Macromolecules **1992,** *25,* 450–453

Hydrophobic Interaction of Ionenes in Aqueous Solution

Li Zhuomei,* Zhang Xuexin, Chen Yuanpei, and Zhong Yuanzhen[†]

Institute of Polymer, Zhongshan University, Guangzhou, People's Republic of China

Received May 3, 1991; Revised Manuscript Received July 12, 1991

ABSTRACT: The effect of hydrophobic interaction on the conformation of three ionene species, 2,10-Br, 6,10-Br, and 6,6-Br, in aqueous solution was studied. In the absence of added electrolytes the polymer molecules behaved as stiff rods, while in the presence of 0.4 M KBr they had a random-coil conformation typical of an ordinary uncharged polymer. The 2,10-Br coiled up more than the other ionenes, and its steric factor σ ($=\langle r_0^2\rangle^{1/2}/\langle r_f^2\rangle^{1/2}$) had the smallest value. This is probably due to the different distribution of CH_3 groups and the hydrophobic interaction between the "hydrophobic domain" along the backbone of the chain. A conformational change on electrolyte addition was interpreted in terms of a simultaneous decrease in electrostatic repulsion and an increase in hydrophobic attraction among the methyl groups.

Introduction

Although substantial studies on the effect of hydrophobic interaction on macromolecular behavior in solution have been carried out,[1-10] only a limited number of investigations have been performed to elucidate the effect of the distribution of hydrophobic groups on the conformation of macromolecules. Since ionenes have quaternary ammonium ions in the backbone whose charge density as well as hydrophobic group density can be adjusted at will by choosing the proper monomers, they are ideally suited for studies of the effect of the distribution of hydrophobic groups on the polyelectrolyte behavior. Casson and Rembaum[11] have studied the solution behavior of ionenes, but they used only the symmetric or nearly symmetric ionenes 6,6-Br and 3,4-Br and did not discuss the effect of hydrophobic interaction.

The present paper describes the conformation of ionenes in aqueous solutions for three species, 2,10-Br, 6,10-Br, and 6,6-Br. It was found that the hydrophobic interaction between the CH_3 groups was the main factor governing their conformations when the polyelectrolyte effect was suppressed by added salts in which case the distribution of CH_3 groups along the backbone of the polymer played an important role.

Experimental Section

Polymer Preparation. The monomers *N,N,N′,N′*-tetramethyl-1,6-hexanediamine, 1,6-dibromohexane, and 1,10-dibromodecane were synthesized according to the methods described in the literature.[12,13] *N,N,N′,N′*-Tetramethylethylenediamine was purchased as an analytical reagent and used without further purification. Polymerizations were carried out in the DMF–CH_3OH mixed solvent.[14]

Characterization. The IR (KBr) spectra of all the ionenes show strong absorption bands at 1420 cm^{-1} (due to the C–H torsional vibration in the $-CH_2{}^+N<$ moiety) while the bands at 2800 cm^{-1} (due to the C–H stretching vibration in the $-N(CH_3)_2$ moiety), 1240 cm^{-1} (due to the C–H stretching vibration in $-CH_2Br$), and 550 cm^{-1} (due to the C–Br stretching vibration in $-CH_2Br$) disappear. The results of the elemental analysis of the ionenes are summarized in Table I.

Molecular Weight Determination. Weight-average molecular weights (M_w) were determined by SALLS with a KMX-6 light scattering photometer. Measurements were made at λ = 6328 Å, θ = 4.96°, and t = 26 °C, with 0.4 M KBr as solvent. To remove dust, each polymer solution was pressure filtered through 0.22-μm GS filter paper. The dn/dc's of the polymer in 0.4 M KBr were determined with a KMX-16 differential refractometer at λ = 6328 Å and t = 26 °C, using 0.4 M KBr as the reference.

Viscosity Measurement. The viscosity of the polymer solution was determined at 30 °C with an Ubbelohde dilution viscometer. Corrections for kinetic energy and shear rate were found to be negligible. The concentration of the polymer solution was expressed in grams per deciliter.

