe emission could not be sensitized. At high pH, ANS is expected to remain in the bulk solution due to charge repulsion, and the spectrum resembles that of ANS in pure water. As the polymer is protonated, the ANS begins to be incorporated into the collapsing coil and associates with the naphthalene clusters. The increased degree of hydrophobicity enhances and blue shifts the emission, as shown in Figure 4. The probe fluorescence reflects the sharp collapse of the coil, as the intensity increases by ca. 25% over the pH range 8.3–3.6 and then increases by an additional 140% on lowering to pH 2.75.

Fluorescence Quenching by Copper(II) Ions. Fluorescence quenching by copper(II) ions was studied as a function of pH and polymer concentration. Figure 5 shows examples of Stern–Volmer plots for pH 8 and 3. Emission was monitored at 342 nm. As has been observed for other polyelectrolyte-bound fluorophore systems, the quenching is highly efficient, and with second-order rate constants well in excess of diffusion-controlled values.[1f–h] This can be attributed to the combined effects of electrostatic quencher–polymer attraction and facile energy migration between chromophores.

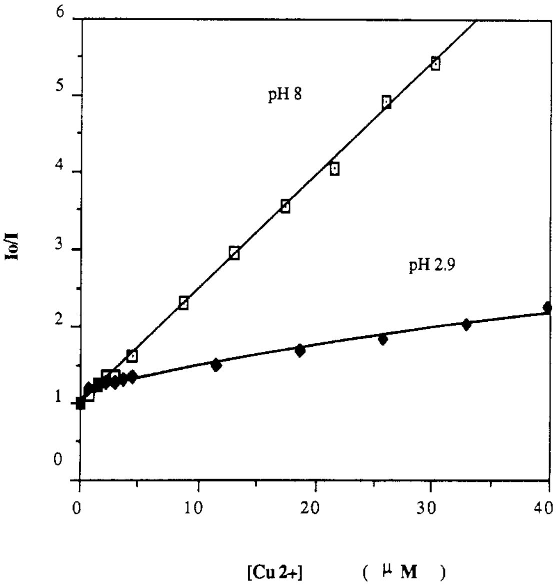

Figure 5. Stern–Volmer quenching plots for pH 8 and 2.9. Polymer concentration: 0.01 mg/mL.

In basic solution at higher polymer concentrations, the Stern–Volmer plots exhibit a slight degree of upward curvature, similar to P(2VN-α-MAA).[1g] It is possible that with increased Cu^{2+} concentration the coil is perturbed. However, it should be noted that addition of NaCl up to 0.01 M did not alter the steady-state emission spectrum of the polymer at pH 8, so ionic strength effects do not seem to be important in this concentration range. A modified Stern–Volmer plot of I_0/I versus the ratio $[Cu^{2+}]/[Naph]$ for pH 8 was constructed for several polymer concentrations. It was found that K_{SV} increases with decreasing polymer concentration. If a simple "condensation" model were appropriate, these curves should coincide.[1a] At pH 8, the addition of copper(II) ions caused a slight shortening of the average fluorescence decay time, but the lifetime quenching constant was much less than the intensity quenching constant (Figure 6). This implies significant static quenching, with the copper and naphthalene forming a stable contact complex whose excitation is immediately extinguished.

At low pH, the quenching is much less efficient and shows a curious saturation effect for both steady-state and time-dependent quenching (Figure 6). By use of the average decay time determined from single-photon-counting experiments, k_q was determined to be ca. 7.7×10^{11} M^{-1}

