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Micelle-Mimetic Ionene Polyelectrolytes

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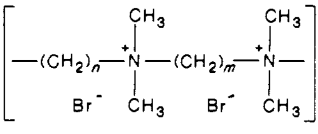
Abstract: The properties of a series of linear cationic polyelectrolytes of the [*n*,*m*]-ionene type (dimethylammonium charge centers interconnected by alternating chain segments containing *n* and *m* CH_2 groups, respectively) have been investigated in aqueous solution. Ionenes with short segments, i.e., the [6,10]-ionene and the [3,*m*]-ionenes with $m \leq 14$, exhibit behavior typical of polyelectrolytes with extended or rodlike conformations. In contrast, the aqueous solution properties of the [3,*m*]-ionenes with $m > 14$ are quite distinct. Thus, increasing *m* beyond 14 results in a progressive increase in the net degree of bromide counterion association to the ionene (conductivity data), enhanced solubilization of hydrophobic substrates (pyrene) in a progressively less aqueous environment, a gradual increase in the fluorescence anisotropy of an ionene-adsorbed anionic fluorescein derivative, and an increase in the selectivity of chloride/bromide counterion exchange at the ionene surface. These *m*-dependent changes in solution properties, which correlate nicely with the *m*-dependent onset and rise of catalytic activity (acceleration of the rate of alkaline hydrolysis of *p*-nitrophenyl octanoate), are consistent with a change in ionene conformation, going from extended to progressively more compact (globular or micellelike) as the segment length *m* is increased beyond 14. Indeed, the observed effects of the [3,10]-, [3,16]-, and [3,22]-ionenes on reaction rate can be quantitatively reproduced by using the pseudophase ion-exchange formalism originally developed for micellar systems. The marked similarity between the [3,22]-ionene and the CTAB micelle with respect to counterion binding, counterion-exchange selectivity, substrate solubilization, and catalytic rate enhancement suggests that amphiphilic ionenes of this type should be excellent prototypes for the rational design of micelle-mimetic polyelectrolytes.

It is now generally appreciated that the primary factor responsible for the acceleration of the rates of bimolecular reactions by micelles is their ability to concentrate the reactive species in a relatively small reaction volume at their surface.[1-4] In this context, the key structural feature of an ionic micelle is the presence of a rather compact hydrophobic core region delimited by a hydrocarbon-water interface of high surface charge density (Stern layer), both of which are formed concomitantly upon aggregation of the surfactant monomers. This confers upon the ionic micelle the dual capability of solubilizing relatively hydrophobic neutral substrates and of attracting or binding counterionic reagents in a small surface reaction zone. In addition, other characteristics of the micelle represent particularly desirable features for a "catalyst" of bimolecular reactions. Thus, the micellar aggregates themselves are thermodynamically stable, are formed spontaneously in solution, have a dynamic and rather flexible packing arrangement that permits accommodation of substrates of widely differing size and shape, and can be modified by merely changing the molecular structure of the surfactant monomer.[1,2]

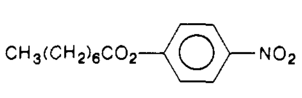
The potential utility of micelles (or any other related type of association colloid) as catalysts is, however, compromised by the dynamic nature of the aggregation phenomenon. Since micelles are in equilibrium with free surfactant monomer, they cannot be immobilized on solid supports and are typically not retained by semipermeable membranes due to the permeability of the monomer. Moreover, the elevated tensoactivity of the free surfactant monomer at both the air-water and oil-water interfaces can lead to complications in situations where isolation of micelle-incorporated solutes or reaction products is of interest. Although this last complication can often be overcome by precipitating out the detergent in some insoluble form or by ingenious design of surfactants that can subsequently be destroyed chemically,[5] a more general approach would be to design polyelectrolytes consisting of interconnected amphiphilic subunits capable of ordering themselves in solution, preferably spontaneously, to form intrapolymeric domains with micellelike solubilizing and counterion-binding properties.

In an earlier preliminary work,[6] we showed that, by appropriate structural modification, one could obtain linear aliphatic [*n*,*m*]-ionenes capable of accelerating the rate of alkaline hydrolysis of *p*-nitrophenyl octanoate (NPO). Although the hydrophilic [6,10]- and [3,10]-ionenes had no effect whatsoever on the rate of this reaction, two ionenes with longer interconnecting segments, viz., the [3,16]- and the [3,22]-ionene, were capable of accelerating the reaction rate. Indeed, with the [3,22]-ionene, the maximum rate acceleration was virtually identical with that observed[7] for the same reaction in micellar hexadecyltrimethylammonium bromide (CTAB). This marked difference in catalytic properties was tentatively attributed[6] to a structure-dependent change in preferred conformation, from extended or rodlike in the hydrophilic [6,10]- and [3,10]-ionenes to globular or "micellelike" in the more hydrophobic [3,16]- and [3,22]-ionenes, a hypothesis consistent with the observed intrinsic viscosities (high for the [6,10]- and [3,10]- and very low for the [3,22]-ionene).



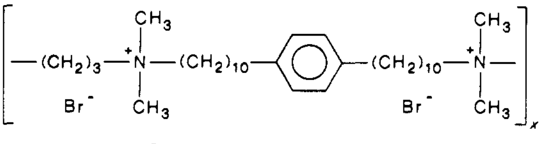
$$\left[-(CH_2)_n-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-(CH_2)_m-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}- \right]_x \quad Br^- \quad Br^-$$

[*n*, *m*]-ionene



NPO

In the present work, we report a systematic study of nine ionene polyelectrolytes: the [6,10]-ionene, seven homologous [3,*m*]-ionenes (m = 6, 10, 12, 14, 16, 18, 22), and the [3,10-phenyl-10]-ionene.



[3,10-phenyl-10]-ionene

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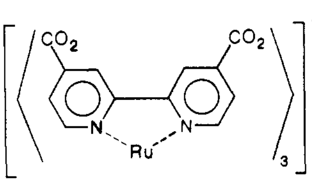
The results nicely confirm our previous hypothesis[6] that the formation of micellelike domains, governed by the interplay between ionene structure and ionene conformation, is responsible for the observed catalytic activity. Moreover, for the homologous [3,*m*]-ionenes, the onset of folding of the ionene chain is found to occur at about $m = 14$, as previously predicted[6] on the basis of simple free energy considerations. The concepts developed here should provide a basis for the rational design of a wide range of potentially useful micelle-mimetic polyelectrolytes, with perspectives for immobilization on appropriate supports and for straightforward inclusion of additional auxiliary functionality.

