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Dimensions of Polyelectrolytes Using the "Spectroscopic Ruler". 3. Experimental Studies of Poly(*N-tert*-butylaziridine hydrogen chloride) Chains

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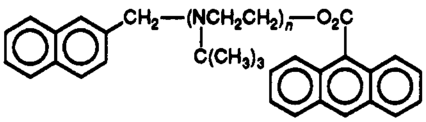
ABSTRACT: Change in effective end-to-end distances of poly(*N-tert*-butylaziridine hydrogen chloride) (PTBA·HCl) as a function of ionic strength and molecular weight is monitored by using the "spectroscopic ruler" technique. In the formulation of the efficiency of energy transfer from a donor to an acceptor group, both attached to the ends of a polyelectrolyte chain, the end-to-end distance distribution function proposed in a concurrent paper is used.

I. Introduction

In a previous paper in this series,[1] it was pointed out that, despite their fundamental importance, neither the theoretical treatment nor the experimental treatment of the conformation and dimensions of polyelectrolytes is satisfactory. This paper explores the feasibility of using the "spectroscopic ruler" technique, developed by Förster and subsequently modified by us,[2,3] to measure end-to-end distances of polyelectrolyte samples.

The determination of root-mean-square end-to-end distances of polyelectrolytes using the spectroscopic ruler requires polyelectrolyte samples end-labeled with energy donor and acceptor groups. To monitor the change in the end-to-end distances of poly(*N-tert*-butylaziridine hydrogen chloride) (PTBA·HCl, PTBA for the free polymer) as a function of ionic strength and molecular weight, polymer NA–PTBA–AN (reaction with HCl yielding NA–PTBA·HCl–AN) was synthesized, where the energy donor is a naphthyl group and the acceptor is an anthryl group. In the absence of significant diffusion of polymer chain ends during the donor fluorescence lifetime, the efficiency for energy transfer is[3]


NA–PTBA–AN

$$\langle E \rangle = \int_{N_1}^{N_2} P(N)\,\mathrm{d}n \int_0^{m_x} P(N,R,W) \frac{R_0^{\,6}}{R_0^{\,6} + R^6}\,\mathrm{d}R \qquad (1)$$

where R is the end-to-end distance, which can take values from 0 to m_x, the contour length of a polyelectrolyte chain with N repeating units, R_0 is the critical distance for energy transfer, $P(N)$ is the distribution function of the number of repeating unit N, and $P(N,R,W)$ is the end-to-end distance distribution function for a PTBA·HCl chain possessing N repeating units.

The end-to-end distance distribution function of polyelectrolytes is not Gaussian under most experimental conditions. In this paper, the expression for $P(N,R,W)$ proposed previously[1] will be used. According to Noda et al.,[5] $P(N,R,W)$ can be approximated as a Gaussian form $P(N,R)$ multiplied by a Boltzmann energy weighting factor, i.e.,

$$P(N,R,W) = P(N,R) \exp\left[-\frac{W_{\mathrm{el}}(R) + W_{\mathrm{hp}}(R)}{k_{\mathrm{B}}T}\right] \qquad (2a)$$

or

$$P(N,R,W) = 4\pi R^2 \left[\frac{1}{2\pi N\beta^2}\right]^{3/2} \exp\left[-\frac{1}{2}\frac{R^2}{N\beta^2}\right] \times \exp\left[-\frac{W_{\mathrm{el}}(R) + W_{\mathrm{hp}}(R)}{k_{\mathrm{B}}T}\right] \qquad (2b)$$

where $W_{\mathrm{el}}(R)$ and $W_{\mathrm{hp}}(R)$ are the statistically averaged electrostatic and hydrophobic interaction energies for a polyelectrolyte chain possessing an end-to-end distance of R at an ionic strength μ_{I}, respectively. The root-mean-square end-to-end distance calculated from the hypothetical Gaussian distribution function $P(N,R)$ is $R_n^{\,0}$ or $(3N)^{1/2}\beta$ for a chain with N repeating units and each unit consisting of three bonds, and $k_{\mathrm{B}}T$ is the thermal energy. The $W_{\mathrm{hp}}(R)$ term was further approximated by Liu and Guillet[1] as being independent of ionic strength and equal to $W_{\mathrm{el}}^{\,0}(R)$, the statistically averaged electrostatic interaction energy at a Θ state with an ionic strength of $\mu_{\mathrm{I}}^{\,0}$. Thus

$$P(N,R,W) = 4\pi R^2 \left[\frac{1}{2\pi N\beta^2}\right]^{3/2} \exp\left[-\frac{1}{2}\frac{R^2}{N\beta^2}\right] \times \exp\left[-\frac{W_{\mathrm{el}}(R) - W_{\mathrm{el}}^{\,0}(R)}{k_{\mathrm{B}}T}\right] \qquad (3)$$

