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Dimensions of Polyelectrolytes Using the "Spectroscopic Ruler". 2. Conformational Changes of Poly(methacrylic acid) Chains with Variation in pH

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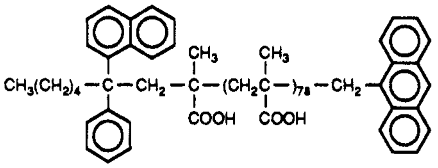
ABSTRACT: Conformational changes of poly(methacrylic acid) (PMAA) chains as a function of the degree of backbone ionization have been monitored by using three energy donor-acceptor pairs of different critical energy-transfer distances, R_0. The trends observed from this technique are compared with results from previous studies.

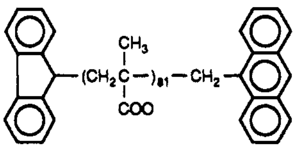
I. Introduction

Changes in conformation of poly(methacrylic acid) (PMAA) as a function of the degree of PMAA backbone ionization, α, in dilute aqueous solutions have been probed by using various experimental techniques.[1] These include viscometry measurement,[2-6] potentiometric titration,[7-11] UV photometric studies,[7,12,13] small-angle neutron scattering,[14-16] studies of the solubilization of hydrophobic molecules in aqueous PMAA coils,[17-19] and light scattering.[20] Previous results have indicated that PMAA chains exist as hypercoils[1] at a low degree of ionization, $\alpha < 20\%$. In these hypercoils, most of the methyl groups, due to hydrophobic interactions, are in the interior, providing nonpolar cores for the solubilization of hydrophobic molecules. At a high degree of ionization and low ionic strength, PMAA samples of low molecular weights, ~10 000, are generally believed to possess planar zigzag structures.[1] However, conflicting experimental results are obtained concerning the behavior of PMAA at a high degree of ionization. Moan et al.,[5] for example, measured the radius of gyration, R_G, of a PMAA sample with $M_v = 1.3 \times 10^4$ at 10% ionization and a polyelectrolyte concentration of 1.0×10^{-2} g/mL from a neutron-scattering experiment. The value was found to be 88 Å, close to the 100-Å radius of gyration calculated for a fully stretched chain. Plestil et al.,[15] carried out a neutron-scattering experiment for a PMAA sample with an average molecular weight (M_w = 23 000, PD = 1.2) almost twice as high as that used by Moan et al.[5] and obtained a R_G value of 66.8 Å at $\alpha = 100\%$ and a similar ionic strength.

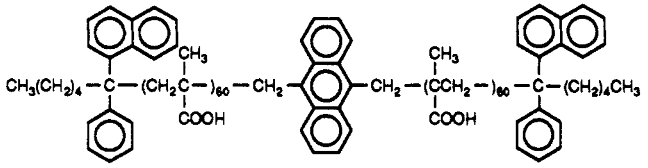
The present study employs the "spectroscopic ruler" technique, developed by Förster[21] and then modified by us,[22,23] to monitor the variation in root-mean-square end-to-end distances of PMAA chains as a function of α. Three polymers were used: PMAA labeled with naphthalene and anthracene groups (N-P-A), PMAA labeled with fluorene and anthracene end groups (F-P-A), and PMAA labeled at the two ends with naphthalene groups and in the middle with an anthracene group (N-P-A-P-N). The purpose of this study is 3-fold. (1) It extends the use of the technique developed previously[22,23] to a new system. The use of different donor-acceptor pairs with varying R_0 values would provide further confirmation of the validity the spectroscopic ruler technique. (2) It may help to gain insight into the PMAA conformational behavior. (3) It may provide evidence for the decreased separation distances between the hydrophobic end groups at a low α value. Our samples possess hydrophobic end groups and are similar in structure to those PMAA samples containing porphyrin and quinone groups, which were synthesized for electron-transfer reaction studies.[24] According to Guillet et al.,[24] because of ground-state hydrophobic interaction between porphyrin to quinone groups, electron donation from excited-state porphyrin to ground-state quinone was very efficient despite the fact that on the average they were separated by 30 methacrylic acid repeat units.



N-P-A



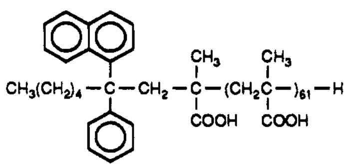
F-P-A



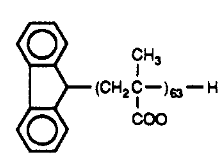
N-P-A-P-N

II. Experimental Section

Synthesis of the Polymer. N-P-A, F-P-A, N-P-A-P-N, N-P-H, and F-P-H were all synthesized by using anionic polymerization.[25] N-P-H is PMAA labeled at one end with a naphthalene group, and F-P-H is PMAA end-labeled with a fluoryl group. To synthesize N-P-A, for example, equal moles



N-P-H



F-P-H

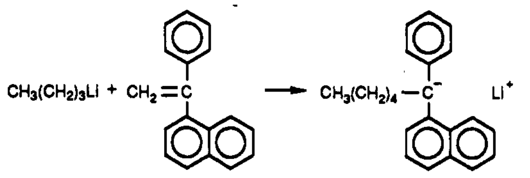
0024-9297/91/2224-0068$02.50/0

Table I
Characterization of the Polyelectrolyte Samples

sample	$\bar{M}_w \times 10^{-4}$ GPC	$\bar{M}_n \times 10^{-4}$ GPC	UV[a]	NMR[b]	$\bar{n}$ MB[c]	GPC[d]	UV	NMR	av	T, % UV	NMR	av	$\bar{M}_w/\bar{M}_n$ GPC
N-P-A	1.11	0.89	0.74	0.72	100	98	80	78	79	96	93	94	1.25
F-P-A	1.04	0.95	0.71	0.74	100	106	80	82	81	57	63	60	1.09
N-P-A-P-N	1.37	1.09	1.16	1.07	50	60	62	57	60	-	96	96	1.25
N-P-H					60			62					
F-P-H					60			63					