Results and Discussion

The [3,*m*]-ionenes employed in this work were prepared by reacting 1,3-dibromopropane with an equimolar quantity of the appropriate 1,*m*-bis(dimethylamino)alkane. Under our polymerization conditions, the molecular weights of the ionenes obtained would appear to be of the order of 10000–15000 (roughly 15–30 repeat units, depending on the ionene). This inference is based on our previously reported[6] viscosity average molecular weight of ~15 000 (ca. 30 repeat units) for the [6,10]-ionene and an estimate of the molecular weight of the [3,22]-ionene based on an adaptation of the Turro–Yekta method[8] for determining micellar aggregation numbers. This adaptation involved the use of [3,22]-ionene-solubilized 9-methylanthracene (9-MeAn) to quench the emission of the anionic probe[9] $(dcbpy)_3Ru$. The fact that only about 95% of the emissive probe is bound to the [3,22]-ionene or to typical cationic micelles such as TTAB and CTAB, even in the absence of added salt,[10] required the introduction of a correction for emission from the non-ionene-bound probe, which modifies the original Turro–Yekta[8] equation to eq 1, where I^0 and

$$-\ln [1 - (1 - I/I^0)(I^0/I_p^0)] = (2N)[\text{9-MeAn}]/[\text{P}] \qquad (1)$$

I are the emission intensities of $(dcbpy)_3Ru$ in the absence and presence of 9-MeAn, respectively; I_p^0, the emission intensity of the ionene-bound probe in the absence of 9-MeAn, was determined by extrapolation of data for the selective quenching of the emission of the residual aqueous probe by the *N*-methyl-4-carboxamidopyridinium ion[11] to infinite quencher concentration. This value was confirmed by parallel experiments using Cu^{2+} and the *N*-methyl-4-cyanopyridinium ions as quenchers[9] of the non-ionene-bound probe. Analysis of the experimental data in terms of eq 1 provided an average number of repeat units of $N = 17.5 \pm 2$, corresponding to an unhydrated number average molecular weight of ~11 000 ± 1,000 for the [3,22]-ionene.[12]



$(dcbpy)_3Ru$

Scheme I. Photophysical Model for Quenching of Pyrene (M) Fluorescence by the *N*-Ethylpyridinium (NEP) Cation in Aqueous Ionene (P) Solutions

$$\mathrm{M_{aq}} \xrightarrow{f_{aq}I_0} \mathrm{M_{aq}}^{*1} \text{ excitation (aqueous pyrene)}$$

$$\mathrm{M_p} \xrightarrow{f_pI_0} \mathrm{M_p}^{*1} \text{ excitation (ionene pyrene)}$$

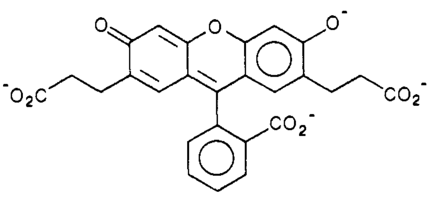
$$\mathrm{M_{aq}}^{*1} \xrightarrow{1/\tau_{aq}^0} \mathrm{M_{aq}} \text{ unimolecular decay (aqueous pyrene)}$$

$$\mathrm{M_p}^{*1} \xrightarrow{1/\tau_p^0} \mathrm{M_p} \text{ unimolecular decay (ionene pyrene)}$$

$$\mathrm{M_{aq}}^{*1} + \mathrm{P} \xrightarrow[k_-]{k_+} \mathrm{M_p}^{*1} \text{ ionene entry and exit}$$

$$\mathrm{M_{aq}}^{*1} + \mathrm{NEP} \xrightarrow{k_q} \mathrm{M_{aq}} \text{ quenching (aqueous pyrene)}$$

In order to determine whether the more hydrophobic ionenes do, in fact, form micellelike domains, we investigated the ionenes with respect to their ability to solubilize a neutral hydrophobic substrate (pyrene), to bind and exchange counterions (measured via conductivity and fluorescence quenching techniques), and to adopt folded or more globular conformations (measured via fluorescence anisotropy of an adsorbed fluorescein derivative BCF).



BCF

Incorporation coefficients for the solubilization of pyrene by the ionenes were estimated by using the hydrophilic, ionene-excluded *N*-ethylpyridinium (NEP) cation as a selective quencher of the fluorescence of pyrene in the aqueous phase. In homogeneous aqueous solution, NEP is a diffusion-controlled quencher of pyrene fluorescence ($k_q = 1.4 \times 10^{10}$ M^{-1} s^{-1} assuming[13] $\tau_{aq}^0 = 65$ ns). In contrast, in micellar CTAB or aqueous solutions of the [3,18]-, [3,22]-, and [3,10-phenyl-10]-ionenes, there is no detectable quenching of pyrene fluorescence by NEP. For the remaining ionenes, the apparent quenching efficiency depends on both the structure and concentration of the ionene and simple Stern–Volmer quenching plots are noticeably nonlinear. These results are consistent with electrostatic exclusion of the hydrophilic NEP cation from the immediate vicinity of the cationic ionene, such that the quenching occurs only in the aqueous phase (Scheme I). On the basis of this scheme, conventional steady-state analysis[14] leads to eq 2 for the ratio of pyrene fluorescence intensities in the presence (I) and absence (I^0) of NEP, where

$$I^0/I = (1 + K_{sv}'[\text{NEP}])/(1 + BK_{sv}^0[\text{NEP}]) \qquad (2)$$

$K_{sv}^0 = k_q\tau_{aq}^0$ is the Stern–Volumer quenching constant in the absence of the ionene. The term B, given by eq 3, depends on the ionene

$$B = f_p\Phi_p^0[\Phi_p^0(f_p + K_+^0) + \Phi_{aq}^0(f_{aq} + K_-^0)] \qquad (3)$$

concentration ([P], as ionic bromide), the intrinsic fluorescence quantum yields (Φ^0) of pyrene in the ionene and aqueous phases, and the parameters $K_+^0 = k_+\tau_{aq}^0/2N$ and $K_-^0 = k_-\tau_p^0$, which are functions of the probe lifetimes and the rates of probe entry and exit from an ionene with an average number of repeat units N. Finally, the "apparent" Stern–Volmer quenching constant K_{sv}' in the presence of ionene can be related to K_{sv}^0 via eq 4.

$$K_{sv}^0/K_{sv}' = 1 + K_+^0[\text{P}]/(1 + K_-^0) \qquad (4)$$

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[10] The adsorbed $(dcbpy)_3Ru$ can be readily displaced from these cationic surfaces by addition of NaBr, displacement (followed by emission intensity) being essentially total at ~0.1 M NaBr. 9-Methylanthracene is totally solubilized in the [3,22]-ionene under these conditions.