$W_{\mathrm{el}}(R)$ has been previously derived by Katchalsky and Lifson.[6] According to these authors,

$$W_{\mathrm{el}}(R) = \frac{3(nd)^2 q^2}{\epsilon R (R_n^{\,0})^2} \times \exp\left[-\frac{3}{2}\left(\frac{R}{R_n^{\,0}}\right)^2\right] \int_0^{m_x} \frac{\exp(-\kappa r)}{r}\,\mathrm{d}r \times \int_{|r-R|}^{r+R} r_1 \exp\left[-\frac{3}{2}\left(\frac{r_1 + r}{R_n^{\,0}}\right)^2\right] \mathrm{d}r_1 \qquad (4)$$

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Table I
Characterization of the Samples

fraction	$10^{-3}M_w$ GPC[a]	$10^{-3}M_n$ GPC	UV[b]	NMR[c]	N UV	NMR	av	T UV, %	NMR, %	av	M_w/M_n GPC
1	7.2	6.1	10.3	10.4	98	102	100	91	97	94	1.2
3	6.2	4.9	8.2		80		80	93		93	1.3
5	3.5	2.6	6.2	5.8	59	55	57	99	92	95	1.4
6	2.8	2.0	4.4		41		41	99		99	1.4
8	1.8	1.4	4.2		39		39	93		93	1.3

[a] Obtained by using a calibration curve generated from polystyrene standards. [b] Error is about ±5%. [c] Error is about ±5%.

Table II
Extinction Coefficients of 9-Methylanthracene (ϵ_A) and 2-Methylnaphthalene (ϵ_N) at Selected Wavelengths

λ, nm	$10^{-3}\epsilon_A$, cm^{-1} M^{-1}	$10^{-3}\epsilon_A$, cm^{-1} M^{-1}
270	3.2	6.6
276	1.33	6.9
280	0.84	6.4
284	0.58	5.4
346	6.2	*a*
364	8.8	*a*
382	7.6	*a*

[a] Values approach zero.

where

$$R_n^{\,0} = (3N)^{1/2}\beta \qquad (5)$$

r is the separation distance between a segment and one end of a polyelectrolyte chain, r_1 is the separation distance between the segment and the other end, the upper integration limit m_x is equal to the contour length of a chain with N repeating units, ϵ, the local dielectric constant of each repeating unit, is approximated by the bulk dielectric constant, n is the number of charged sites on the polyelectrolyte chain, q is the electronic charge on the individual site, d is the degree of ionization multiplied by an activity coefficient, σ, for the backbone charges, and κ is the Debye–Hückel parameter

$$\kappa = \left(\frac{8\pi e^2}{\epsilon k_B T}\right)^{1/2} \mu_I^{\,1/2} \qquad (6)$$

In eq 6, e is the electronic charge and μ_I is the ionic strength of the added salt defined by

$$\mu_I = \frac{1}{2}\sum_i c_i z_i^{\,2} \qquad (7)$$

with i summing over all ions except the polyelectrolyte itself. c_i and z_i in eq 7 are the concentration and valence of the ith ionic component.

II. Experimental Section

Synthesis of NA–PTBA–AN. A solution of 442 mg (2 mmol) of 2-(bromomethyl)naphthalene and 426 mg (2 mmol) of silver trifluoromethanesulfonate in 25 mL of dry methylene chloride was stirred under a dry nitrogen atmosphere at 20 °C for 30 min. After sedimentation of the silver bromide, the clear solution was transferred to a two-necked reaction flask equipped with a nitrogen inlet, after which 9.9 g (100 mmol) of TBA was added while stirring under a slight dry nitrogen flow. After 10 min, 535 mg (2.5 mmol) of 9-anthrylcarboxylic acid, dissolved in 10 mL of methylene chloride, was added, and the solution was stirred for another 20 min at room temperature.

The polymer was precipitated in 250 mL of methanol, filtered off, washed with methanol, and dried in vacuo. Yield 9.5 g.

GPC Fractionation and Analysis of the Sample. The polymer NA–PTBA–AN was fractioned in HPLC chloroform (Caledon) by using Ultrastyragel columns (Waters, 10^4, 10^3, and 500 Å). Eight fractions were collected. Analysis of each fraction was done in THF (Caledon, HPLC grade) by using Ultrastyragel columns (Waters, 10^3, 500, and 100 Å). Mark–Houwink constants,[7] k and α, are not known for the polymer in any organic solvents. As an approximation, polystyrene standards were used to generate a calibration curve for the characterization of the fractions. The results are summarized in Table I.

NMR Characterization. NMR spectra were obtained for fractions 1 and 5 in CD_2Cl_2 or $CDCl_3$ on a Varian XL400 spectrometer. The termination efficiency, T, determined from the relative proton peak areas of the naphthyl and the anthryl end groups, was 91 ± 5%. The number-average number of repeating units, $\bar{N}$, for fraction 5, calculated by taking the ratio of peak area of polymer backbone protons to that of end group protons, was found to be 55 ± 3. In a like manner, the average number of repeating units and termination efficiency for fraction 1 were calculated to be 102 ± 4 and 97 ± 3%, respectively (Table I).