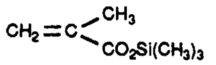
[a] Error ca. ±3%. [b] Error ca. ±5%. [c] Calculated from the concentration ratio of monomer to initiator used for polymerization. [d] Error ca. ±10%. [e] Difficult to estimate.

of butyllithium and 1-phenyl-1-α-naphthylethyl were reacted in dry THF in the absence of O_2 to yield the initiator



(1)

The initiator reacts with trimethylsilyl methacrylate (1)[26] to initiate the polymerization.


$CH_2{=}C(CH_3)CO_2Si(CH_3)_3$
1

Polymerization was terminated with 9-(bromomethyl)-anthracene. The polymer obtained was hydrolyzed in methanol to yield PMAA. To purify the polymer, the sample was dissolved in methanol, precipitated from methylene chloride or pentane, and dried under reduced pressure for 2 days.

F-P-A was synthesized by using lithium fluorene to initiate the polymerization. N-P-A-P-N was synthesized using equal moles of butyllithium and 1-phenyl-1-α-naphthylethylene as initiator and 9,10-bis(bromomethyl)anthracene as the terminator.

NMR Characterization of the Polymers. All NMR spectra were obtained by using a Varian XL-400 spectrometer. Approximately 20 mg of sample was used for each measurement. All samples were dissolved in deuterated methanol. Two hundred or more pulses were required to get an acceptable signal-to-noise ratio.

The number-average number of repeat units, $\bar{n}$, or molecular weight, $\bar{M}_n$, of each sample was determined by using the NMR peak area ratios between the aromatic group protons and the backbone protons. Some proton peaks of two different aromatic end-group chromophores in each sample were well resolved. From the peak area ratios of these peaks, the termination efficiencies could be determined. The number-average number of repeat units, $\bar{n}$, for N-P-A, F-P-A, N-P-A-P-N, N-P-H, and F-P-H are 78 ± 4, 82 ± 4, 57 ± 3, 62 ± 2, and 63 ± 2, respectively (Table I). The termination efficiency for N-P-A is 93 ± 4%, and the corresponding values for F-P-A and N-P-A-P-N are 63 ± 3% and 96 ± 5%, respectively.

UV Characterization. All UV spectra were recorded on a Hewlett-Packard 8451 diode array spectrophotometer. N-P-H was used as the model compound for the naphthyl group in N-P-A and N-P-A-P-H. F-P-H was used as the model compound for the fluorene group in F-P-A. 9-Methylanthracene was used as the model compound for the anthryl groups in all samples. Absorption peak shapes of 9-methylanthracene are assumed to resemble those of the anthryl groups in N-P-A, F-P-A, and N-P-A-P-N, while the absolute values of the extinction coefficients and the positions of maxima can be different.

The extinction coefficients of N-P-H and F-P-H were determined by measuring the absorbance of these solutions at known concentrations. In methanol, the extinction coefficient of N-P-H at its absorption maximum, λ = 284 nm, is 7.2×10^3 (M cm)$^{-1}$. The extinction coefficients of F-P-H at 292- and 302-nm maxima are 4.1×10^3 and 5.5×10^3 (M cm)$^{-1}$, respectively. The extinction coefficient of 9-methylanthracene at wavelength λ, $\epsilon(\lambda)$, in methanol was determined in a similar fashion. According to previous assumptions, $\epsilon(\lambda)$s are related to those of the anthryl groups in the three polymers $\epsilon'(\lambda)$ by

Table II
Extinction Coefficients of 9-Methylanthracene

wavelength, nm	$\epsilon \times 10^{-3}$, (M cm)$^{-1}$	wavelength, nm	$\epsilon \times 10^{-3}$, (M cm)$^{-1}$
284	0.34 ± 0.01	366	8.4 ± 0.3
348	5.4 ± 0.2	386	8.0 ± 0.3

$$\epsilon'(\lambda+L) = a\epsilon(\lambda) \qquad (2)$$

where L represents the red shift in the absorption spectra of the anthryl group in each polymer relative to that of 9-methylanthracene and a is the reduction factor in the extinction coefficients of anthryl groups in polymers relative to those of 9-methylanthracene. The extinction coefficients of 9-methylanthracene at selected wavelengths are summarized in Table II.

In Figure 1, the UV absorption spectrum of N-P-A in methanol is compared with those of N-P-H and 9-methylanthracene. The absorption maxima of the anthryl group in N-P-A are red-shifted by 2 nm relative to those of 9-methylanthracene, i.e., L = 2 nm, but the shape of the absorption envelopes are similar. As an approximation, it is assumed that the extinction coefficients of the anthryl group in N-P-A are equal to those of 9-methylanthracene; i.e., $\epsilon'(\lambda+2) = \epsilon(\lambda)$. Figure 1 (curve a) is a UV absorption spectrum of N-P-A obtained by superimposing that of a 0.94×10^{-4} M solution of 9-methylanthracene on that of 1.01×10^{-4} M of N-P-H. Different concentrations of N-P-H and 9-methylanthracene were used to correct for the 93% termination efficiency (determined from NMR measurement) for the N-P-A sample. In comparison with the experimentally observed absorption spectrum (Figure 1, curve d), the agreement between curves a and d is good. Exact calculations, however, indicate that a termination efficiency of 96% is required to generate N-P-A absorption curves from those of N-P-H and 9-methylanthracene. A termination efficiency of 93% determined from NMR measurement and that of 96% from UV measurement match one another within experimental error. The assumption $\epsilon'(\lambda+2) = \epsilon(\lambda)$, therefore, holds in methanol. From UV end-group concentration determination, the number-average molecular weight for N-P-A is 0.74×10^4.