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[12] Given the incomplete adsorption of the emissive probe to the ionene, this value is probably only approximate. It does, however, appear to rule out significant interpolymeric aggregation to form vesiclelike structures. Although the formation of such structures has been reported for the symmetrical hydrophobic [20,20]-ionene in aqueous solution, no such structures were observed with the unsymmetrical hydrophobic [16,20]-ionene: (a) Kunitake, T.; Nakashima, N.; Takarabe, K.; Nagai, M.; Tsuge, A.; Yanagi, H. *J. Am. Chem. Soc.* **1981**, *103*, 5945-5947. (b) Kunitake, T.; Tsuge, A.; Takarabe, K. *Polym. J. (Tokyo)* **1985**, *17*, 633-640.

[13] Geiger, M.; Turro, N. J.; *Photochem. Photobiol.* **1975**, *22*, 273-276.

[14] This kinetic situation is treated in detail by: Shetlar, M. D. *Mol. Photochem.* **1974**, *6*, 191-205.

Table I. Vibronic Intensity Ratios of Pyrene Fluorescence, Partitioning Coefficients (K_s) for Incorporation of Pyrene, Apparent Degrees of Bromide Counterion Dissociation (α), and Fluorescence Anisotropies (r) and Maxima (λ_{max}) of BCF

ionene or micelle	concn,[a] M × 10^3	I/III[b] ratio	K_s,[c] M^{-1} water	K_s,[c] M^{-1} NaBr[d]	α	r	λ_{max}, nm
	water	1.81				0.022	517
[6,10]	6.9	1.81	85	110	0.89	0.051	522
[3,6]	10	1.81	11	15	0.71	0.044	522
[3,10]	7.9	1.81	6	17	0.95	0.054	522
[3,12]	13	1.81	45	65	0.81	0.055	524
[3,14]	14	1.81	200	410	0.82	0.081	527
[3,16]	9.7	1.60	1400	2800	0.61	0.134	529
[3,18]	10	1.60	7300	1.4 × 10^4	0.34	0.186	532
[3,22]	9.7	1.58	2.4 × 10^5	4.9 × 10^5	0.25	0.226	532
[3,10-phenyl-10]	9.3	1.58	>10^4	>10^4	0.25	0.196	532
CTAB	20	1.36	1.7 × 10^5		0.20	0.133	529
	methanol	1.36				0.026	522

[a] As equivalent ionic bromide. [b] Vibronic bands designated as in ref 17. [c] Values for the [6,10]-, [3,6]-, and [3,10]-ionenes are K_s^* estimated from the ratios $K_+/(1 + K_-)$ (eq 4) assuming $k_+/2N = 6 \times 10^9$ M^{-1} s^{-1}; values for the [3,18]- and [3,22]-ionenes were estimated by extrapolation of eq 7 (Figure 2, inset); value for CTAB from ref 26. [d] In 0.050 M NaBr.

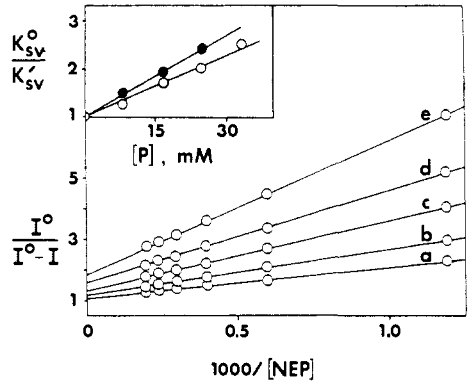

Figure 1. Data for quenching of pyrene (1 × 10^{-7} M) fluorescence by the *N*-ethylpyridinium (NEP) cation in (a) water and in (b) 0.0082 M, (c) 0.0164 M, (d) 0.0246 M, and (e) 0.0328 M [3,12]-ionene (expressed as ionene-derived bromide), plotted according to eq 5. The inset shows the corresponding plot of K_{sv}^0/K_{sv}' versus [3,12]-ionene concentration in the absence (○) and presence (●) of 0.050 M NaBr.

From a practical standpoint, the quenching data are more conveniently analyzed by using the corresponding reciprocal relationship of eq 5. When plotted in this form, the value of K_{sv}'

$$I^0/(I^0 - I) = [1/(K_{sv}' - BK_{sv}^0)](K_{sv}' + 1/[\mathrm{NEP}]) \quad (5)$$

is given by the intercept/slope ratio and B can be calculated from the intercept. When probe entry and exit are sufficiently slow, $K_{sv}' = K_{sv}^0$ and the intercept, which reduces to $1/(1 - B)$, can be directly related to the ground-state pyrene incorporation coefficient (K_s) via eq 6.[15] This behavior was observed for the [3,14]- and

$$1/(1 - B) = 1 + K_s(\Phi_p^0/\Phi_{aq}^0)[P] \quad (6)$$

[3,16]-ionenes. On the other hand, if probe entry and exit do occur during the probe lifetime, the experimental value of K_{sv}' will be less than K_{sv}^0. This behavior was encountered for the [6,10]-, [3,6]-, and [3,12]-ionenes (Figure 1). In these cases, incorporation coefficients (actually $K_s^* = k_+/k_-N$ for excited pyrene) were estimated from the ratio $K_+^0/(1 + K_-^0)$, given by the slope of linear plots of K_{sv}^0/K_{sv}' versus ionene concentration (eq 4; Figure 1, inset).

The values of K_s for solubilization of pyrene by the ionenes in the absence and presence of 0.050 M NaBr are collected in Table I. For the homologous [3,*m*]-ionenes with m = 10–16, there is a good linear correlation between ln K_s and m (Figure 2, inset) of the type shown by eq 7, where $\Delta\Delta G$ is the incremental free

$$\ln K_s = A - m\Delta\Delta G/RT \quad (7)$$

energy contribution per methylene group. The salt-independent value of $\Delta\Delta G = -0.88RT$ is consistent with solubilization due to a predominantly hydrophobic interaction[16] between pyrene and the hydrocarbon segments of the ionene. Extrapolation of these correlations to higher m permits one to estimate the K_s values for the [3,18]- and [3,22]-ionenes (Table I) and to compare the percentage of the total pyrene incorporated into the homologous [3,*m*]-ionenes (Figure 2) at any given fixed ionene concentration.