Synthesis of Methyl 9-Anthroate. The compound methyl 9-anthroate was prepared following the procedure of Parrish and Stock.[8] 9-Anthroic acid (2.0 g, 0.009 mol, Aldrich, 98%) was suspended in 40 mL of benzene (Caledon, reagent grade) and treated with trifluoroacetic anhydride (5.0 mL, 0.036 mol, Aldrich, 99+% Gold Label). All of the 9-anthroic acid was dissolved after 10 min of gentle warming. Methanol (5 mL, Caledon, reagent grade) was then added. The mixture was allowed to stand for 20 min without further heating. Potassium hydroxide solution (10%, 30 mL) was subsequently added with stirring, and the aqueous phase was removed. The orgnanic phase was washed with water until it was neutral, then dried on anhydrous sodium sulfate, filtered, and rotor-evaporated to dryness. The residue was recrystallized from methanol. Yield 70%. Thin-layer chromatography revealed one product. UV spectra coincided with those obtained by Parrish and Stock[8] (maxima 346 nm, $\epsilon = 5.11 \times 10^3$; 364 nm, $\epsilon = 7.19 \times 10^3$; and 382 nm, $\epsilon = 6.25 \times 10^3$).

UV–Visible Characterization of NA–PTBA–AN. All UV spectra were recorded on a Hewlett-Packard 8451 diode array spectrometer. The molar extinction coefficient, $\epsilon(\lambda)$, of 2-methylnaphthalene at wavelength λ was different from that, $\epsilon'(\lambda)$, of the naphthyl group in NA–PTBA–AN but the absorption envelopes of the two were quite similar. It was assumed that eq 8 holds; i.e.,

$$\epsilon'(\lambda) = b\epsilon(\lambda) \qquad (8)$$

A similar relation was assumed between the extinction coefficients of methyl 9-anthroate and the anthracene end group in the polymer:

$$\epsilon'(\lambda) = d\epsilon(\lambda) \qquad (9)$$

The concentration of end groups for fractions 1 and 5 was determined by NMR (Table I). The b and d values were calculated from the absorbances of NA–PTBA–AN of known concentration and were found to be 1.50 ± 0.09 and 1.22 ± 0.03, respectively, in methylene chloride. The extinction coefficients of the naphthalene and anthracene end groups in NA–PTBA–AN at the wavelengths of interest were calculated in this way and are summarized in Table II.

Number-average molecular weights and termination efficiency for each fraction was then evaluated using $\epsilon'(\lambda)$ values and are also tabulated in Table I.

Fluorescence Measurement. All fluorescence spectra were recorded on a Spex Fluorolog 2 spectrometer. Figure 1 shows a typical fluorescence spectrum of NA–PTBA·HCl–AN in water. There are two phenomena to note in the spectrum. *First*, the

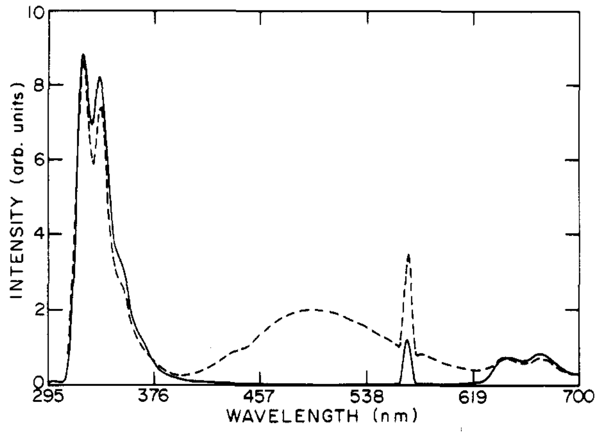


Figure 1. Fluorescence spectra of NA-PTBA·HCl-AN (- - -) and polymer II (—) in pH = 2.0 HCl aqueous solution.

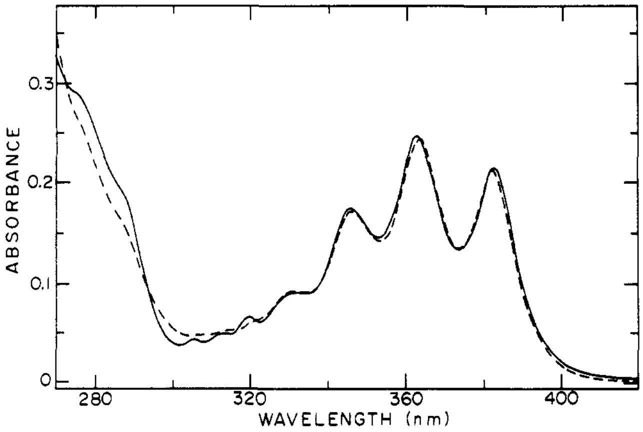


Figure 2. Comparison of the experimentally observed absorption spectrum of NA-PTBA-AN (—) with that of 2-methylnaphthalene superimposed on that of methyl 9-anthroate (- - -).

anthracene emission is structureless, strongly Stokes-shifted, and has a maximum at 500 nm. This has been explained as being caused by the rotation of the carboxylic group into the plane of anthracene ring in the excited state.[9] Second, an emission band around 650 nm was observed. The structure of the band is similar to naphthalene fluorescence emission and has two maxima, 643.5 and 670 nm. These peaks have the scattering overtone wavelengths of the naphthalene fluorescence band, which has maxima at 321.5 and 334 nm, respectively, and are therefore the second-order scattering of the emission band of the naphthyl group. The sharp peak around 568 nm is from the second-order scattering of the incident light.