Following the same methodology, the termination efficiency in F-P-A was found to be 60% and $\bar{M}_n = 0.71 \times 10^4$. $\bar{M}_n$ for N-P-A-P-N determined from naphthyl end-group concentration is 1.16×10^4. Since NMR was used to determine the termination efficiency for this sample, the extinction coefficients of the anthryl group could be estimated from the intensities of the absorption peaks of the anthryl group relative to that of the naphthyl groups. In methanol, the reduction factor, a, is 0.63 or

$$\epsilon'(\lambda+6) = 0.63\epsilon(\lambda) \qquad (3)$$

Energy-transfer efficiencies between the chromophores of the polymer samples were determined in aqueous solutions. The extinction coefficients of the anthryl group in each polymer in water at even wavelengths, $\epsilon'(\lambda)$, are required for calculating the J-integral (see below). In water, the extinction coefficients of the anthryl group in N-P-A-P-N are related to those of 9-

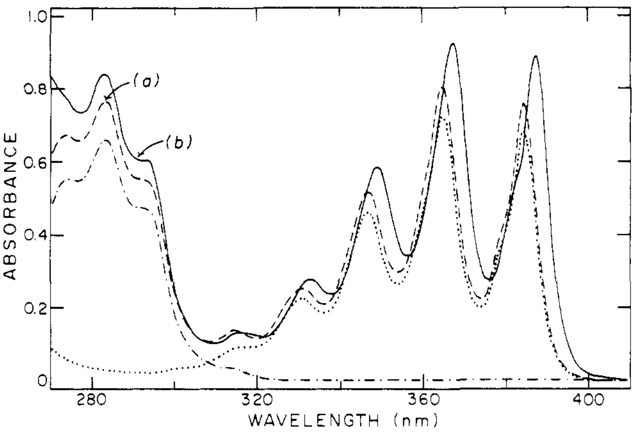


Figure 1. UV absorption spectrum for N-P-A (- - -) in methanol obtained from that of N-P-H (– • –) superimposed on that of 9-methylanthracence (• • •). (—) Absorption spectrum experimentally obtained for a 1.08 × 10^{-4} M N-P-A sample.

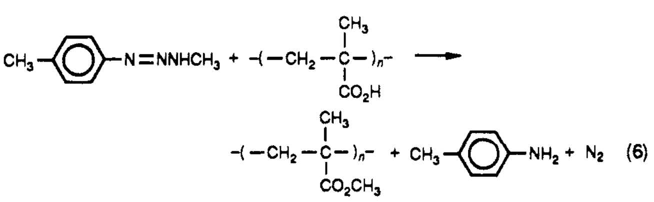
methylanthracene dissolved in methanol by

$$\epsilon'(\lambda+12) = 0.50\epsilon(\lambda) \tag{4}$$

In water or a solution of 0.1 N NaCl, the expression relating the extinction coefficients of the anthryl group in N-P-A and F-P-A and those of 9-methylanthracene dissolved in methanol is given by

$$\epsilon'(\lambda+4) = 0.82\epsilon(\lambda) \tag{5}$$

Esterification of PMAA. N-P-A, F-P-A, and N-P-A-P-N were esterified prior to GPC measurement by use of 3-methyl-*p*-tolyltriazene, a safe and clean methylating reagent recommended by Blumstein et al.:[27]

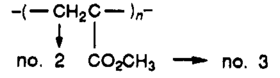


(6)

A typical experiment was performed as follows. 3-Methyl-1-*p*-tolyltriazene (0.35 g) was added to 0.20 g of end-labeled PMAA suspended in 5 mL of benzene. The mixture was brought to 40 °C, and 0.1 g of 3-methyl-1-*p*-tolyltriazene was added every 8 h. The reaction was terminated when nitrogen bubbles no longer evolved after addition of 3-methyl-1-*p*-tolyltriazene. Four days were usually required to complete the esterification.

p-Tolylamine was extracted from the reaction mixture by using dilute hydrochloric acid. The organic phase was dried over potassium sulfate, concentrated, and precipitated from methanol. After two precipitations, 0.045 g of product (yield = 20%) was obtained.

The NMR spectrum of esterified N-P-A-P-N is shown in Figure 2. The peak assignments are as follows:



$$-(-\overset{\overset{\text{no. 2}}{\uparrow}}{CH_2}\overset{\overset{CH_3 \rightarrow \text{no. 1}}{|}}{\underset{\underset{CO_2CH_3 \rightarrow \text{no. 3}}{|}}{C}}-)_n-$$

Assignments: δ 0.8–1.0 (two peaks, 3 H, protons no. 1, area = 5.34); δ 1.8–2.0 (band, 2 H, protons no. 2, interfered by solvent peaks); δ 3.58 (s, 3 H, protons no. 3, area = 5.36). The triplet at δ 1.2, the singlet at δ 2.0, and the quartet at δ 4.06 are from ethyl acetate. The sample was prepared in ethyl acetate for GPC analysis and subsequently dried for NMR analysis. The ratio between the areas of the peak at δ 3.58 and the band at δ 0.8–1.0 approaches unity. The esterification is quantitative, as determined by NMR.