Results and Discussion

1. Conformation of Ionenes in Water in the Absence of Added Electrolytes. All aqueous solutions of ionenes have the typical polyelectrolyte behavior in the absence of added electrolyte. The viscosity of the polymer solution could be represented by the Fuoss relation

$$\frac{\eta_{sp}}{C} = \frac{A}{1 + BC^{1/2}} + D$$

D was first approximately obtained from the $\eta_{sp}/C - C^{-1/2}$ plot at higher concentrations of polymer, and then the linear plot of $(\eta_{sp}/C - D)^{-1}$ vs $C^{1/2}$ gave the intercept $1/A$. All the Fuoss parameters were evaluated by the least-squares method with the correlation coefficients $r \rightarrow 1$. The results are shown in Table II.

Because of the small magnitude of $1/A$, it was impossible to determine the value of A very precisely. However, a plot of log A vs log M_w for all systems was close to linear, with slopes approximately equal to 2.0. In practice, A can be considered as the intrinsic viscosity of the polymer in pure water; i.e., $A = [\eta]_{H_2O}$.

The A values were proportional to M^2, indicating that the ionenes in water without added electrolytes behave as stiff rodlike molecules, independently of the charge density and the distribution of CH_3 groups. It is surprising that the electrostatic repulsion between the cationic groups is sufficient to produce a rodlike chain, even in the case of 2,10-Br and 6,10-Br, which have flexible segments containing 10 methylene groups in the main chain.

2. Effect of the Distribution of CH_3 Groups on the Conformation of Ionene in 0.4 M KBr Aqueous Solution. After suppression of the polyelectrolyte effect by 0.4 M KBr, $[\eta]$ is related to the molecular weight by the Mark–Houwink relation $[\eta] = KM^a$. The parameters K and a are summarized in Table III. The a parameters for 2,10-Br and 6,10-Br are close to 0.6, similar to those for 6,6-Br and 3,4-Br, indicating that the ionenes have a random-coil conformation typical of ordinary uncharged polymers.

In order to investigate the effect of the distribution of CH_3 groups on the extent of coiling, we compared the value of A ($=[\eta]_{H_2O}$) with that of $[\eta]_{0.4\ M\ KBr}$ for ionenes

---

* To whom all correspondence should be addressed.

[†] Present address: GAF Chemicals Corp., 1361 Alps Road, Wayne, NJ 07470.

0024-9297/92/2225-0450$03.00/0

Table I
Elemental Analysis of Ionenes

	calcd, wt %					exptl, wt %					
x,*y*-Br	C	H	N	Br	C/N	C	H	N	Br	C/N	N/Br[a]
2,10	46.16	8.72	6.73	38.39	6.86	44.11	8.71	6.36	37.07	6.94	0.99
6,10	50.83	9.39	5.93	33.84	8.57	47.89	9.04	5.52	31.34	8.68	1.01
6,6	46.16	8.72	6.73	38.39	6.86	43.13	8.74	6.23	35.88	6.92	1.01

[a] Atomic ratio.

Table II
Fuoss's Parameters for Ionenes

x,*y*-Br	$M_w \times 10^{-4}$	*D*	1/*A*	*A*
2,10	0.49	0.063	0.105	9.5
	1.18	0.075	0.018	55.5
	1.52	0.078	0.012	83.3
	1.78	0.082	0.009	111.1
6,6	0.75	0.102	0.071	14.1
	1.97	0.159	0.009	111.1
	2.64	0.136	0.006	166.6
	3.42	0.148	0.003	333.3
	4.08	0.132	0.002	500
6,10	2.06	0.136	0.010	100
	2.76	0.146	0.006	166.6
	2.83	0.145	0.006	166.6
	3.33	0.097	0.004	250
	4.66	0	0.002	500

Table III
Mark–Houwink Parameters

x,*y*	solvent	*t*, °C	*K*	*a*
2,10-Br	0.4 M KBr	30	3.85×10^{-4}	0.59
6,10-Br	0.4 M KBr	30	6.86×10^{-4}	0.58
6,6-Br[a]	0.4 M KBr	25	6.22×10^{-4}	0.58
3,4-Br[a]	0.4 M KBr	25	6.94×10^{-4}	0.61
6,6-Cl[a]	0.4 M KCl	25	1.02×10^{-5}	1.00