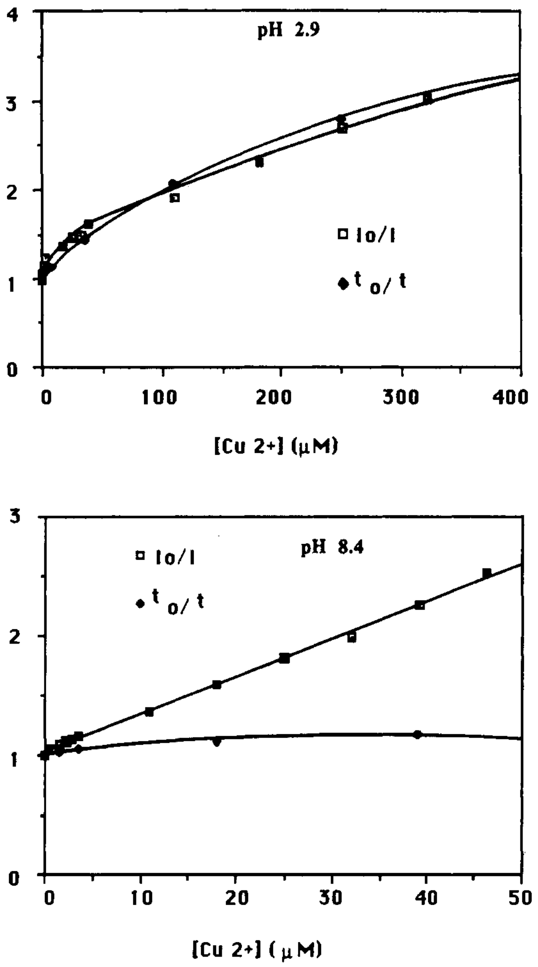

Figure 6. Steady-state and lifetime quenching plots for pH 8.4 and 2.9. Polymer concentration: 0.1 mg/mL.

s^{-1}. This compares to (1.5–9) × 10^{12} M^{-1} s^{-1} for the high-pH case. This decreased rate of quenching can be attributed to the negligible attraction of the cationic copper species to the now fully neutralized backbone. The diminished Cu^{2+} binding could be partially compensated by the enhanced singlet energy diffusion with decreased coil dimensions. Figure 6 shows that the lifetime shortening is roughly commensurate with the intensity quenching, indicating a dynamic process.

The results from dynamic light scattering studies indicated that the onset of polymer aggregation was pH and concentration dependent. The generation of aggregates would present two distinct types of chromophores with different characteristic quenching rates, those with readily accessible surface sites and protected inner sites. This would account for the saturation seen in the low-pH Stern–Volmer plots and is supported by the fact that these plots show more pronounced negative curvature with increasing polymer concentration and, hence, degree of aggregation. (It should be pointed out that, while the concentrations used in the quenching study were below those for which aggregation was observed via light scattering, the solutions were ca. 1 pH unit more acidic, and for the most concentrated samples, the solutions were slightly turbid.)

Energy Transfer to Anthracene. Several studies have been reported that utilize anthracene as an energy trap in polymeric naphthalene systems.[21] Some systems of this type have been found to be highly efficient, funneling more than 50% of the absorbed excitation to the trap. This efficiency has been attributed to energy migration between identical naphthalene chromophores and the relatively large Forster radius for naphthalene to anthracene energy transfer. In an attempt to learn more about the coil structure and the role of energy migration in the present system, anthracene was employed as an intrinsic and extrinsic energy trap.

Quenching of naphthalene emission by the addition of a DMF solution of anthracene proved to be efficient and highly pH dependent. Stern–Volmer constants for pH 10 and 3 were found to be 2 × 10^2 and 3 × 10^4, respectively. The high pH value is consistent with approximately diffusion-controlled quenching, while the drastically enhanced quenching in acidic solution may indicate the greater ability of the fully neutralized polymer to micellize the hydrophobic small molecule.

9-Anthraceneethanol was reacted with the anhydride form of the polymer to yield an alternating copolymer with 0.9 mol % anthracene (relative to naphthalene). With the energy trap thus covalently bound to the polymer backbone, the local concentration of quencher is fixed, and the effect of energy migration along the chain can be observed.

The energy-transfer quantum efficiency χ can be interpreted as the fraction of photons absorbed by donor naphthalene that localize as excitation on the acceptor anthracene. χ was determined by deconvoluting the polymer emission and excitation spectra into anthracene small-molecule and P(2IPN-*a*-MAA) components. The fractional contributions of each are determined as f_a and f_n, respectively, and we define $r = f_a/f_n$. It can be shown that $\chi = r^{em} - r^{exc}/r^{em} + 1$.[22] Transfer efficiencies were found to increase steadily from 0.57 at pH 8.3 to 0.79 at pH 2.9.

This increase in χ is consistent with a collapsing coil structure in which the average chromophore separation, both naphthalene–naphthalene and naphthalene–anthracene, is diminished, thus facilitating down-chain migration and single-step Forster transfer.

