Chain Characteristics of Poly(2-acrylamido-2-methylpropanesulfonate) Polymers. 2. Comparison of Unperturbed Dimensions and Persistence Lengths

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ABSTRACT: The effect of the nature of solvents and counterions on chain flexibility was investigated for poly(2-acrylamido-2-methylpropanesulfonic acid) (H–PAMS) and its sodium, cesium, and tetrabutylammonium salts (Na–PAMS, Cs–PAMS, and TBA–PAMS). The characteristic ratios, C_∞, estimated by the intrinsic viscosity–molecular weight extrapolation technique, are as follows: 23 for TBA–PAMS in aqueous TBA–Br, 19 for TBA–PAMS in organic solvents, and 11–12 for all salts of H–PAMS in aqueous NaCl or CsCl. The persistence lengths of these polymers were also calculated by applying the wormlike-chain model to light-scattering and viscosity data. These polymers are highly expanded at low ionic strength but exhibit coillike behavior with small persistence lengths if enough supporting electrolyte is added.

In part 1 of this series,[1] we have reported light-scattering and intrinsic-viscosity data for several salts of poly(2-acrylamido-2-methylpropanesulfonic acid) (H–PAMS) in a number of organic solvents and aqueous salt solutions. We have found that while these polymers are highly expanded in these solvents, they exhibit coillike behavior if enough supporting electrolyte is added. In the present paper, we examine chain flexibility of these polymers as affected by the nature of the solvents and counterions having different ionic size and extents of binding. Also to be discussed are the calculated persistence lengths of these systems by applying the wormlike-chain model[2] to light-scattering and intrinsic-viscosity data.[3–5]

Among various theories published in the literature, the Stockmayer-Fixman extrapolation technique[6] appears to be the most convenient and commonly employed method for estimating unperturbed dimensions from intrinsic viscosity ($[\eta]$)–molecular weight (M) data. This method is particularly useful where direct measurements of $[\eta]$ and radius of gyration ($\langle s^2\rangle^{1/2}$) at a theta condition are difficult. This type of extrapolation is often applicable to flexible coils with moderate coil expansion (i.e., the Mark–Houwink exponent, ν, is in the range of 0.5 to 0.8).[7,8] Caution must be exercised, however, in using this procedure for systems with $\nu > 0.8$ where partial draining and/or stiffness of chains is normally expected.[7–9] This need has been demonstrated for two nonionic, stiff-chain molecules in organic media.[7,9] Incorrect unperturbed dimensions were predicted for cellulose derivatives when linear extrapolation of plots of $[\eta]^{2/3}/M^{1/3}$ against either $M^{2/3}/[\eta]^{1/2}$ or $M/[\eta]$ were used.[9] Much smaller and erroneous unperturbed dimensions were also derived from the Stockmayer–Fixman plots for a ladder polymer, cis-syndiotactic poly(phenylsilsesquioxane).[7]

The above limitation for the application of linear extrapolations has been demonstrated, however, for stiff molecules in organic solvents only. These systems[7] generally possess large values of ν even at a theta condition where the second virial coefficient $A_2 = 0$. Behavior for polyelectrolyte–salt systems represents a somewhat different case. The intrinsic viscosity–molecular weight data of these systems can also be described by the Mark–Houwink relation.[10–14] Although the exponents are rather large at low ionic strengths (C_s), they are accompanied by large values of A_2. These quantities are greatly reduced and approach the theta condition, i.e., $\nu = 0.5$ and $A_2 = 0$, if enough salt is added (see Figure 6 of part 1), indicating the coillike nature of these polyions. Because the high value of A_2 is partly due to contributions from ionic repulsions among the charged sites, high values of ν at low ionic strength may not necessarily indicate local chain stiffness or partial draining of the polymer.