[a] Cited from the literature.[11]

Table IV
Comparison of A (=$[\eta]_{H_2O}$) with $[\eta]_{0.4\ M\ KBr}$

x,*y*-Br	$M_w \times 10^{-4}$	*n*	*A*	$[\eta]_{0.4\ M\ KBr}$
2,10	1.78	599.3	111	0.127
6,10	2.06	785.9	100	0.219
6,6	1.97	663.3	111	0.192

in which the number of bonds in the main chain is nearly equal. The results are shown in Table IV. In pure water 2,10-Br has *A* equal to 100, which is similar to 6,10-Br and 6,6-Br, but in 0.4 M KBr solution its $[\eta]$ decreases to 0.127, much smaller than that of 6,10-Br and 6,6-Br.

The extent of coiling of a polymer chain is closely related to its flexibility which can be characterized by the steric factor $\sigma \equiv \langle r_0^2\rangle^{1/2}/\langle r_f^2\rangle^{1/2}$ where $\langle r_0^2\rangle^{1/2}$ and $\langle r_f^2\rangle^{1/2}$ denote the unperturbed polymer dimension and freely rotating polymer dimension, respectively.

Unperturbed dimensions of flexible linear macromolecules can be obtained from[15]

$$\langle r_0^2\rangle = (K_0^{2/3}/\phi)M$$

and K_0 can be obtained by plotting $[\eta]/M^{1/2}$ vs $M^{1/2}$ (see Figure 1) according to the Stockmayer–Fixman equation[16]

$$[\eta]/M^{1/2} = K_0 + 0.51\phi B M^{1/2}$$

The intercept and slope (Stockmayer–Fixman parameters) are shown in Table V.

The dimensions of freely rotating polymers can be obtained by

$$\langle r_f^2\rangle = nl^2\frac{1 + \cos\theta}{1 - \cos\theta}$$

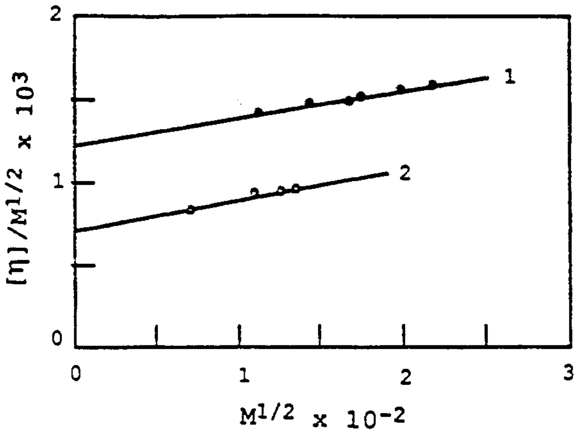

Figure 1. Plot of $[\eta]/M^{1/2}$ vs $M^{1/2}$ for ionenes in 0.4 M KBr aqueous solution: (1) 6,10-Br; (2) 2,10-Br.

Table V
Stockmayer–Fixman Parameters

x,*y*-Br	solvent	$K_0 \times 10^4$	$0.51\phi B \times 10^6$
2,10	0.4 M KBr	7.32	1.71
6,10	0.4 M KBr	13.5	1.08

Table VI
$\langle r_0^2\rangle^{1/2}$, $\langle r_f^2\rangle^{1/2}$, and σ for Ionenes in 0.4 M KBr Aqueous Solution

x,*y*-Br	$M_w \times 10^{-4}$	$\langle r_0^2\rangle^{1/2}$, Å	$\langle r_f^2\rangle^{1/2}$, Å	σ
2,10	0.50	49	27	1.81
	1.18	76	42	1.81
	1.52	87	48	1.81
	1.78	94	52	1.81
6,10	1.28	98	47	2.07
	2.06	124	60	2.07
	2.76	143	69	2.07
	3.01	150	72	2.07
	3.99	172	83	2.07
	4.66	184	90	2.07
3,4[a]	3.57	136	65	2.09
6,6[a]	1.32	95	45	2.11

[a] Cited from the literature.[11]

For ionenes the average bond length is 1.52 Å, θ = 71°, and $n = (M/M_0)b$ where M and M_0 denote the molecular weight of polymer and structure unit, respectively, and b is the number of bonds in one structural unit. The results for 2,10-Br and 6,10-Br ionenes of different molecular weight are summarized in Table VI, together with the corresponding σ calculated from $\langle r_0^2\rangle$ and $\langle r_f^2\rangle$. The σ values of 2,10-Br are evidently smaller than those of 6,10-Br, 3,4-Br, and 6,6-Br, indicating that the chain of 2,10-Br is more flexible. This is consistent with the results shown in Table IV.