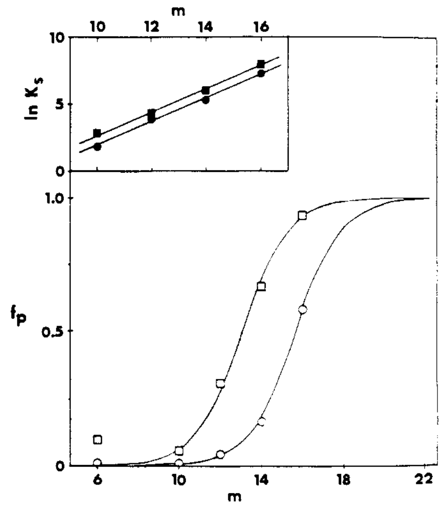

Figure 2. Fraction (f_p) of total pyrene (1 × 10^{-7} M) incorporated into the homologous [3,*m*]-ionenes ((○) 0.001 M and (□) 0.010 M equivalent ionene–derived bromide) in water. Data points, calculated from the K_s values of Table I, are compared with curves calculated via eq 7. The parameters of eq 7 were determined from the plots in the inset in the absence (●, $A = -6.89$ and $\Delta\Delta G/RT = -0.88$) and presence (■, $A = -6.19$ and $\Delta\Delta G/RT = -0.88$) of 0.050 M NaBr.

On the basis of these K_s values, the highly aqueous average microenvironment of pyrene in solutions of the [6,10]-, [3,6]-, [3,10]-, and [3,12]-ionenes, which can be inferred[17] from the vibronic intensity ratio data of Table I, merely reflects the fact that pyrene is predominantly localized in the aqueous phase. In the case of the [3,14]-ionene, pyrene is apparently largely, but not totally, solubilized in the ionene. For the [3,16]- [3,18]-, [3,22]-, and [3,10-phenyl-10]-ionenes, however, solubilization of pyrene is essentially complete; for these ionenes, the vibronic intensity ratios suggest a partially nonaqueous solubilization microenvironment for pyrene (somewhat more aqueous than that in the CTAB micelle), with a modest decrease in aqueous character upon going from the [3,16]- to the [3,22]-ionene.

The K_s values are also consistent with the effects of added NaBr and KCl on pyrene fluorescence. In solutions of the [3,12]-ionene

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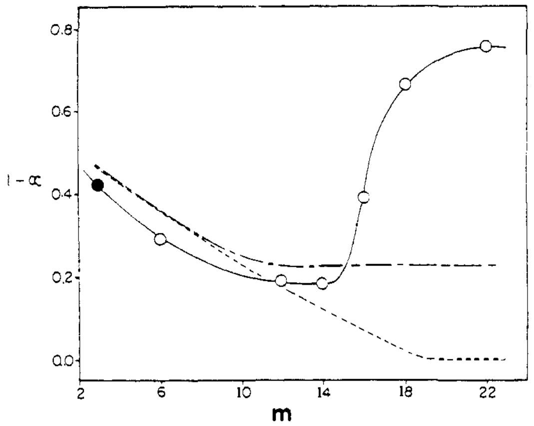

Figure 3. Comparison of the experimental degrees of counterion association ($1 - \alpha$, Table I) to the homologous [3,*m*]-ionenes with values predicted for rodlike polyelectrolytes from counterion condensation theory (eq 8) assuming (1) $\alpha_{3,m} = (\alpha_{3,3} + \alpha_{m,m})/2$ (— - —) or (2) $\alpha_{3,m} = \alpha_{(3+m)/2,(3+m)/2}$ (- - -). Data point for the [3,3]-ionene (●) from Fujii.[21]

(0.013 M), the quenching of the fluorescence of pyrene by added bromide ion (0–0.1 M NaBr) is indistinguishable from that in water in the absence of the ionene. Similar results were obtained for the [6,10]-ionene (0.017 M), the quenching being about $^2/_3$ as efficient as in water. In contrast, added NaBr has no effect at all on the fluorescence of pyrene solubilized in either the [3,22]- or the [3,10-phenyl-10]-ionenes (0.01 M). In the case of the [3,14]-, [3,16]-, and [3,18]-ionenes (all ca. 0.01 M), initial addition of NaBr (0.01 M) provokes a decrease in pyrene fluorescence intensity (by about 6%, 4%, and 1%, respectively) with little or no additional quenching effect at higher [NaBr], a behavior that can be rationalized in terms of enhanced solubilization of pyrene in the ionene due to the salt-dependent increase in K_s (Table I). The effects of added KCl (0–0.1 M) on pyrene fluorescence, which are complimentary to those with NaBr, range from no effect for the [6,10]-ionene and only a very slight (5%) increase for the [3,12]-ionene to a rather large increase (asymptotically approaching a value of $I^0/I = 0.65$ at high KCl) for the [3,10-phenyl-10]- and [3,*m*]-ionenes with $m \geq 14$. Treatment of data for the effect of added KCl on the fluorescence of pyrene at two fixed ionene concentrations and three fixed NaBr concentrations (0.005, 0.010, and 0.020 M) according to the method of Abuin et al.,[18] using experimentally determined degrees of counterion dissociation (vide infra), provided selectivity coefficients for chloride/bromide counterion exchange ($K_{Cl/Br}$) at the ionene surface of 0.55, 0.28, and 0.23 for the [3,18]-, [3,10-phenyl-10]-, and [3,22]-ionenes, respectively.[19]

Apparent degrees of dissociation (α) of the bromide counterions of the ionenes were determined by conductivity with micellar CTAB as the reference. For CTAB, the ratio between the slopes of plots of specific conductivity versus detergent concentration above (β_{CTAB}) and below (β_0) the critical micelle concentration provided a value of $\alpha = 0.20$, in good agreement with other literature values.[1,3,4] If the mobilities of the ionenes and the CTAB micelle are similar, one can use the slope (β_{ionene}) of a plot of specific conductivity versus ionene concentration (expressed as bromide) to estimate the values of α for the ionenes via $\alpha = 0.2\beta_{ionene}/\beta_{CTAB}$. The α values thus determined are collected in Table I.

According to counterion condensation theory,[20] the degree of dissociation of a rodlike polyelectrolyte at infinite dilution is given by $\alpha = b/l_B \leq 1$, where l_B is the Bjerrum length (0.7135 nm in water at 25 °C) and b is the linear charge density or effective spacing between the charge centers along the polyelectrolyte chain. Recently, Fujii[21] has shown that experimental values of $\alpha_{k,k}$ for symmetrical aliphatic [*k*,*k*]-ionenes can be calculated from the relationship of eq 8, where the numerator corresponds to the

$$\alpha_{k,k} = (0.045k + 0.0112)^{1/2}/l_B \leq 1 \qquad (8)$$

average distance between the extremities of a freely rotating methylene chain. Since our ionenes are nonsymmetrical ($n \neq m$), we calculated what should be upper and lower limits on $\alpha_{n,m}$ for a rodlike conformation by assuming that (1) $\alpha_{n,m} = (\alpha_{n,n} + \alpha_{m,m})/2$, i.e., the mean of the α values of an [*n*,*n*]- and an [*m*,*m*]-ionene, or (2) $\alpha_{n,m} = \alpha_{k,k}$, where $k = (n + m)/2$ is the mean segment length. As shown in Figure 3, up to about $m = 14$, the experimental data for the [3,*m*]-ionenes, plotted as the apparent degree of counterion association ($1 - \alpha$) versus *m*, are in quite good agreement with the range of predicted α values. Similar agreement is found for the [6,10]-ionene (calculated $\alpha = 0.85$). However, the assumption that all of the ionenes adopt extended or rodlike conformations in aqueous solution clearly breaks down for the [3,*m*]-ionenes with $m > 14$ (Figure 3) and for the [3,10-phenyl-10]-ionene (calculated $\alpha = 0.77$–1.0). Indeed, the linear charge spacings (*b*) that would be required to generate the experimental values of α for rodlike [3,16]-, [3,18]-, [3,22]-, and [3,10-phenyl-10]-ionenes (0.44, 0.24, 0.18, and 0.18 nm, respectively) are in themselves clearly inconsistent with any conceivable rodlike conformation for these ionenes.