GPC Characterization. Molecular weights and molecular weight distributions for N-P-A, F-P-A, and N-P-A-P-N were determined by using a Waters high-pressure liquid chromatography equipped with Waters Ultrastyragel columns (10^4, 10^3, and 500 Å). The columns were calibrated in ethyl acetate by using monodisperse PMMA standards (Polymer Laboratories; $M_w/M_n < 1.10$) in the 2400–60 000 MW range. The calibration curve is given by

$$\ln M_p = -0.4187t + 19.34 \tag{7}$$

where t is the retention time. The molecular weights and polydispersity for each sample are presented in Table I. The GPC chromatograms are shown in Figure 3.

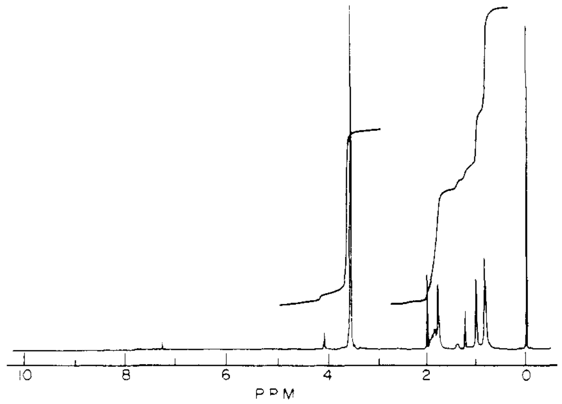


Figure 2. NMR spectrum for esterified N-P-A-P-N.

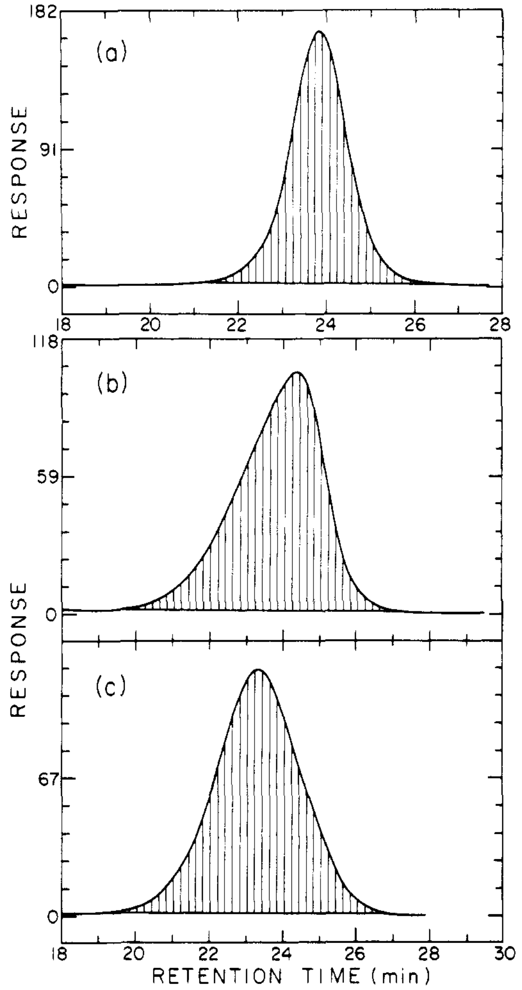


Figure 3. GPC chromatogram of esterified samples: (a) F-P-A; (b) N-P-A; (c) N-P-A-P-N. Mobile phase, ethyl acetate; flow rate, 1 mL/min; calibration curve, $\ln M = -0.4187t + 19.34$, where t is retention time in minutes.

Measurement of E, the Energy-Transfer Efficiency, as a Function of pH or α. The pH value for each sample was

Table III

End-to-End Distances R_{nG} Fitted at Different pH

pH	α, %	E, %	β, Å	R_{nG}, Å
		N–P–A ($\bar{n}$ = 79)		
2.00	0.26	80	0.95	11.9
3.93	2.6	80	0.95	11.9
5.15	10.1	79	0.96	12.1
5.66	17.2	74	1.05	13.2
6.44	34.4	71	1.10	13.8
6.92	48.2	58	1.32	16.6
7.21	56.8	34	1.88	23.6
7.45	63.7	15.2	2.80	35.2
7.66	69.2	6.2	4.10	51.5
8.69	88.5	2.07	6.2[a]	78
10.98	99.2	2.11	6.1[a]	77
		F–P–A ($\bar{n}$ = 81)		
1.92	0.24	92	0.62	7.9
3.81	2.2	92	0.62	7.9
5.11	9.7	88	0.69	8.8
5.44	13.7	86	0.73	9.3
6.14	26.9	75.4	0.88	11.2
6.44	34.4	55.9	1.17	14.9
6.77	43.8	19.0	2.14	27.2
7.58	67.2	1.50	5.8[a]	74
8.67	88.2	1.21	6.3[a]	80
10.48	98.5	1.11	6.4[a]	82
		N–P–A–P–A ($\bar{n}$ = 60)		
2.00	0.26	30.0	2.16	23.2
3.88	2.4	29.0	2.20	24.1
5.38	12.9	25.9	2.34	25.6
6.42	33.9	22.5	2.51	27.5
6.98	50	15.6	3.00	32.9
7.19	56.2	9.6	3.70	40.5
7.40	62.3	3.3	5.64	62
8.52	86.3	0.36	[b]	
10.76	98.9	0.44	19[b]	208

[a] Errors may result from too high β values. [b] The contour length is 164 Å. The considerably higher value observed is probably caused by experimental error, since the E values are too low and a small change in E values corresponds to a drastic change in β value. The β values fitted suggest a planar zigzag conformation. Error is therefore also expected due to the assumption of a Gaussian form for the end-to-end distance distribution function.

monitored by using a digital pH meter (Corning pH/ion meter Model 150). For pH adjustment, 0.1 N NaOH and HCl solutions were used.