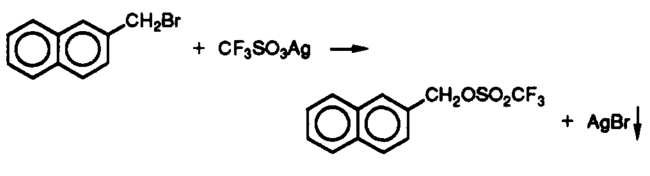
Computer Programming. Numerical solutions were obtained on a Gould computer. To solve eqs 1 and 4, one first needs to define a reference state, the Θ state. At the Θ state, $\langle E\rangle$ is given by

$$\langle E\rangle = \int_{N_1}^{N_2} P(N)\,\mathrm{d}n \int_0^{m_x} P(N,R)\frac{R_0^{6}}{R_0^{6}+R^{6}}\,\mathrm{d}R = \int_{N_1}^{N_2} P(N)\,\mathrm{d}N \int_0^{m_x} 4\pi R^2\left(\frac{1}{2\pi N\beta^2}\right)^{3/2} \times \exp\left[-\frac{1}{2}\frac{R^2}{N\beta^2}\right]\frac{R_0^{6}}{R_0^{6}+R^{6}}\,\mathrm{d}R \quad (10)$$

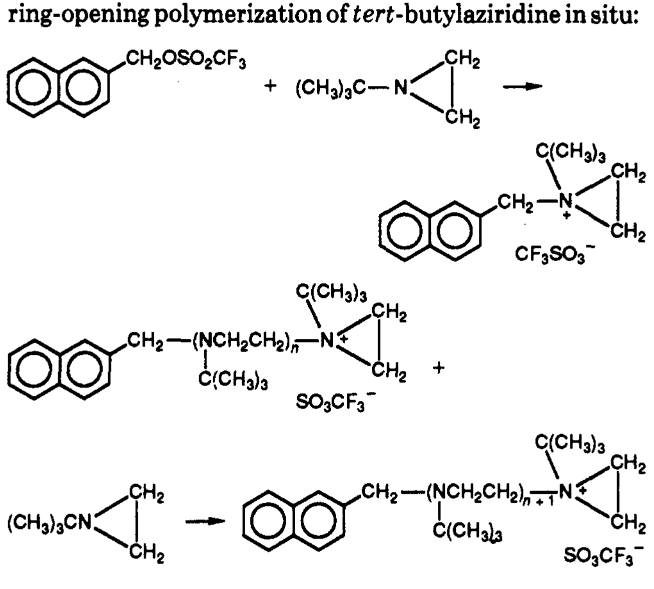
where $P(N,R)$ is a Gaussian end-to-end distance distribution function. Numerical solution of eq 10 yields the fitting parameter β at the Θ state, β^{Θ}. The value of $W_{\mathrm{el}}^{0}(R)$ is determined by inserting β^{Θ} into eq 4. Inserting eq 4 and $W_{\mathrm{el}}^{0}(R)$ into eq 1 allows one to fit $\langle E\rangle$ at any ionic strength μ_I.

III. Results and Discussion

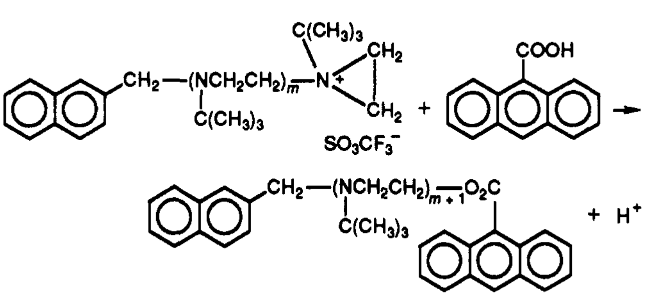
Synthesis of NA-PTBA-AN. NA-PTBA-AN was synthesized by cationic ring-opening polymerization of TBA.[10] 2-(Bromomethyl)naphthalene undergoes reaction with silver triflate



yielding 2-naphthyl methyl triflate, which initiates the ring-opening polymerization of *tert*-butylaziridine in situ:



The polymerization was terminated with 9-anthrylcarboxylic acid:



Characterization of the Polyelectrolytes. Molecular weights of certain fractions of NA-PTBA-AN determined by using various techniques are summarized in Table I. NMR measurement is an absolute technique. Molecular weights determined from NMR measurement were then used to determine the extinction coefficients of the end groups. By using these extinction coefficients, molecular weights were also obtained from UV measurements. GPC data were obtained by using the calibration curve generated from employing polystyrene standards. The molecular weights obtained from the GPC technique are, therefore, in error. The GPC chromatogram of each fraction was linearly shifted on the retention time axis so as to generate the $\bar{M}_n$ determined from NMR or UV technique. The shifted chromatogram was then used for the calculation of $P(N)$ in eq 1 as an approximation. The average termination efficiency, T, determined from UV measurement was 95 ± 3%.