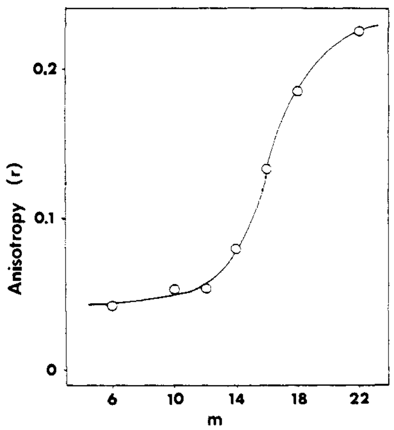

Figure 4. Experimental fluorescence anisotropies (*r*, Table I) of BCF adsorbed onto the homologous [3,*m*]-ionenes in slightly alkaline (pH 9–10) aqueous solution.

Measurements of the fluorescence anisotropy (*r*) of a tetraanionic fluorescein derivative (BCF) adsorbed into the ionenes provide much more direct evidence for a structure-dependent change in the conformation of the ionenes. In alkaline aqueous solution, BCF exhibits absorption and emission maxima at 498 and 517 nm, respectively, and has a fluorescence quantum yield of 0.6, a fluorescence lifetime of 4.37 ns, and a residual anisotropy of 0.022. Addition of BCF to slightly alkaline aqueous ionene solutions or to micellar CTAB results in a red shift of both the absorption and emission maxima, accompanied by an increase in *r* (490 nm excitation and 520 nm emission) with little or no change in fluorescence lifetime. At low to moderate ionic strengths, the spectral shifts and *r* values depend on the structure (Figure 4) but not the concentration of the ionene (0.002–0.03 M equivalent bromide), indicating complete adsorption of BCF onto the ionenes under these conditions.

For hydrophilic ionenes with extended or rodlike conformations, the adsorption of BCF onto the ionene should be predominantly electrostatic in nature. The linear disposition of the cationic charge centers and the greater segmental flexibility of the polyelectrolyte chain in the extended conformation should permit relatively rapid rotational relaxation of the adsorbed probe. This expectation is consistent with the observation of a moderately small *m*-independent anisotropy ($r = 0.050 \pm 0.005$) and similar small spectral

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shifts for BCF adsorbed onto the [6,10]-ionene and the [3,*m*]-ionenes with $m < 14$ (Table I). In contrast, for a hydrophobic ionene with a globular conformation, the higher net surface charge density and the possibility of additional nonelectrostatic (hydrophobic) contributions should result in much stronger adsorption of BCF to the ionene and, consequently, much slower rotational relaxation of the adsorbed BCF. In the limit of very strong adsorption of BCF to a compact, globular ionene, the anisotropy should be governed by the rate of isotropic rotation of the ionene as a whole. Under these conditions, the observed anisotropy can be related to the hydrated molar volume (V_h) of the ionene via eq 9,[22] where $r_0 = 0.35$ is the intrinsic anisotropy (determined for

$$V_h = (RT\tau/\eta)[r/(r_0 - r)] \qquad (9)$$

BCF in a rigid polymeric matrix), $\tau = 4.4$ ns is the BCF fluorescence lifetime, and η is the solvent viscosity. Indeed, for the [3,*m*]-ionenes with $m > 14$, the anisotropy increases significantly with *m* (Table I) and is accompanied by much larger spectral shifts. For the [3,22]-ionene, the observed anisotropy corresponds (assuming a density of ~1) to a *hydrated* molecular weight of ~25 000 ± 5,000, a value about twice the *unhydrated* number-average molecular weight estimated by using $(dcbpy)_3Ru$ as probe (vide supra). Together with our more limited intrinsic viscosity data[6] (vide introduction), these *m*-dependent differences in fluorescence anisotropy imply that BCF is in fact detecting, via its relative rotational mobility at the ionene surface, differences in the conformation of the ionenes in aqueous solution.

For the homologous [3,*m*]-ionene bromides, the onset of the changeover from rodlike or extended conformations to progressively more compact or more globular conformations occurs at about $m = 14$, as predicted in our earlier work[6] on the basis of simple free energy considerations (hydrophobic effect compensating electrostatic repulsion). Although the nature of the counterion does influence the ionene conformation slightly,[19] it is the relative hydrophobicity of the segments that plays the dominant role in determining the preferred conformation in aqueous solution. The importance of hydrophobic interactions is further reinforced by the observation that, in pure methanol,[19] the anisotropy of BCF adsorbed to the [3,22]-ionene is virtually identical with that for the [3,6]-ionene ($r = 0.050$ vs $r = 0.051$).

Relationship to Ionene Catalysis. The results outlined above show that the [3,10]-ionene binds both hydrophobic substrates and counterions poorly, with little or no selectivity in counterion exchange.[19] At the other extreme, the [3,22]-ionene appears to be quite CTAB-like, not only in terms of its ability to solubilize hydrophobic substrates and bind counterions, but also in its ion-exchange selectivities. The [3,16]-ionene exhibits intermediate behavior with respect to solubilization, counterion binding, and exchange selectivity (extrapolation of the data for the [3,18]- and [3,22]-ionenes provides an estimate of $K_{Cl/Br} = 0.75$ for the [3,16]-ionene). This picture is entirely consistent with the experimentally observed[6] effects of these three ionenes on the rate of alkaline hydrolysis of *p*-nitrophenyl octanoate (NPO) in buffered (0.02 M borate, pH 9.4–9.5) solution, which range from no effect at all ([3,10]-ionene) to a modest rate acceleration ([3,16]-ionene) to a very CTAB-like rate profile ([3,22]-ionene).