Experiments have shown that the degree of dissociation, α, of a polyacid can be described by[28]

$$\mathrm{pH} = \mathrm{p}K_a' - b \log [(1 - \alpha)/\alpha] \tag{8}$$

where $\mathrm{p}K_a'$ is the apparent $\mathrm{p}K_a$ of the polyacid, and b is an experimental constant. The experimental parameters $\mathrm{p}K_a'$ and b vary with polymer concentration, added salt, and the cations used in the titration base. The expression for PMAA in salt-free water titrated by using NaOH at the PMAA concentration of 0.02 N was found to be[15]

$$\mathrm{pH} = 6.98 - 1.98 \log [(1 - \alpha)/\alpha] \tag{9}$$

Using eq 9, the degrees of dissociation at different pH's for the samples are summarized in Table III.

Efficiencies of energy transfer from energy donor to energy acceptor groups in N–P–A, F–P–A, and N–P–A–P–N were determined from the enhancement of the intensities of anthryl group fluorescence due to energy transfer.[22,23] A Spex Fluorolog 2 fluorescence spectrometer was used for measurement. The equation used was

$$E = \frac{1}{PT}\left[\frac{I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_1)\,(1 - 10^{-A(\lambda_2)})}{I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_2)\,(1 - 10^{-A(\lambda_1)})}\right] \tag{10}$$

where λ_2 (352 nm) is the wavelength at which only the energy acceptor group absorbs, λ_1 (292 nm) is the wavelength at which predominantly energy donor groups absorb, T, the termination efficiency, accounts for the incomplete incorporation of the anthryl groups in the synthesis of the polymers, and P is the efficiency at which energy donors (naphthyl or fluoryl group) absorb at λ_1. At λ_1, both energy donor and acceptor groups absorb incident radiation energy. The efficiency of energy donor absorption is given by

$$P = \frac{1 - 10^{-A_{\mathrm{D}}(\lambda_1)}}{2 - 10^{-A_{\mathrm{D}}(\lambda_1)} - A^{-A_{\mathrm{A}}(\lambda_1)}} \tag{11}$$

where $A_{\mathrm{D}}(\lambda_1)$ and $A_{\mathrm{A}}(\lambda_1)$ are the absorbances of the energy donor and acceptor groups at λ_1, respectively. $I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_1)$ and $I_{\mathrm{Af}}{}^{\mathrm{R}}(\lambda_2)$ in eq 10 are acceptor fluorescence intensities measured in the ratio mode by exciting the samples at λ_1 and λ_2, respectively.

Measurement of E began at low pH. Samples were usually changed at pH 5 to minimize the salt effect from the neutralization reaction between NaOH and HCl. Low optical densities (~0.05) were used with all samples. Energy-transfer efficiencies for N–P–A, F–P–A, and N–P–A–P–N are summarized in Table III.

III. Results and Discussion

Characterization of the Polyelectrolytes. Table I summarizes the results for the characterization of the labeled PMAA using the three techniques. The number-average molecular weights from UV measurement agreed with those from NMR measurement within an error of ±5%.

Methacrylic acid groups on the backbone of labeled PMAA samples were esterified before GPC measurements. The molecular weights reported are those of esterified samples. The values were corrected to obtain the molecular weights of the polymers in their acidic form. The corrected values are presented in Table I for comparison with results obtained by using other techniques. The number-average molecular weight of N–P–A–P–N evaluated from GPC is the same as the value determined from NMR and UV measurements for the polymers. The values for F–P–A and N–P–A from GPC determination are, however, higher than those from NMR and UV measurements. We are unaware of the cause of this discrepancy. In subsequent calculations, $\bar{M}_n$ will be determined by using NMR and UV techniques.

The termination efficiency in N–P–A–P–N is not the concentration ratio between anthracene end-group concentration, c_{A}, and naphthalene end-group concentration, c_{N}. Rather, it is defined as

$$T = \frac{c_{\mathrm{A}}}{(1/2)c_{\mathrm{N}}} \times 100\%$$

The termination efficiency of 96 ± 5% means that, for every 2 mol of naphthyl end groups, there is 0.96 mol of anthracene groups. The 0.96 mol of anthracene groups can be attached to the polymer chain either at both of the 9,10-positions or at the 9-position only. The description of the system becomes very complicated. Since the experimentally observed T is very close to unity, the termination efficiency of 100% is accepted in subsequent calculations. This approximation can be justified by the ±5% uncertainty in the measurement.