$\langle r_0^2\rangle$ can be calculated also from

$$\langle r_0^2\rangle = (K_0^{2/3}/\phi)(nM_0/b)$$

Then it is possible to compare $\langle r_0^2\rangle$ for ionenes with an equal number of bonds (n) by

$$\frac{\langle r_0^2\rangle_1}{\langle r_0^2\rangle_2} = \left(\frac{K_{0,1}}{K_{0,2}}\right)^{2/3}\frac{(M_0/b)_1}{(M_0/b)_2}$$

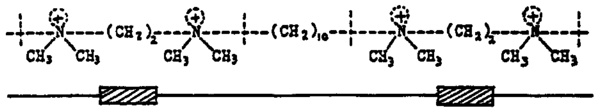

Figure 2. Schematic diagram of a "hydrophobic domain" in a 2,10-Br chain: dotted circles around pluses indicate shielded "+" charges on N atom; crosshatched rectangulars indicate hydrophobic domains including four CH_3 and one CH_2CH_2; solid lines indicate flexible segments.

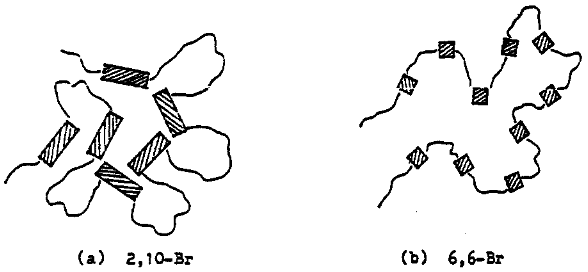
(a) 2,10-Br (b) 6,6-Br

Figure 3. Conformation of ionenes in 0.4 M KBr solution.

The ratios (abbreviated as $(x,y)_1/(x,y)_2$) are as follows:

6,10/6,6 = 0.98; 6,10/3,4 = 0.98;
3,4/6,6 = 0.99; 6,10/2,10 = 1.33; 6,6/2,10 = 1.37;
3,4/2,10 = 1.37

(K_0's for 3,4-Br and 6,6-Br are cited from the literature.[11]) The results are quite interesting. Ratios of 6,10 to 6,6 and 6,10 to 3,4 are close to unity, reflecting similar flexibilities after the polyelectrolyte effect is suppressed. On the other hand, ratios of other ionenes to 2,10 are obviously larger than unity, showing that 2,10-Br is more flexible.

It has been shown by Tan et al.[2] that the characteristic ratio C_∞ of poly(methacrylic acid) in aqueous media is much smaller than that of poly(acrylic acid) due to the hydrophobic interaction between the methyl groups. It is probable that the facts mentioned above may stem from a different distribution of methyl groups along the backbone of the chains. In 2,10-Br the nearest-neighbor methyl groups, separated by only two methylene groups, may form a rigid hydrophobic domain. In this domain, there are one CH_2CH_2 and four CH_3 groups clustering closely and the ammonium groups are shielded by counterions. We call this a "hydrophobic domain" (see Figure 2). Two adjacent domains are connected by a chain of 10 methylene groups sufficiently flexible for coiling. Thus, due to the movement of the flexible connecting segments and the dispersion attraction force of the hydrophobic domains, the 2,10-Br chain can contract more compactly as shown in Figure 3a. In the case of 6,6-Br, there are only two CH_3 groups in the hydrophobic domain, leading to a smaller dispersion attraction, and the connecting segments consist of only six methylene groups, leading to a smaller flexibility. These two factors render 6,6-Br less contractible than 2,10-Br as shown in Figure 3b. In 6,10-Br the density of CH_3 in the hydrophobic domain is lower than that in 2,10-Br, and in 3,4-Br the connecting segment is less flexible. Thus, both 6,10-Br and 3,4-Br cannot coil up as much as 2,10-Br.