Discussion

Alternating copolymers can be viewed as homopolymers constructed from the appropriate difunctional monomer. In some respects, then, alternating copolymers represent a well-characterized molecular skeleton upon which to investigate photophysical phenomena. It is well-known, however, that equimolar composition is not always achieved, and perfect alternation is difficult to prove experimentally. It has become apparent, furthermore, that the photophysical response of these types of systems may be strongly influenced by those portions of the polymer backbone that depart from ideality, so-called "defects". Excimer formation is known to occur at both adjacent and non-nearest-neighbor chromophores.[23] For a perfectly alternating copolymer, nearest-neighbor excimer formation is necessarily eliminated. If, however, there are defects along the backbone, which lead to a naphthalene–naphthalene diad, this could serve as an excimer site similar to those in a 2VN homopolymer,[18] for which excimer emission is dominant, or P2IPN, which exhibits excimer fluorescence exclusively.[24] Morishima et al. have recently shown that the excimer-to-monomer ratio increases rapidly with the fraction of vinylnaphthalene in the feed for P-(2VN-*a*-MAn).[8] Presumably, this is due to the increased propensity for 2VN–2VN propagation or termination with increasing concentration.

The consecutive naphthalene–naphthalene diad fractions were calculated by Morishima et al. from the following equation: $F_{11} = r_1\beta/(2 + r_1\beta + r_2/\beta)$, where r_1 and r_2 are the reactivity ratios for 2IPN and MAn, respectively, and β is the molar ratio of monomers in the feed, [2IPN]/[MAn].[25] In the present study, β was varied from 0.25 to 4.9 and the corresponding F_{11} values ranged from

1% to 18%. The polymer whose photophysical properties are reported was found to contain 52 mol % naphthalene, and F_{11} was calculated as 3%. GPC molecular weight estimates imply ca. 35 alternating repeat units (70 monomers) per coil. Thus, each chain contains on average two naphthalene defects and one maleic anhydride defect.

It is proposed that these naphthalene defects can act as preformed excimer sites which are populated by efficient down-chain energy migration. R_0 for 2-methylnaphthalene–2-methylnaphthalene self-transfer is 11.4 Å,[26] a far less restrictive distance than the 3-Å separation that is required for excimer formation. Computer modeling of different conformations indicated that the naphthalene-to-naphthalene center distance varies from 5 to 10 Å. If the average chromophore spacing were 8 Å for the fully ionized form at high pH, then according to random walk theory, we would expect that the excitation would make only ca. 10 hops down the chain within its lifetime.[27] Assuming that only nearest-neighbor transfer is possible, this represents ca. 25% probability that excitation will migrate to an excimer trap. For low pH, however, the average spacing may decrease to ca. 5 Å as the coil collapses. Under these conditions, the average number of hops is in excess of 200, sufficient to provide a sampling of nearly the entire backbone (recall that the net displacement in a random walk process is proportional to the square root of the number of steps). The fluorescence spectrum is thus drastically altered as the probability of trap sensitization approaches unity.

Energy migration to preformed excimer sites is apparently not the only pathway giving rise to excimer emission, however. The comparison of excitation spectra in the excimer and monomer regions indicated that a small fraction of the lower energy emission derives from red-shifted chromophores which do not contribute to the monomer fluorescence. It is reasonable to assume that the defects, which comprise ca. 10% of the total chromophores, are responsible for such absorption. In addition, there may be a component of excimer fluorescence that arises from the classical dynamic mechanism. This was suggested by the observation that for all pHs the excimer intensity decreased upon going from a room-temperature solution to a 77 K glass. Alternatively, this could be the effect of thermodynamically disfavored excimer sites. Excimers could be formed dynamically from isolated neighboring naphthalenes or from chromophores that are remote from each other along the chain sequence but are brought into close contact because of a collapsed or folded macromolecular conformation. This latter mode is operative for excimer formation in acenaphthalene-containing polymers.[7]

Regardless of the exact mechanism, it is obvious that defect sites will promote excimer emission most effectively. Alexandru and Somersall recognized this in a 1977 paper that reported that the degree of alternation of a styrene–acrylonitrile copolymer was highly correlated with the excimer-to-monomer emission ratio for the phenyl group.[28] It was assumed that the probability of excimer formation between isolated chromophores was negligibly small compared to that between what we term "defect" chromophores. This assumption could break down in a poor solvent such as the acidic water used for the present system.