In Figure 2, the UV-absorption spectrum of NA-PTBA-AN experimentally observed is compared with that of 2-methylnaphthalene superimposed on that of methyl 9-anthroate by assuming a termination efficiency of 95%. The agreement is fairly good.

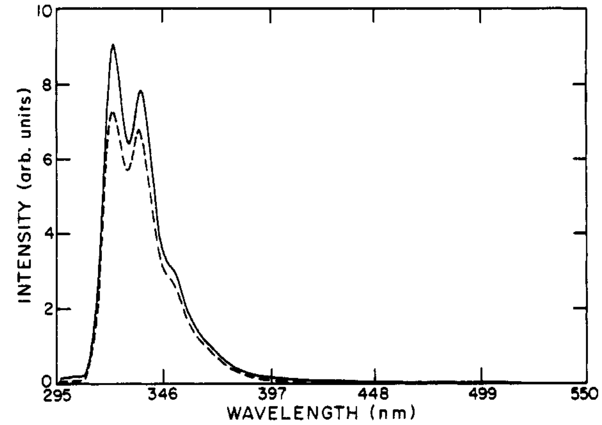


Figure 3. Comparison of the fluorescence spectra of the naphthyl group in polymer II at 0.01 M (—) and 0.62 M (- - -) ionic strength.

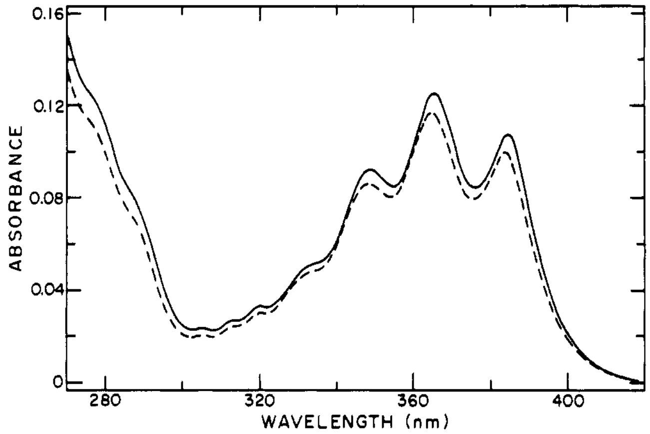


Figure 4. Comparison of the absorption spectra of the anthryl group in NA-PTBA·HCl-AN at 0.01 M (—) and 0.62 M (- - -) ionic strength.

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

$$J = \int_0^\infty \lambda^4 I_\lambda \epsilon_\lambda \, d\lambda \tag{11}$$

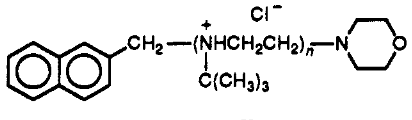
where by definition

$$\int_0^\infty I_\lambda \, d\lambda = 1 \tag{12}$$

The overlap integral was approximated by using[4]

$$J = \sum_{i=1}^{65} \epsilon(290 + 2i)(290 + 2i)^4 I(290 + 2i)(2 \times 10^{-28}) \tag{13}$$

where $\epsilon(290 + 2i)$ is the extinction coefficient of the anthryl group in NA-PTBA·HCl-AN at wavelength $290 + 2i$ nm; $I(290 + 2i)$ is the intensity reading from corrected and normalized fluorescence spectrum of polymer II at wavelengths $290 + 2i$.



polymer II

Figure 3 shows the fluorescence spectra of the naphthyl group in polymer II at 0.01 and 0.61 M ionic strength. The shape of the fluorescence peaks is barely changed with ionic strength.

The extinction coefficients of the anthracene group in NA-PTBA·HCl-AN were approximated by the those of methyl 9-anthroate in methylene chloride multiplied by the correction factor $d = 1.22$. The absorption maxima between those of methyl 9-anthroate and those of the anthracene group in NA-PTBA·HCl-AN were found to match in position well within the resolution of the spectrometer. Figure 4 demonstrates the small change in the UV absorption spectrum of the anthryl group in the NA-PTBA·HCl-AN sample by increasing the ionic strength. No shift in absorption maxima was observed at the two ionic strengths used, 0.01 and 0.61 M, and the change in absorbances was <7%. By using eq 13, the J integral was calculated to be 2.49×10^{-15} L cm^3/mol.