Overlap Integral, *J*. J is the overlap integral between the normalized fluorescence intensity of wavelength λ, I_λ, of the donor group and the extinction coefficient, ϵ_λ, of the acceptor group

$$J = \int_0^\infty \lambda^4 I_\lambda \epsilon_\lambda \, \mathrm{d}\lambda \tag{12}$$

where, by definition

$$\int_0^\infty I_\lambda \, \mathrm{d}\lambda = 1 \tag{13}$$

The extinction coefficients of the donor groups in N–P–A and F–P–A in aqueous and 0.1 M NaCl solutions are

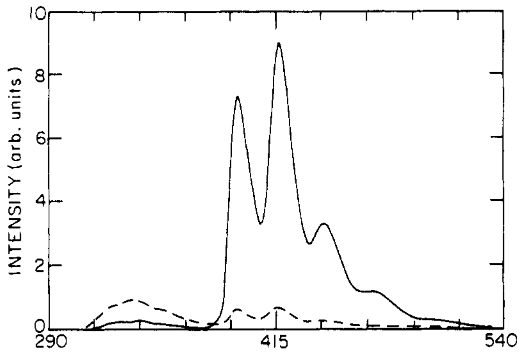


Figure 4. At high pH (10.54), PMAA coils are more expanded than at low pH (2.00). The coil expansion lowers energy-transfer efficiency and therefore the emission intensity of the anthracene group.

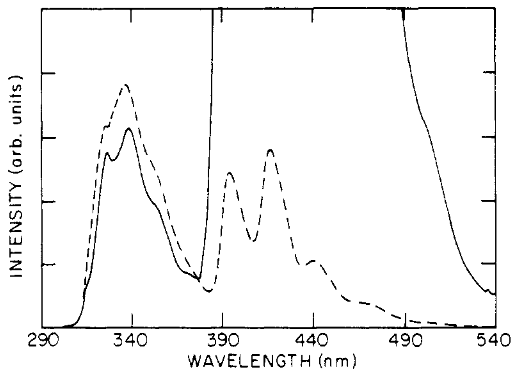


Figure 5. Comparison of the emission band shape of the naphthyl group in N-P-A at pH 10.54 and 2.00.

related to those of 9-methylanthracene by eq 5 as discussed previously. A similar relation was found for the anthracene group in N-P-A-P-N (eq 4). The extinction coefficients of the anthracene group in the three polymers studied did not change within experimental error over the pH range used for energy-transfer studies.

Fluorescence spectra of N-P-A at pH = 2.00 and 10.54 are compared in Figure 4. At high pH, the stretching of the polymer chain causes a decrease in energy-transfer efficiency and, therefore, a decrease in anthracene fluorescence quantum yield and an increase in naphthalene fluorescence quantum yield. In Figure 5, the spectrum obtained at pH = 10.54 is divided by 3 so that the naphthalene emission intensities match for the two spectra. The naphthalene emission band structure did not change with pH. The normalized fluorescence spectrum for the donor group naphthalene was obtained by integrating the fluorescence spectrum from 300 to 600 nm and then dividing the intensities at wavelength λ by the integrated intensity.

The J-integral for each sample was calculated using eq 14,[23] where 2 is the integration increment, $\epsilon(290+2i)$ is the

$$J = \sum_{i=1}^{55} \epsilon(290+2i) \times (290+2i)^4 \times I(290+2i) \times 2 \times 10^{-28} \tag{14}$$

extinction coefficients of the acceptor group of the sample at wavelength 290 + $2i$ nm, and $I(290+2i)$ is the intensity of the normalized fluorescence spectrum of the donor group at wavelength $290+2i$. The J values were calculated to be 1.32×10^{-15}, 6.45×10^{-16}, and 4.39×10^{-16} L cm^3/mol for the donor–acceptor pairs in N-P-A, N-P-A-P-N, and F-P-A, respectively.

Table IV
Examination of Additional Quenching

sample	χ_e, %	χ, %	E, %	$\phi_D{}^0$	$\phi_{DA}{}^0$
N-P-A	80	84	74	0.22 ± 0.03	0.14 ± 0.02
F-P-A	58	97	92	0.30 ± 0.05	0.11 ± 0.02
N-P-A-P-N	43	43	26	0.22 ± 0.03	0.17 ± 0.02

Fluorescence Quantum Yields. The fluorescence quantum yields, $\phi_D{}^0$, of the naphthalene and fluorene groups in N-P-H and F-P-H were measured by comparing the fluorescence intensities of the samples with those of naphthalene and fluorene molecules in cyclohexane. The technique has been described in detail previously.[23] The fluorescence quantum yields of the naphthalene and fluorene molecules in cycloyhexane[29] are 0.23 and 0.80, respectively. The corresponding $\phi_D{}^0$ values determined by this method for the N-P-H and F-P-H are 0.22 and 0.30, respectively (Table IV).

Additional Quenching. The fluorescence quantum yield, $\phi_D{}^0$, of the naphthyl end group in N-P-H is not necessarily equal to that of the naphthyl group in N-P-A in the absence of energy transfer, $\phi_{DA}{}^0$. The introduction of an anthracene end group to N-P-H, resulting in N-P-A, not only introduces a quenching mechanism for naphthyl group fluorescence through energy transfer but also may affect the quantum yield in other ways. For example, the introduction of an anthryl end group can significantly change the environment of the naphthyl end group due to the tendency for the two end groups to cluster together in an aqueous medium. The change in the local environment for the naphthyl group may cause its fluorescence quantum yield to vary, even in the absence of an energy-transfer process. If the fluorescence quantum yield of the naphthyl group in N-P-A in the absence of energy transfer is reduced relative to that in N-P-H, we say that additional quenching other than quenching through energy transfer for naphthyl group fluorescence is present.