In addition to these qualitative considerations, the present results also permit more quantitative analysis of the rate data for these ionenes in terms of the pseudophase ion-exchange model[3,4,23] originally developed for micellar solutions. Within the framework of this model, the observed pseudo-first-order rate constant (k_ψ) for alkaline hydrolysis of NPO in buffered ionene bromide solution is given by eq 10,[7] where k_{2aq} and k_{2p} are the second-order rate

$$k_\psi = k_{2aq}[OH_{aq}][(k_{2p}/k_{2aq}\bar{V})K_s K_{OH/Br}[Br_p]/[Br_{aq}] + k_{2aq}]/(1 + K_s[P]) \qquad (10)$$

constants for hydrolysis of NPO in the aqueous phase and at the ionene surface, $\bar{V}$ is the reaction volume (per mole of quaternary

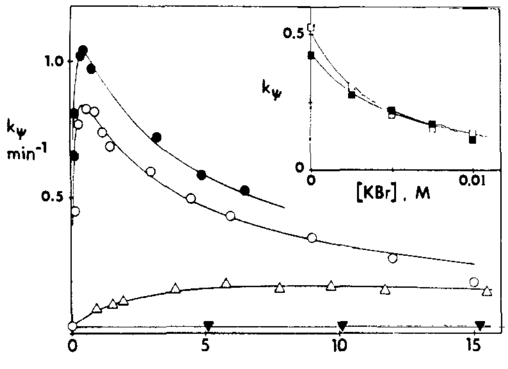

Figure 5. Comparison between experimental[6] and calculated (eq 10, see text) profiles of the effect of the [3,10]- (▼, pH 9.4), [3,16]- (Δ, pH 9.4), and [3,22]-ionenes (○, pH 9.4; ●, pH 9.5) on the pseudo-first-order rate constant for alkaline hydrolysis of *p*-nitrophenyl octanoate (NPO) in 0.020 M borate buffer. The inset shows the corresponding fit of eq 10 to the data for the inhibitory effect of added KBr on the rate constant at two concentrations of the [3,22]-ionene (□, 0.0042 M; ■, 0.0056 M; pH 9.4).

ammonium groups) at the ionene surface, K_s is the NPO incorporation coefficient, [P] is the ionene concentration (as equivalent bromide), and $K_{OH/Br}$ is the selectivity coefficient for OH^-/Br^- counterion exchange at the ionene surface. The aqueous hydroxide ion concentration ($[OH_{aq}]$) is determined by the buffer pH. The ratio of bromide ion concentrations at the ionene surface ($[Br_p]$) and in the aqueous phase ($[Br_{aq}]$) can be calculated from relationships entirely analogous to those used to analyze this same reaction in micellar CTAB.[7] In calculating this ratio, we employed the experimental values of α for counterion dissociation (Table I) and values of $K_{OH/Br}$ estimated from the relationship $K_{OH/Br}(\text{ionene}) = K_{OH/Br}(\text{CTAB})[K_{Cl/Br}(\text{ionene})/K_{Cl/Br}(\text{CTAB})]$, where $K_{OH/Br}(\text{CTAB}) = 0.08$[3,24,25] and $K_{Cl/Br}(\text{CTAB}) = 0.20$;[18,25] as in the case of CTAB,[7] hydroxide–borate (B) exchange was taken into account via a best fit value of $K_{OH/B}(\text{ionene}) = 0.80$. On the basis of K_s values for solubilization of pyrene[26] and NPO[7] by micellar CTAB and for solubilization of pyrene by the ionenes (Table I), the K_s values for solubilization of NPO by the [3,10]-, [3,16]-, and [3,22]-ionenes were estimated to be of the order of 1, 100, and 10000 M^{-1}, respectively. As shown in Figure 5, this parameter set gives excellent agreement with the experimental kinetic data,[6] both as a function of ionene concentration and of added KBr, with values[27] of $k_{2p}/k_{2aq}\bar{V} = 1.20–1.25$ comparable to that (0.78) for the same reaction in borate-buffered micellar CTAB.[7]

Implications for the Design of Micelle-Mimetic Polyelectrolytes. In essence, there are three distinct manners in which charged amphiphilic subunits can be interconnected to produce a polymeric structure: (1) by linking together the hydrophilic ionic headgroups of the subunits to form a polyelectrolyte with lateral hydrophobic side chains: (2) by linking together the hydrophobic portions of the subunits to form a polymer with lateral side chains distally terminated by the ionic headgroups; or (3) as in the aliphatic ionenes described here, by joining the subunits together in head-to-tail or in alternating head-to-head and tail-to-tail fashion to form a linear polyelectrolyte structure. The available literature data,[28,29] together with the results of this study, suggest that this

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[27] The lack of a significant rate acceleration in the case of the [3,10]-ionene is consistent with a large range of parameter values, including $k_{2p} = k_{2aq}$, no counterion exchange selectivity, $\alpha = 0.75–1.0$, and $K_s(\text{NPO}) \leq 1\ M^{-1}$. In view of our earlier results[7] in micellar CTAB, we attribute the similar values of $k_{2p}/k_{2aq}\bar{V}$ for the [3,16]- and [3,22]-ionenes to compensation between changes in k_{2p} and $\bar{V}$.

last type of structural arrangement has several distinct advantages.

There are a number of examples of amphilic polyelectrolytes or "polysoaps" with the first type of subunit arrangement. Those that have been shown to accelerate rates of bimolecular reactions include long-chain *N*-alkylpoly(vinylpyridinium)s,[28c,30–32] poly(vinylethylimidazolium)s,[31,33] poly(ethyleneiminium)s,[28c,d] and poly(diethyldiallylammonium)-SO_2 copolymers.[30] A rather typical finding[31–34] for polyelectrolytes of this type is that the incorporation of both short and long side chains, as opposed to only long side chains, tends to enhance the "catalytic" efficiency while simultaneously reducing the intrinsic viscosity or effective volume occupied by the polyelectrolyte in aqueous solution. In addition, the optimal proportion of short side chains becomes progressively higher as the length of the long side chain increases.[31–34] This is perhaps not surprising since the juxtapositioning of the charged headgroups necessarily requires that the intrapolymeric aggregation of the hydrophobic side chains be subject to restrictions imposed by the conformational mobility and coiling of the main polymer chain.

Interesting examples of the second type of polysoap structure include polymer-anchored amphiphiles, which produce modest reaction rate accelerations,[35] and sodium poly(styrene-styrene-undecanoate),[36] which is capable of solubilizing relatively large quantities of cholesterol. Although this disposition of the amphiphilic subunits should potentially be conducive to the formation of hydrophobic domains, restrictions on packing imposed by the radial attachment of the subunits to the main polymer chain should ultimately limit the net charge density that can be achieved at the surface of these hydrophobic domains.