Critical Energy-Transfer Distance. Förster's critical energy-transfer distance, R_0, was calculated by using[2]

$$R_0 = \left(\frac{9000 \ln 10 \kappa^2 \phi_D}{125 \pi^5 n^4 N_0} J \right)^{1/6} \tag{14}$$

where ϕ_D is the donor fluorescence quantum yield in the absence of energy transfer, n is the refractive index of the solvent at the excitation wavelength, and N_0 is Avogadro's constant. The relative orientation between the transition dipole of the donor group and that of the acceptor group is characterized by κ^2 (different from κ, the Debye–Hückel parameter defined by eq 6). J is the overlap integral defined earlier.

The fluorescence quantum yield, ϕ_D, of the naphthyl group in polymer II was determined by comparing its fluorescence intensity (I_1) with that of naphthalene in argon-purged cyclohexane (I_2). The fluorescence quantum yield, ϕ_2, of naphthalene in cyclohexane was reported by Berlman[11] to be 0.23. When equal optical densities are used for the two solutions, eq 15[3] was used for calculating

$$\phi_D = \frac{n_2^2 I_1}{n_1^2 I_2} \phi_2 \tag{15}$$

ϕ_D. The values were found to be 0.022 ± 0.005 and 0.021 ± 0.005 for ionic strengths of 0.01 and 0.61 M, respectively.

The refractive indices of salt water at different ionic strengths were taken from the *CRC Handbook*.[12] Pure water has an n_D of 1.3330, and the 0.6 M NaCl solution has a refractive index of 1.3390. The value of 1.34 was employed in the R_0 calculation.

The orientation factor κ^2 was taken as $^2/_3$.

The critical energy transfer distance, R_0, as shown in Table III, was calculated to be 14.7 Å. The calculated error[4] was ±0.5 Å.

Energy-Transfer Efficiencies. Efficiencies of energy transfer from energy donor to energy acceptor groups in the polymers were determined from the enhancement of the intensities of anthryl group fluorescence due to energy transfer.[3,4] The equation used was

$$E = \frac{1}{PT} \left[\frac{I_{Af}^{R}(\lambda_1)(1 - 10^{-A(\lambda_2)})}{I_{Af}^{R}(\lambda_2)(1 - 10^{-A(\lambda_1)})} \right] \tag{16}$$

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

Table III
Förster Critical Energy-Transfer Distance R_0 for NA–PTBA·HCl–AN

J integral, L cm^3/mol	ϕ_D	n	k^2	R_0, Å
2.49×10^{-15}	0.021 ± 0.004	1.34	2/3	14.7 ± 0.05

Table IV
Energy-Transfer Efficiencies, E, for Fractions 1, 3, and 5 at Different Ionic Strengths

ionic strength, M	fraction 1 ($\bar{N}$ = 100), %	fraction 3 ($\bar{N}$ = 80), %	fraction 5 ($\bar{N}$ = 57), %
0.01	4.3 ± 0.7	4.9 ± 0.7	7.6 ± 0.5
0.06	4.9 ± 0.7	7.9 ± 0.9	10.5 ± 0.5
0.11	6.9 ± 0.6	9.3 ± 0.5	15.1 ± 0.2
0.16	7.9 ± 0.5	9.3 ± 0.5	15.1 ± 0.2
0.21	9.0 ± 0.5	12.4 ± 0.8	19.3 ± 0.8
0.31	8.3 ± 0.5	12.0 ± 0.3	24.6 ± 0.5
0.62	12.8 ± 0.5	15.4 ± 0.4	23.8 ± 0.5

Table V
Variation in Energy-Transfer Efficiencies, E, with Number of Repeating Units, $\bar{n}$, of Polyelectrolyte Chains

		E (%) for ionic strength	
fraction	$\bar{n}$	0.62 M	0.01 M
1	100	12.8 ± 0.5	4.3 ± 0.7
3	80	15.4 ± 0.4	4.9 ± 0.7
5	57	23.8 ± 0.5	7.6 ± 0.7
6	41	36.5 ± 0.5	10.5 ± 0.7
8	39	41.0 ± 1.0	18.1 ± 0.9

Table VI
Effect of Viscosity η on Energy-Transfer Efficiencies, E

solvent	η, cP	fraction 1	fraction 5
water, IS = 0.62 M[a]	1.0	12.8 ± 0.5	23.8 ± 0.5
W/G,[b] IS = 0.62 M[a]	8.33	10.3 ± 0.5	18.7 ± 0.5

[a] IS = ionic strength. [b] W/G is a water/glycerol mixture (v/v = 50%).

radiation energy. The efficiency of energy donor absorption is given by

$$P = \frac{1 - 10^{-A_D(\lambda_1)}}{2 - 10^{-A_D(\lambda_1)} - A^{-A_A(\lambda_1)}} \qquad (17)$$

where $A_D(\lambda_1)$ and $A_A(\lambda_1)$ are the absorbances of the energy donor and acceptor groups at λ_1, respectively. $I^R_{Af}(\lambda_1)$ and $I^R_{Af}(\lambda_2)$ in eq 16 are acceptor fluorescence intensities measured in the ratio mode by exciting the samples at λ_1 and λ_2, respectively.