Linear plots of $[\eta]/M^{1/2}$ against $M^{1/2}$ have been illustrated for a number of polyelectrolyte–salt systems.[10,12,13,15,16] A single common intercept was found for these data at various ionic strengths, even for those systems with $\nu > 0.8$. In the case of salt-free or extremely low C_s media, however, different intercepts were observed,[15] indicating the inapplicability of this method for obtaining unperturbed dimensions. In this paper, linear plots of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ are examined for the present polymers in various solvents, counterions, and ionic strengths. The unperturbed dimensions derived are discussed in terms of solvent polarity and extent of counterion binding.

Calculations of the persistence lengths of the present polymer and of other polyelectrolytes are presented in order to obtain insight into the local conformation of the polymer backbone. Although the value of the persistence length gives a relative measure of the stiffness of the polymer, it is the total number of statistical chain segments which reveals the coillike or rodlike behavior of the molecule. Comparison of the persistence lengths in the unperturbed state is useful for investigating the effect of side groups on the vinyl backbone flexibility.

Results and Discussion

Unperturbed Dimensions. The Stockmayer–Fixman extrapolation according to

$$[\eta]/M^{1/2} = K_0 + 0.51\Phi_0 B M^{1/2} \tag{1}$$

was applied to the viscosity data reported in part 1 (Figure 3a–e).[1] Here, K_0 is the intercept and is equal to the Mark–Houwink constant K at a theta condition, B is related to the second virial coefficient, and Φ_0 is the Flory viscosity constant. The value K_0 is related to the characteristic ratio, C_∞, and the mean-square unperturbed end-to-end distance, $\langle r_0^2\rangle$, by[17]

$$C_\infty = \left(\frac{K_0}{\Phi_0}\right)^{2/3}\frac{M_0}{2l^2} = \frac{\langle r_0^2\rangle}{nl^2} \tag{2}$$

where M_0 is the monomer molecular weight, l is the bond length (i.e., 1.54 Å for a C–C bond), and n is the total number of backbone bonds.

The tetrabutylammonium salt of H–PAMS (TBA–PAMS) was chosen for the study of unperturbed dimensions in different solvents because it is soluble in organic as well as in aqueous salt media. The plots of $[\eta]/\overline{M}_w^{1/2}$ against $\overline{M}_w^{1/2}$ according to eq 1 for TBA–PAMS in organic solvents are shown

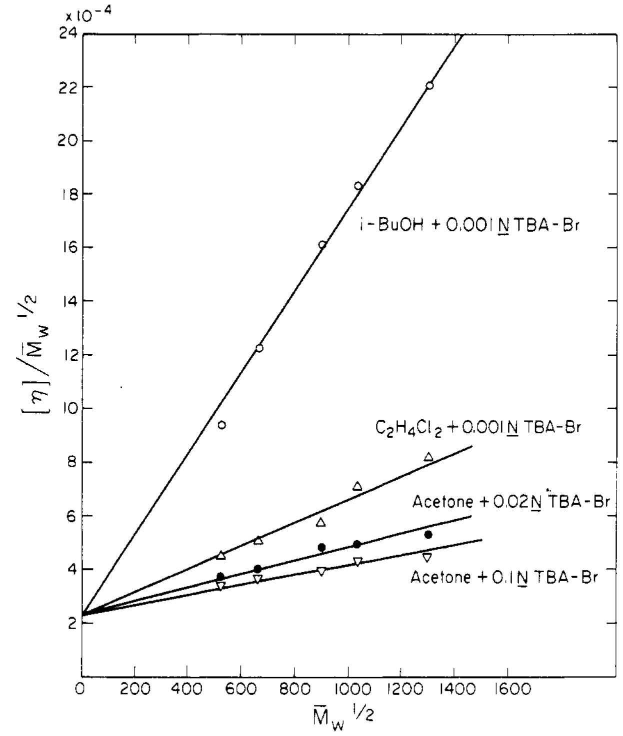

Figure 1. Stockmayer-Fixman plots, $[\eta]/\overline{M}_w^{1/2}$ vs. $\overline{M}_w^{1/2}$, for TBA-PAMS in organic media.