While model studies would be required in order to quantify the efficiency of energy migration, copper-quenching and anthracene-sensitization experiments present possible additional evidence for such a process. The upper limit on χ can be predicted for the case of no energy migration if the appropriate model is chosen. If we assume a nearly rigid rod conformation at high pH and an R_0 for 2-methylnaphthalene–anthracene transfer of 24.6 Å,[26] than the maximum quantum efficiency of transfer is given by summing the joint probabilities for excitation of a given naphthalene and single-step Forster transfer to the trap over the entire coil. Assuming only fluorescence and transfer as deactivation pathways, the probability of energy transfer is given by $P(R) = (R_0/R)^6/(R_0/R)^6 + 1$, where R is the intermolecular separation. Assuming an 8-Å naphthalene–naphthalene separation, χ was calculated to be 0.17. This compares with the experimentally determined value of 0.57, which supports our contention that energy migration between naphthalene moieties does occur. The unidimensional extended-rod model is strictly required only for a radius of ca. $2R_0$ about the trap, and this appears to be reasonable for a polyanion. Increased efficiency at lower pH can be ascribed to a combination of enhanced migration and sensitization as the overall coil dimensions are reduced. These conclusions will be tested by more extensive modeling in the future.

The method of comparative fluorescence quenching has been utilized by several workers in order to quantify energy migration rates in polymers where the quenching occurs more rapidly than the diffusion-limited maximum. While such a study was not done for the present system, the highly efficient quenching that was observed does provide evidence for energy migration between like chromophores. At high pH, where k_q was ca. 5×10^{12} M^{-1} s^{-1}, the situation is complicated by the fact that the copper(II) cations are expected to electrostatically bind to the anionic backbone of the polymer. Thus, the effective quencher concentration local to the naphthalenes is much higher than the analytical concentration.

At low pH, it is expected that the binding of the copper(II) ions to the protonated carboxylic acid groups is diminished. The rate of quenching, however, is still characterized by second-order rate constants which are roughly 2 orders of magnitude in excess of those for a purely diffusional process. In addition to very large initial slopes, the low-pH Stern–Volmer plots exhibit a downward curvature similar to that observed by Morishima for amphiphilic phenanthrene-containing copolymers in aqueous solution.[29] These workers presented a kinetic model based upon a multistep equilibrium for the binding of amphiphilic quenchers to the hydrophobic microdomains, including contributions from both static and dynamic quenching processes. Further studies are required to fully understand the interesting quenching behavior observed here, but a modified version of this model might be expected to apply.

Conclusions

It was originally presumed that P(2IPN-*a*-MAA) could be compared with P(2VN-*a*-MAA) in order to learn what effect, if any, the extra methyl substituent on the backbone would have on the solution behavior and photophysics. It became apparent, however, that this subtle monomer variance was masked by differences in polymer sequence distributions. It is thus suggested that direct photophysical comparisons of nominally alternating copolymers proceed with caution. The aqueous solution fluorescence spectrum of P(2IPN-*a*-MAA) showed a mixture of monomer and excimer emissions at high pH and shifted to nearly exclusively excimer emission below pH 4.5. It was proposed that consecutive naphthalene diads served as preformed excimer sites and that down-chain energy migration to these defects was highly efficient.

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Organosilylphosphazene Oligomers and Polymers: Synthesis via (Lithioaryloxy)phosphazenes[1]

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ABSTRACT: (Lithioaryloxy)phosphazenes have been used as reaction intermediates for the synthesis of phosphazenes that bear organosilicon side groups. The synthetic pathways were developed at two levels, first with the use of small-molecule cyclic phosphazenes as reaction models and second with high polymeric phosphazenes. The cyclic small molecule $N_3P_3(OPh)_5OC_6H_4Br$-*p* was first lithiated to $N_3P_3(OPh)_5OC_6H_4Li$-*p*, and this compound was allowed to react with a range of organochlorosilanes or with hexamethylcyclotrisiloxane to yield the species $N_3P_3(OPh)_5OC_6H_4R$-*p*, where R is $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiMe_2CH{=}CH_2$, $SiMe_2(OSiMe_2)_2OSiMe_2Bu$, and $SiMe_2(OSiMe_2)_2OSiMe_3$. At the high polymer level, the macromolecule $[NP(OC_6H_4Br)_2]_n$ was subjected to partial lithiation followed by coupling to chlorosilanes or to ring-opening addition of $(OSiMe_2)_3$ to generate polymers with OC_6H_5 and OC_6H_4Br-*p* side groups as well as OC_6H_4R'-*p* units, where R′ is $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, or $SiMe_2(OSiMe_2)_2OSiMe_3$. Molecular structural characterization was obtained by NMR, IR, microanalytical, and mass spectrometric methods. Glass transition temperatures for the high polymers were in the range +45 to −68 °C.

The synthesis of new macromolecules derived from the inorganic elements provides opportunities for the extension of both polymer chemistry and inorganic chemistry into fields as diverse as solid-state science, electronics research,

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