Additional quenching results in quenching efficiencies, χ, greater than energy-transfer efficiencies, E. Energy-transfer efficiencies were determined from the enhancement in the fluorescence quantum yields of energy acceptor groups (anthryl groups) due to energy transfer. Quenching efficiencies were determined from the reduction in fluorescence quantum yields of energy donor groups (naphthyl or fluoryl group) due to the introduction of an energy acceptor group to a polymer chain. For N-P-A and F-P-A chains with a termination efficiency of T, the experimentally observed fluorescence quantum yield, ϕ_{DA}, for the energy donor group is

$$\phi_{DA} = T(1-E)\phi_{DA}{}^0 + (1-T)\phi_D{}^0 \tag{15a}$$

or

$$\phi_{DA} = T(1-\chi)\phi_D{}^0 + (1-T)\phi_D{}^0 \tag{15b}$$

Careful examination of eqs 15a and 15b shows that

$$(1-\chi)\phi_D{}^0 = (1-E)\phi_{DA}{}^0 \tag{16a}$$

or

$$\phi_{DA}{}^0 = (1-\chi)/(1-E)\phi_D{}^0 \tag{16b}$$

Dividing both sides of eq 15b and noticing that $\phi_{DA}/\phi_D{}^0$ is related to the experimentally observed quenching efficiency, χ_e, by

$$\chi_e = 1 - \phi_{DA}/\phi_D{}^0 \tag{17}$$

Table V
Calculation of the Critical Energy-Transfer Distances, R_0, for Three Different Donor–Acceptor Pairs

sample	J-integral × 10^{15}, L·cm^3/mol	ϕ_{DA}^0	n_D	κ^2	R_0, Å
N–P–A	1.32	0.14 ± 0.02	1.333	2/3	18.0 ± 0.6
F–P–A	0.44	0.11 ± 0.02	1.333	2/3	14.4 ± 0.5
N–P–A–P–N	0.65	0.17 ± 0.02	1.333	2/3	15.9 ± 0.5

one obtains

$$\chi = \chi_e / T \tag{18}$$

The results for ϕ_{DA}^0 calculated by using eq 16b for N–P–A, F–P–A, and N–P–A–P–N are summarized in Table V for R_0 calculations.

R_0 Calculation. The critical energy transfer distances, R_0, for the three donor–acceptor pairs were calculated by using

$$R_0 = \left[\frac{9000 \ln 10 \kappa^2 \phi_{DA}^0}{125\pi^5 \mathbf{n}^4 N_0} J\right]^{1/6} \tag{19}$$

where ϕ_{DA}^0 is the donor fluorescence quantum yield in the absence of energy transfer, **n** is the refractive index of the solvent at the wavelength of excitation, N_0 is Avogadro's constant, κ^2 characterizes the relative orientation between the transition dipole of the donor group and that of the acceptor group and is taken to be $^2/_3$, and J is the overlap integral between the normalized fluorescence intensity and the acceptor extinction coefficient.[23] R_0 values thus obtained are shown in Table V.

End-to-End Distances Fitted by Using Gaussian Distribution Functions. Strictly speaking, the end-to-end distance distribution function developed previously[30] should be used to describe that of PMAA chains. We are interested in changes in PMAA chain conformations over the whole range of degree of ionization, α. The description of the change in the end-to-end distance distribution function of a PMAA chain as a function of α in such a system is of tremendous experimental difficulty. In this paper, a Gaussian functional form is used as an approximation.

When a Gaussian form is assumed, the numerical expression of energy-transfer efficiency is given by[23]

$$\langle E \rangle = \sum_{n_1}^{n_2} P(n)\, \Delta n \sum_{i=1}^{m_x} (0.01i)^2 \exp[-1.5(0.01i)^2] \times \frac{R_0^{\,6}}{R_0^{\,6} + (0.01i)^6 (2n\beta)^3} \Big/ \sum_{i=1}^{m_2} (0.01i)^2 \exp[-1.5(0.01i)^2] \tag{20}$$

where $P(n)$, the distribution function for the number of repeat units n, can be obtained from GPC chromatograms shown in Figure 3, β is the statistical bond length of the PMAA backbone to be fitted, which is related to the root-mean-square end-to-end distance of the chain by

$$R_n = (2n)^{1/2} \beta \tag{21}$$

m_x is defined by

$$m_x = m / [(2n)^{1/2} \beta] \tag{22}$$

where m is the contour length of a chain with n repeat units and R_0 is the critical energy-transfer distance. Using methodology described previously,[23] the end-to-end distances for each sample at different pH were fitted and are tabulated in Table II. The β value for each sample plotted as a function of α is shown in Figure 6.

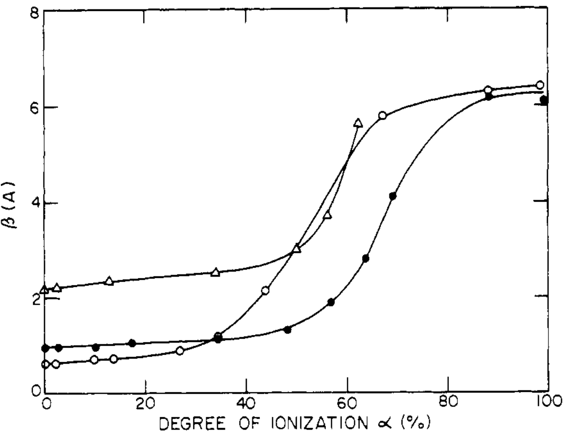


Figure 6. Bond parameter β (Å) plotted against the degree of dissociation, α, for the three samples.