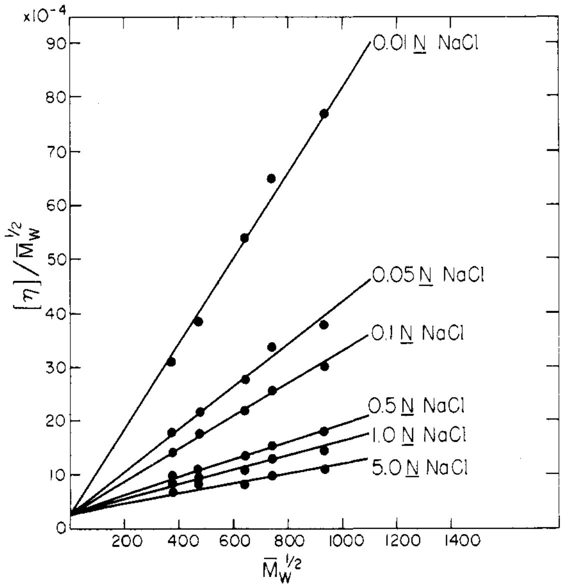

Figure 2. Stockmayer-Fixman plots, $[\eta]/\overline{M}_w^{1/2}$ vs. $\overline{M}_w^{1/2}$, for Na-PAMS in aqueous NaCl solutions.

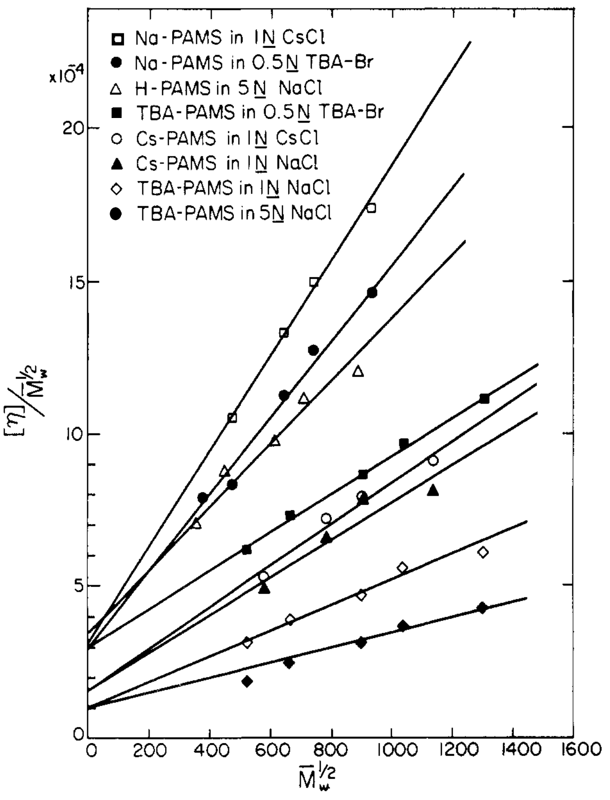

Figure 3. Stockmayer-Fixman plots, $[\eta]/\overline{M}_w^{1/2}$ vs. $\overline{M}_w^{1/2}$, for various salts of H-PAMS in aqueous salt solutions.

in Figure 1. Despite the large value of ν for the polymer in *i*-BuOH + 0.001 N TBA-Br ($\nu = 0.96$), a single common intercept is observed in Figure 1.

Similar plots for Na-PAMS in aqueous NaCl solutions are presented in Figure 2. A single common intercept is also observed even though some of the low ionic strength runs exhibit high values of ν (0.8–1.0). Kay and Treloar[15] reported similar plots for fully and partly neutralized poly(acrylic acid) in aqueous NaCl solutions. The plots for high and moderate ionic strengths gave the same intercept whereas those for salt-free and 0.001 N NaCl polymer solutions gave negative intercepts. These results were interpreted as being due to partial draining of the coil in salt-free and 0.001 N NaCl solutions. In view of the result that a common intercept is obtainable with the present data, we have assumed that the Stockmayer–Fixman extrapolation is likely to be applicable for linear polyelectrolytes with $\nu \leq 1.0$ (or $C_s > 0.01$ N NaCl).