Energy-transfer efficiencies measured for three fractions of the polymer at different ionic strengths are summarized in Table IV, and the variation in energy-transfer efficiency as a function of molecular weight is shown in Table V. In Table VI, energy-transfer efficiencies for two samples at the ionic strength of 0.62 M in solvents at different viscosities are compared.

Θ State. As discussed in section II, the Θ state is an important reference state if one wishes to use the end-to-end distance distribution function $P(N,R,W)$. The Θ state for poly(*tert*-butylaziridine hydrogen chloride) polymer was, however, not known for our treatment. At the Θ state, the Mark–Houwink constant α is 0.5. It has been reported that, in 0.4 M potassium chloride solution, the α value for poly(N-*tert*-butylaziridium chloride) is 0.75.[13] The parameter α is an indication of the flexibility of the polymer chain. The larger the α, the more stretched the chain. The Θ state for this polyelectrolyte lies somewhere at a higher ionic strength. We measured the energy-transfer efficiencies for the samples up to the ionic strength of 0.62 M NaCl. As an approximation, we assume in this treatment that the Θ state occurs at the ionic strength of 0.62 M.

Effective Charges on the Polyelectrolyte Backbones. Due to the condensation of counterions on the backbone of a polyelectrolyte chain, the charges on the chain are less effective than they would otherwise have been in the absence of the counterions. The repulsive interactions between charged segments is therefore weaker. This phenomenon is called charge screening.[14] The reduction in the effect of the charges is manifested by the activity coefficient, σ. The values of σ range between 1 and 0. The smaller the σ, the greater the screening.

There are two principal methods used for the determination of the screening coefficients, the measurement of conductivity and the measurement of the osmotic pressure of a polyelectrolyte solution. These methods have been discussed in some detail by Jannink.[15]

Activity coefficients of poly(methacrylic acid) at different degrees of ionization and ionic strengths were determined by Eisenberg[16] from conductivity measurements. The activity coefficients were found to be strongly dependent on the degree of ionization and also, to a lesser degree, on ionic strength. In the limits of 0 and 100% ionization, the activity coefficients were found to be around 1.0 and 0.4, respectively.

No previous measurement has been performed on the activity coefficients of PTBA·HCl. All of our energy-transfer studies were carried out at pH 2. At this pH, all nitrogen groups in PTBA should be ionized. The 100% ionization could be estimated from the pK_B value of the nitrogen group in PTBA. When PTBA·HCl was dissolved in pyridine-d_5 for NMR measurement, it was found that the PTBA·HCl remained protonated quantitatively. Since pyridine-d_5 was the solvent and was much in excess, the inability of the pyridine-d_5 to form pyridinium-d_5 chloride salt indicated that the K_B value of the N group in PTBA is at least 10^3 times larger than that of the N group in pyridine-d_5. The K_B for pyridine is 1.8×10^{-10} (*CRC Handbook*), which should be similar to that of pyridine-d_5. The K_B for PTBA is therefore estimated to be larger than 10^{-7}. A simple calculation shows that at pH 2 the ionization of the N group in PTBA is 100%. For 100% ionization, the activity coefficient for PTBA·HCl was arbitrarily assumed to be 0.25 and independent of ionic strength.

Root-Mean-Square End-to-End Distances, R_{nE}. Root-mean-square end-to-end distances, R_n, obtained by fitting eq 1 are denoted as R_{nE}. The Θ state was assumed to occur at an ionic strength of 0.62 M. The β^Θ for fractions 1, 3, and 5 fitted from eq 10 were 1.89, 1.87, and 1.77 Å, respectively. Inserting the corresponding β^Θ values into eq 4 enabled the calculation of $W_{el}{}^0(R)$ at the Θ state. $W_{el}(R)$ in eq 1 and defined by eq 4 was varied by insertion of different β values. So was the $\langle E \rangle$ value defined by eq 1. The β values fitted from experimental energy-transfer efficiencies for different fractions of the polyelectrolyte at different ionic strengths are summarized in Table VII. To differentiate, β values obtained by this approach are denoted as β_E in Table VII.

Root-mean-square end-to-end distances for samples at different ionic strengths were calculated by using

$$R_{nE} = \left(\int R^2 P(N,R,W)\, dR\right)^{1/2} \qquad (18)$$

The R_n values are also presented in Table VII.

Table VII
End-to-End Distances Fitted for Fractions 1, 3, and 5 at Different Ionic Strengths

ionic strength, M	fraction 1				fraction 2				fraction 3			
	β_E[a]	β_G[b]	R_{nE}[a]	R_{nG}[b]	β_E	β_G	R_{nE}	R_{nG}	β_E	β_G	R_{nE}	R_{nG}
0.01	1.41	2.93	79	51	1.75	3.02	76	47	1.85	2.97	50	39
0.06	1.28	2.79	61	48	1.45	2.50	56	39	1.64	2.59	40	34
0.11	1.15	2.44	53	42	1.36	2.33	48	36	1.46	2.21	32	29
0.16	1.10	2.31	48	40	1.35	2.33	45	36	1.42	2.11	29	28
0.21	1.06	2.19	44	38	1.24	2.06	38	31	1.35	1.97	26	26
0.31	1.08	2.26	41	39	1.24	2.09	36	32	1.25	1.74	22	23
0.62		1.89		32		1.87		28		1.77		23

[a] Errors in β_E and R_{nE}, both in Å, are 3%. [b] Errors in β_G and R_{nG}, both in Å, are 3%.