End-to-End Distances of PMAA Chains from Previous Studies. The θ-state for PMAA occurs at 30 °C in aqueous 0.002 N hydrochloric acid solution, or at a pH of 2.70.[31] The root-mean-square end-to-end distance of a PMAA sample at the θ-state can be obtained by combining the Mark–Houwink relation[31]

$$[\eta] = 6.6 \times 10^{-4} M^{0.50} \tag{23}$$

and the relation given by Einstein[32]

$$\eta = \eta_0 [1 + (10/3) n_c \pi \bar{R}_h^{\,3}] \tag{24}$$

In eq 24 n_c is the number of polymer molecules per cubic centimeter and is related to polymer solution concentration (g/mL) by

$$n_c = (c/M) \times 6.023 \times 10^{23} \tag{25}$$

where η and η_0 are the solution and solvent viscosities, respectively, and $\bar{R}_h$ is the hydrodynamic radius of the polymer coil. Rearranging eq 24 and noting that

$$100[\eta] = \lim_{c \to 0} (1/c)[(\eta/\eta_0) - 1] \tag{26}$$

yields

$$\bar{R}_h = 2.51 \times 10^{-8} K^{1/3} M^{0.5} \text{ (cm)} \tag{27}$$

where M is sample molecular weight. In eq 23, $[\eta]$ has units in deciliters per gram. $\bar{R}_h$ is related to the radius of gyration of the polymer R_G by[23]

$$R_G = \bar{R}_h / 0.875 \tag{28}$$

and R_G is related to the root-mean-square end-to-end distance, R_n, by

$$R_n = \sqrt{6} R_G \tag{29}$$

The R_n values are related to the statistical bond length, β, by

$$R_n = (2n\beta^2)^{1/2} \tag{30}$$

The statistical bond length calculated from this approach for PMAA is 4.04 Å in the θ-state.

At $\alpha = 27\%$, Moan et al.[5] obtained a radius of gyration value of 33 Å for a PMAA sample of $\bar{M}_v = 13\,000$, and an average number of repeat units, $\bar{n}$, of ~150. Since the chain was still not extensively stretched, eq 29 should apply. After calculating R_n from eq 29, the statistical bond length, β, for the sample at $\alpha = 27\%$ can be calculated from eq 30. The value of β was calculated to be 4.75 Å.

Discussion. The β values for N–P–A, F–P–A, and N–P–A–P–N (Table II) measured at pH = ~2.0 are 0.95, 0.62, and 2.16 Å, respectively, which are all smaller than 4.04 Å. The ratio between β measured from energy-transfer studies and the β value of 4.04 Å are 0.15, 0.24, and 0.53 for F–P–A, N–P–A, and N–P–A–P–N, respectively. The values of β deviate from those determined by using viscometry measurements more severely than those for PMMA samples in organic solvents studied earlier.[23] This arises both because of the contribution to energy-transfer efficiency made by the end-group diffusion and due to the interaction between the hydrophobic end groups in aqueous solution.

The end-to-end distances measured by the spectroscopic ruler technique without correction for end-group diffusion and interaction (i.e., hydrophobic effect) are the "effective" end-to-end distances two reactive end groups have in the media used. Consider an electron-transfer reaction between a hydrophobic electron donor and a hydrophobic electron acceptor group attached to the ends of a polyelectrolyte chain, and suppose that the fluorescence of the donor group is quenched by the acceptor group through an electron-transfer mechanism. The reaction rate and kinetics are closely related to these "effective" distances rather than the "unperturbed" values of polyelectrolyte chains determined by using viscometry, light scattering, etc. Because of these short "effective" separation distances, some reactions that seem unfavorable can actually proceed with high efficiency.

The results for the "effective" distances suggest the following. (1) At low α, PMAA coils expand very little with increasing pH in N–P–A and N–P–A–P–N, indicating that PMAA chains exist as hypercoils[1] under these conditions. (2) The low energy- transfer efficiencies observed for the N–P–A–P–N sample at high pH suggest the planar zigzag conformation postulated by Moan et al.[5] A planar zigzag structure is possible here despite the hydrophobic interactions between naphthyl and naphthyl groups or naphthyl and anthryl groups. Compared with electrostatic repulsion between different segments, the hydrophobic interactions are negligible. However, the β values obtained for the N–P–A and F–P–A samples at high pH are not consistent with the zigzag structure. This is due to the composition differences between the three samples. For N–P–A and F–P–A, both the donor and acceptor groups are located at the ends of the polyelectrolyte chain, but for N–P–A–P–N the acceptor group is in the middle of the polymer chain. The end groups are more mobile and more accessible to each other than the center of mass of a polymer chain according to Kirkwood–Riseman theory.[33] The higher mobility and accessibility contribute to the higher energy-transfer efficiency.

The statistical bond length, β, in N–P–A–P–N is 2.16 Å at pH 2.00, which is considerably longer than β values determined for N–P–A and F–P–A. This is attributed to the different mobility, and possibly accessibility, of the energy acceptor groups located in the center of the polyelectrolyte chain.

IV. Conclusions

Conformational changes of PMAA chains with degree of ionization have been monitored by using the "spectroscopic ruler" technique and three different probes. When this technique was used, PMAA coils were found to expand very insignificantly at low degrees of ionization. This supports the hypercoil structure hypothesis.[1] The chains were found to assume zigzag structure at high degrees of ionization, in agreement with the observations of Moan et al.[5]

The end-to-end distances obtained by using this technique are the "effective" end-to-end distances of two reactive end groups, which undergo reactions on a nanosecond time scale. The values are considerably shorter than those of the unperturbed chains, due partly to the effect of end-group diffusion and partly to the hydrophobic interaction between the end groups.

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