By comparison, polyelectrolytes of the third type, such as the amphiphilic ionenes, with their linear arrangement of alternating charge centers and hydrophobic moieties, should be quite flexible. Consequently, they can take advantage of various folding modes (accordion-like, intrapolymeric segment crossing or intertwining, etc.) and a wide range of packing geometries in order to minimize hydrocarbon–water contact and maximize substrate accommodation. Since the headgroups and hydrophobic segments do not have a predisposed orientation, linear amphiphilic polyelectrolytes of this type could also exhibit rather low tensoactivity. Since, as in micellization of monomeric surfactants, the folding up of the linear polymer chain simultaneously juxtaposes both the hydrophobic segments and the charge centers, the resultant intrapolymeric domains can potentially be quite micellelike in their properties. Moreover, the formation of such domains should be a fairly cooperative process governed by a balance between hydrophobic effects and electrostatic repulsion of the type operative in micellization. This point is nicely demonstrated by the present results, which fully confirm our earlier prediction,[6] based on precisely this line of reasoning, that the onset of chain folding should occur at about $m = 14$ in the [3,m]-ionenes.

This relative predictability of the conformational characteristics of the amphiphilic ionenes, together with the methodology developed here, permits their use as probes for investigating the origin of counterion selectivities and solvophobic effects in mixed solvent systems.[19] The linear repeat sequence and relatively straightforward synthesis of the ionenes facilitate inclusion of additional auxiliary functionality (catalytic, chelating, secondarily polymerizable). The presence of unreacted end groups (terminal tertiary amine and/or alkyl halide) also confers the potential for covalent attachment to appropriate supports.[37] This conjuncture of properties suggests that amphiphilic ionenes are excellent prototypes for the rational design of micelle-mimetic polyelectrolytes tailored to a wide range of potential applications.

Experimental Section

Pyrene (Aldrich, 99%) was purified by the method of Geiger and Turro.[13] The emissive probe[9] $(dcbpy)_3Ru$ [tetrasodium tris[(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II)]] was a gift from Dr. J. B. S. Bonilha (USP-Ribeirão Preto, Brazil). The fluorescent probe bis(carboxyethyl)fluorescein (BCF) was prepared and purified as described elsewhere.[38] CTAB (Merck, p.a.) was recrsytallized from acetone–methanol (85:15). NaBr (BDH, 99+%), KCl (Merck, p.a.), and 9-methylanthracene (Aldrich, 99%) were used as received. *N*-Ethylpyridinium bromide was prepared by reaction (100 h at ambient temperature) of dry pyridine with excess 1-bromoethane; the white crystalline product was filtered, washed with ethyl acetate, and vacuum dried ($\epsilon_{258} = 4200\ M^{-1}\ cm^{-1}$ in methanol). All aqueous solutions were prepared with deionized water, doubly distilled in glass.

Commercial [3,6]-ionene bromide (Polybrene, Aldrich) was used as received. Purified samples of [6,10]-ionene bromide (viscosity MW of ca. 15000) and of [3,10]-ionene bromide were available from prior work.[6] The remaining ionenes were prepared as described[6,39] by heating (70 °C, 24 h, N_2 atmosphere) equimolar quantities of the appropriate 1,m-bis(dimethylamino)alkane (vide infra) and distilled 1,3-dibromopropane (Aldrich) in spectrograde acetonitrile (Aldrich). After being cooled to room temperature, the precipitated ionene polyelectrolyte was collected by filtration, exhaustively extracted with hot ethyl acetate, and vacuum dried. The [3,18]-, [3,22]-, and [3,10-phenyl-10]-ionenes were further purified (extensive loss of material during dialysis precluded application of this procedure to the ionenes with $m < 18$) by dissolution in water, filtration through a 2200-Å Millipore filter, and exhaustive dialysis against distilled water (30 h, with periodic changes) in pretreated[6] dialysis bags, followed by lyophilization to recover the ionene. The ^1H NMR spectra (200 MHz, D_2O, DSS external reference, room temperature) of these three ionenes, which exhibited relatively broad resonances for the methylene protons (0.15–0.3 ppm, spin–spin couplings unresolved, broadening increasing [3,18]- < [3,22]- ≪ [3,10-phenyl-10]-ionene), were consistent with the proposed ionene molecular structure.[40] [3,18]-Ionene: δ 1.34 (28 H, internal methylenes of long segment), 1.80 (4 H, β CH_2s of long segment), 2.30 (2 H, central CH_2 of trimethylene segment), 3.25 (12 H, CH_3), 3.56 (8 H, CH_2-N). [3,22]-Ionene: δ 1.35 (36 H), 1.77 (4 H), 2.31 (2 H), 3.26 (12 H), 3.54 (8 H). [3,10-Phenyl-10]-ionene: δ 0.5–4.5 [58 H, br overlapping resonances with maxima at 1.30 (shoulder at ca. 1.80, internal and β methylenes of long segment), 2.35 (central CH_2 of trimethylene segment and CH_2-Ar?), and 3.25 (shoulder at ca. 3.60, CH_3 and CH_2-N)], 6.80 (4 H, ArH). All three ionenes gave equivalent titrations for ionic bromide and quaternary ammonium groups; after vacuum drying, the [3,22]-ionene analyzed satisfactorily (C, H, N) assuming one residual water of hydration per quaternary ammonium.[41]

Dodecanedioic (Aldrich, 99%) and tetradecanedioic (Aldrich, 99%) acid were used as received. Octadecanedioic acid,[42] docosanedioic

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(40) Both Rembaum and Noguchi[39b,c] and Kunitake et al.[12b] have reported ^1H NMR data for aliphatic ionenes that are generally consistent with those reported here, although our assignments differ somewhat from those assumed by the latter authors.

(41) Stoichiometric [20,20]-ionene hydrates are indicated by the elemental analyses of Kunitake et al.[12b]