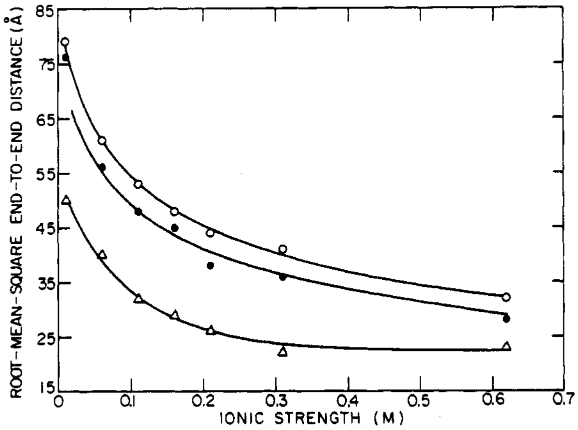


Figure 5. R_{nE} as a function of ionic strength for different fractions of NA-PTBA·HCl-AN: (○) fraction 1, (●) fraction 3, (△) fraction 5.

Discussion of the β_E Values. By definition, β_E values should be independent of ionic strength.[1] In practice, the β_E values obtained do vary with ionic strength. This can be attributed to the following reasons. First, the reference state, the Θ state, was chosen arbitrarily. Second, hydrophobic interactions can be ionic strength dependent. Third, the activity coefficient for the backbone charges can also be ionic strength dependent. A sudden drop of the β value when ionic strength is changed from 0.62 to 0.31 M is probably caused by the first of these effects.

Root-Mean-Square End-to-End Distances, R_{nG}, Fitted from Equation 10. Assuming a Gaussian form for the end-to-end distance distribution function, root-mean-square end-to-end distances, denoted as R_{nG}, could also be obtained from eq 10 by fitting energy-transfer efficiencies experimentally observed. A Gaussian form for the end-to-end distance distribution function of polyelectrolytes at low ionic strengths is erroneous. The end-to-end distances, R_{nG}, are used for comparison to R_{nE} obtained from the previous approach. R_{nG} values for each fraction in solutions of different ionic strengths are also presented in Table VII. β parameters fitted from this approach are denoted as β_G in Table VII for differentiation.

R_{nE} and R_{nG} Values. Root-mean-square end-to-end distances R_{nE} and R_{nG} are compared in Table VII. A significant difference in R_{nE} and R_{nG} values occurs at low ionic strengths. The calculation of R_{nE} and R_{nG} values is preliminary, and until further studies, we can make no comment concerning the different results obtained from the two approaches.

Both the R_{nE} and R_{nG} results indicate that as ionic strength increases, R_n values decrease. Also, as molecular weight increases, R_n increases. The ionic strength dependence of R_{nE} values is illustrated in Figure 5 for fractions 1, 3, and 5.

Effective and Unperturbed End-to-End Distances. R_{nG} and R_{nE} values obtained are not corrected for the diffusion[17-20] of the end groups during the fluorescence lifetime of the naphthyl end group. Furthermore, the hydrophobic interaction between the end groups has not been taken into account explicitly. This approximation is justified at low ionic strengths because the electrostatic repulsion force is so strong that the hydrophobic interaction is negligible. The approximation is, however, crude if the polymer is dissolved in a Θ solvent. The R_{nG} and R_{nE} values obtained are therefore the "effective" end-to-end distances. Consider a diffusion-controlled reaction between two active hydrophobic end groups. If the end groups are active for a period of time on the nanosecond time scale, the reaction rate is determined by these effective end-to-end distances rather than the "unperturbed" values determined from viscosity and light-scattering measurements.[7]

The approximate magnitude of this effect is shown by the data in Table VI, where the viscosity of the solvent was increased from 1 to 8.3 cP by addition of glycerol. The energy-transfer efficiency, E, is reduced by about 20% in the more viscous solvent. The value of R_{nG} calculated from these data should be a closer approximation to the unperturbed value. The effect of end group diffusion is treated in more detail in a previous paper in this series.[19]

IV. Conclusions

Conformational changes of PTBA·HCl with ionic strength were monitored by the spectroscopic ruler relation developed in previous papers.[3,4] End-to-end distances of polyelectrolyte chains of different molecular weights were all found to increase as the ionic strength of the aqueous solution decreased. This is due to less effective screening of the electrorepulsive interaction between the charges on the polyelectrolyte backbone by molecular ions as ionic strength decreases.

The end-to-end distances determined are the effective end-to-end distances. These values constitute the first experimental values of the root-mean-square end-to-end distances of flexible polyelectrolyte chains.

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