3. Effect of the Hydrophobic Interaction between CH_3 Groups on the Change of Conformation of Ionenes in KBr Solutions of Various Concentration. In order to verify the explanation mentioned above, we investigated the decrease of [η] with an increase of the KBr concentration (Cs) from 0.01 to 0.4 M for 2,10-Br and 6,10-Br as shown in Figure 4. In all these plots there is a break which is similar to that observed for copoly(ethyl acrylate–acrylic acid).[2] But for the PAANa–NaCl system the break in the plot of [η] vs log Cs does not occur (see Figure 5). Obviously the hydrophobic interaction between CH_3 groups plays an important role in the conformational change of the ionenes. In the region of low concentration of KBr, the repulsion between the cationic groups is the main factor governing the conformational change due to the incomplete "shielding effect" of counterions. The polymer is in the state of a swollen random coil whose dimension is rather sensitive to Cs, resulting in a larger slope of the [η] vs log Cs plot. However, in the region of high concentration of KBr, where the electrostatic repulsion is already shielded, the polymer is in the state of a compact random coil and the hydrophobic interaction between CH_3 groups becomes the main factor for conformational change. Thus the dimension of the polymer becomes less sensitive to Cs and the [η]–Cs plot has a smaller slope. But for PAANa, due to the absence of intramolecular hydrophobic interaction, the change from a swollen random coil to a compact random coil occurs only gradually with increasing Cs, exhibiting no break in the [η]–Cs plot.

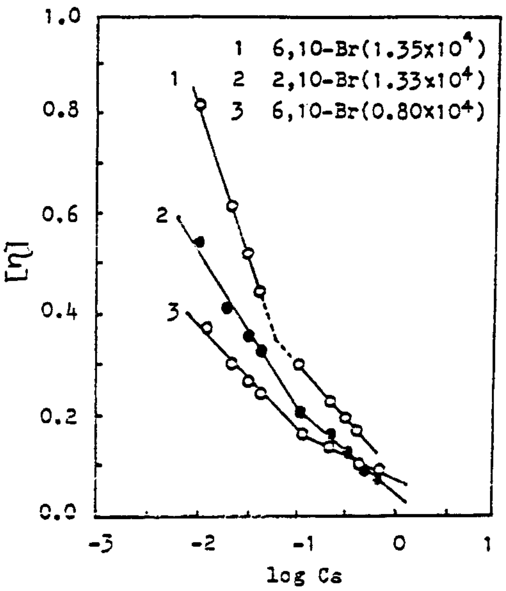

Figure 4. Plot of [η] vs log Cs for 6,10-Br and 2,10-Br.

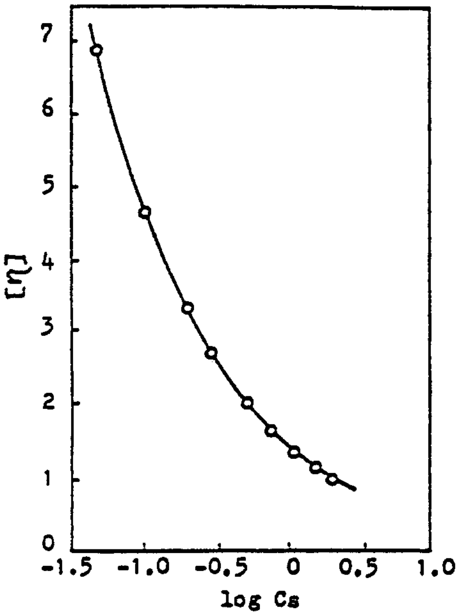

Figure 5. Plot of [η] vs log Cs for a PAANa–NaCl system.