acid,[42,43] and 1,4-benzenedidecanoic acid[44] were prepared by literature procedures and purified via recrystallization of their dimethyl esters from methanol (monitoring purity by mp and glpc on a 2 m × $^1/_8$ in. column of 10% UCW-98 on Chromosorb W), followed by saponification. The diacids were converted to the corresponding *N,N,N',N'*-tetramethyldiamides (characterized by C, H or C, H, N microanalyses and ^{1}H NMR), which were in turn reduced with $LiAlH_4$ to obtain the 1,*m*-bis(dimethylamino)alkanes (characterized by ^{1}H NMR) employed in the ionene synthesis. The following procedure is typical. Octadecanedioic acid (6 g, 0.02 mol) was converted to the diacid chloride by 3-h reflux with 30 mL of thionyl chloride. Excess thionyl chloride was removed by addition of benzene and evaporation at reduced pressure, the diacid chloride redissolved in 70 mL of dry benzene, and the solution slowly saturated with dry gaseous dimethylamine. After being stirred for 2 h at room temperature, the reaction mixture was diluted with water, additional benzene added to dissolve all of the product, and the benzene layer washed exhaustively with water, dried, and evaporated to dryness. Recrsytallization of the residual solid from ethyl acetate (active charcoal) provided 5.4 g (77% yield) of *N,N,N',N'*-tetramethyloctadecanediamide: mp 94–95 °C (lit.[45] mp 98 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (br s, 24 H, internal methylenes), 1.59 (m, 4 H, β CH_2s), 2.28 (tr, J = 7.5 Hz, 4 H, CH_2CO), 2.95 (br s, 12 H, CH_3). The diamide (2.7 g, 0.0073 mol) in 30 mL of dry THF was added to 2 g of $LiAlH_4$ in 20 mL of THF and, after refluxing overnight under a N_2 atmosphere, was worked up by careful addition of 5 mL of ethyl acetate, filtration, and evaporation at reduced pressure. Vacuum distillation provided 1.7 g (70% yield) of 1,18-bis(*N,N*-dimethylamino)octadecane: bp 150 °C (0.3 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.10–1.70 (m with br s at 1.25, 32 H, internal methylenes), 2.20 (br s, 16 H, CH_3-N with underlying CH_2-N). The other aliphatic *N,N,N',N'*-tetramethyldiamides and the corresponding known[12b,45–47] aliphatic 1,*m*-bis(*N,N*-dimethylamino)alkanes, which gave strictly analogous ^{1}H NMR spectra (virtually identical chemical shifts and coupling patterns), exhibited the following physical properties [*m*, diamide mp (from ethyl acetate), diamine bp or mp (from acetonitrile)]: *m* = 12, mp 88–90 °C, bp 160 °C (1 mmHg) [lit. bp 143–145 °C (0.2 mmHg),[41] bp 116–118 °C (0.1 mmHg)[46]]; *m* = 14: mp 87–87.5 °C, bp 140 °C (0.4 mmHg); *m* = 22, mp 99–100 °C, mp 48–48.5 °C. The same procedure was also employed to prepare 1,4-bis[10-(*N,N*-dimethylamino)decyl]benzene [*m* = 10-phenyl-10; mp 43.5–44 °C (from acetonitrile); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.27 (br s, 24 H, internal methylenes), 1.43 (m, 4 H, CH_2CH_2N), 1.58 (m, 4 H, CH_2CH_2Ar), 2.21 (s, 12 H, CH_3), 2.23 (tr, J = 7.5 Hz, 4 H, CH_2-N), 2.55 (tr, J = 7.5 Hz, 4 H, CH_2Ar), 7.07 (s, 4 H, ArH)] from the corresponding *N,N,N',N'*-tetramethyldiamide [mp 84–85 °C (from ethyl acetate); satisfactory C, H, N analysis; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.27 (br s, 20 H, internal methylenes), 1.61 (m, 8 H, CH_2CH_2Ar and CH_2CH_2CO), 2.29 (tr, J = 7.5 Hz, 4 H, CH_2CO), 2.55 (tr, J = 7.5 Hz, 4 H, CH_2Ar), 2.96 (s, 12 H, CH_3), 7.07 (s, 4 H, ArH)]. 1,16-Bis(*N,N*-dimethylamino)hexadecane[12b,47] was available from our previous study.[6] The amines were stored under vacuum and, when necessary, freshly distilled prior to use in the ionene synthesis.

Concentrations of aqueous stock solutions of *N*-ethylpyridinium bromide (0.18–0.20 M), CTAB (0.020 M), and the ionenes (expressed as ionene-derived bromide) were checked by titration.[48] Aqueous stock solutions of NaBr and KCl (3.00 M) and ethanolic stock solutions of pyrene (10^{-4} M) were prepared by weight. The concentration of aqueous stock solutions of BCF was estimated by absorption spectroscopy assuming[49] ϵ = 90 000 M^{-1} cm^{-1} at 498 nm.

All measurements were performed at 30 ± 1 °C on solutions contained in 1-cm path-length quartz fluorescence cells (Hellma). Relative vibronic intensities were determined from pyrene fluorescence spectra recorded at small band pass (0.5 nm) on a Hitachi Perkin-Elmer MPF-4 fluorescence spectrometer. All other fluorescence measurements were performed on a Perkin-Elmer LS-5 spectrometer. Fluorescence lifetimes were determined by single-photon counting (PRA system at the University of Rochester). Fluorescence quenching and counterion-exchange experiments were performed by adding successive aliquots of quencher or salt stock solution to 2.00 mL of aqueous ionene solution containing pyrene ((1–5) × 10^{-7} M final, excitation at 310 nm, emission at 393 nm). Selectivity coefficients for chloride–bromide counterion exchange were calculated from the pyrene fluorescence intensity data as previously described.[18] The solutions used to estimate the degree of polymerization of the [3,22]-ionene by emission quenching were prepared by mixing different amounts of two aqueous solutions of $(dcbpy)_3Ru$ (1.3 × 10^{-5} M) and ionene (5.64 × 10^{-3} M equivalent bromide), one of which also contained ionene-solubilized 9-methylanthracene (9.62 × 10^{-5} M, solubilized by overnight stirring in the dark). The quencher *N*-methyl-4-carboxamidopyridinium (MAP) chloride[11] was added to the solution without 9-methylanthracene in order to estimate the emission contribution from residual aqueous $(dcbpy)_3Ru$ not bound to the ionene. Emission intensities of $(dcbpy)_3Ru$ were determined at 605 nm with 465-nm excitation. Fluorescence anisotropies (r) of BCF (1 × 10^{-7} M) in slightly alkaline (pH 9–10) aqueous ionene solutions were determined on the Perkin-Elmer LS-5 equipped with polarization accessory (right-angle geometry), employing excitation and emission wavelengths of 490 and 520 nm, respectively, and the relationship[22] given in eq 11, where G =

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \qquad (11)$$

I_{HV}/I_{HH} is an instrumental correction factor and I_{VV}, I_{VH}, I_{HV}, and I_{HH} refer to the resultant emission intensities polarized in the vertical or horizontal detection planes (second subindex) upon excitation with either vertically or horizontally polarized light (first subindex). The intrinsic anisotropy (r_0) was determined with a 1-cm-diameter rod prepared by thermal polymerization (60 °C, 1 week, sealed test tube) of styrene polyester resin (Polilite T208-Resapol, Resana S.A. Ind. Quim., São Paulo) containing 3 × 10^{-7} M BCF. Conductivity measurements were performed at 25 °C with a Micronal B-331 conductimeter using a cell with Pt electrodes and a constant of 0.12 cm^{-1}; the initial ionene solution was progressively diluted with water, measuring the conductivity after each dilution. All calculations were performed on a CCE Exato Apple II+ compatible microcomputer.

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