By plotting $[\eta]/M^{1/2}$ vs $M^{1/2}$ we have obtained the Stockmayer–Fixman parameter B for 6,10-Br at various con-

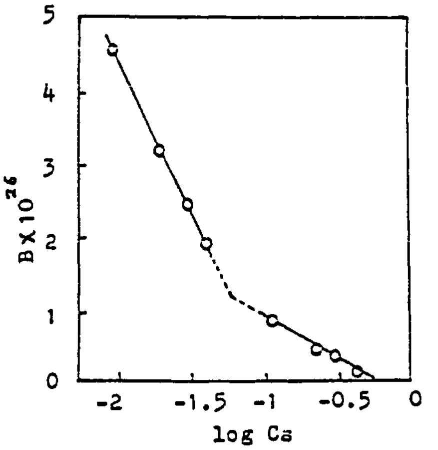

Figure 6. Plot of *B* vs log Cs for 6,10-Br in a KBr aqueous solution.

centrations of KBr. The *B* vs log Cs plot (Figure 6) is very similar to the [η]–log Cs plot; a break is also present around Cs ≈ 0.05 M. This result relates also to the conformational transformation of ionene. Since *B* is related to the solvent–polymer interaction parameter χ by[16] $B = 2(1/2 - \chi)/V_1\rho_2{}^2N_0$, the decrease of *B* implies a decrease of solvation. At low Cs, 6,10-Br is in a swollen state favorable for hydration of N^+, but the hydration would be reduced in the presence of added salts due to the shielding effect of counterions. Thus, *B* descends rapidly as Cs ascends. At high Cs, the chains are tightly coiled, most N^+'s have been shielded or some of the unshielded N^+'s would be imbedded inside the coil protected by CH_3 groups, so that the effect of counterions on the hydration of N^+ is not as sensitive as at low Cs. Thus, the change of slope from the low Cs to the high Cs region also occurs in the plot of *B* vs log Cs.

References and Notes

(1) Braud, C.; Muller, G.; Fenyo, J.-C.; Selegny, E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2767.
(2) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1785.
(3) Strauss, U. P. In *Microdomains in Polymer Solutions*; Dubin, P., Ed.; Plenum: New York, 1985; pp 1–12.
(4) Strauss, U. P.; Chiao, Y.-C. *Macromolecules* **1986**, *19*, 355.
(5) Mifune, S.; Kubodera, K.; Kaneko, M. *Kobunshi Ronbunshu* **1987**, *44*, 107.
(6) Hsu, J. L.; Strauss, U. P. *J. Phys. Chem.* **1987**, *91*, 6238.
(7) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1987**, *20*, 2133.
(8) Duveneck, G. L.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *J. Phys. Chem.* **1988**, *92*, 2028.
(9) Borbely, S.; Cser, L.; Ostanevich, Yu. M.; Vass, Sz. *J. Phys. Chem.* **1989**, *93*, 7967.
(10) Binana-Limbele, W.; Zana, R. *Macromolecules* **1990**, *23*, 2731.
(11) Casson, D.; Rembaum, A. *Macromolecules* **1972**, *5*, 75.
(12) Pine, H. S.; Sanchez, L. B. *J. Org. Chem.* **1971**, *36*, 829.
(13) Vogel, I. A. A. *Textbook of Practical Organic Chemistry*; Longman Group Limited: London, 1956; p 271.
(14) Rembaum, A.; Noguchi, H. *Macromolecules* **1972**, *5*, 261.
(15) Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 14.
(16) Stockmayer, H. W.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.

Registry No. KBr, 7758-02-3; 1,10-dibromodecane/*N,N,N′,N′*-tetramethylethylenediamine (copolymer), 59407-11-3; 1,10-dibromodecane/*N,N,N′,N′*-tetramethylethylenediamine (SRU), 52270-19-6; 1,10-dibromodecane/*N,N,N′,N′*-tetramethyl-1,6-hexanediamine (copolymer), 27789-53-3; 1,10-dibromodecane/*N,N,N′,N′*-tetramethyl-1,6-hexanediamine (SRU), 28728-57-6; 1,6-dibromohexane/*N,N,N′,N′*-tetramethyl-1,6-hexanediamine (copolymer), 29322-35-8; 1,6-dibromohexane/*N,N,N′,N′*-tetramethyl-1,6-hexanediamine (SRU), 31622-88-5.