Figure 3 shows similar plots for the various salt forms of H-PAMS in various salt solutions. The intercepts obtained from Figures 1–3 and the corresponding calculated values for C_∞ according to eq 2 and using the corresponding M_0 for each salt form are listed in Table I.

(1) The Effect of the Nature of Solvents on the Unperturbed Dimensions of TBA-PAMS. Although many nonionic polymers show different K_0 values in different solvent media,[18-22] no definite correlation was obtained between these K_0 values and the dielectric constants of the solvent media. Nevertheless, most polymers seem to show smaller K_0 in solvents with larger dielectric constants. Our results for TBA-PAMS, with a smaller K_0 in aqueous NaCl than in organic media, follow this generalization. The unperturbed dimensions in organic media are approximately 1.3 times those in aqueous media.

Similar results were also reported for other carboxylated polymers, e.g., a copolymer of acrylic acid and ethylacrylate[13] and for poly(methacrylic acid).[23-25] In all cases, the unperturbed dimensions or C_∞ values are larger in organic than in aqueous media. These results are not unexpected if one follows the argument of Ptitsyn.[26] At the theta point, the total effective excluded volume for a polyelectrolyte–salt system is zero (i.e., $A_2 = 0$), and the excluded volume due to the uncharged polymer analogue would have to be negative in order to compensate for the positive ionic interactions.[26] Consequently, the dimensions of the polyion under this condition ($A_2 = 0$) would be expected to be less than those for the uncharged analogue with zero excluded volume.

Two types of interaction are expected to prevail in these polyelectrolytes: hydrophobic interactions and hydrogen bonding. In the case of copoly(ethylacrylate–acrylic acid),[13]

Table I
Characteristic Ratios of PAMS Polymers

	TBA–PAMS			Na–PAMS			Cs–PAMS		H–PAMS
	(Organic)	(NaCl)	(TBA–Br)	(NaCl)	(TBA–Br)	(CsCl)	(CsCl)	(NaCl)	(NaCl)
$K_0 \times 10^4$	2.3	1.0	3.0	3.0	3.0	3.2	1.6	1.6	3.5
C_∞ (±10%)	19	11	23	12	12	12	11	11	12

the collapse of the coil in aqueous media is attributed to the hydrophobic interaction of the ester groups. In the case of poly(methacrylic acid), the collapse of the coil in aqueous media is attributed to the hydrophobic interactions of α-methyl groups. The larger unperturbed dimensions of poly(methacrylic acid) in organic media, however, are attributed to intramolecular hydrogen bonding among the COOH groups possibly forming helical structures.[27]

The values of C_∞ for TBA–PAMS in organic and in aqueous NaCl media, as listed in Table I, can be interpreted in light of the above discussion. The tendency for intramolecular hydrogen bonding between the -CONH- groups may be enhanced in organic media. The presence of the bulky and much less dissociated TBA groups in organic media probably enhances extended coil formation (possibly helical form) caused by hydrogen bonding. In aqueous media, these TBA$^+$ ions, although still diffusely bound to the sulfonate sites,[28] are completely dissociated and may be replaced by the smaller sodium counterions present in the media. As a result of the counterion screening effect, the polymer coils are relaxed and more flexible than those in organic media. Consequently, the unperturbed dimensions are contracted beyond the values for the un-ionized TBA–PAMS in organic media. These results are in good agreement with those of polycarboxylic acids discussed above.[23–25]

(2) The Effect of Counterions on PAMS Backbone Chain Conformation in Aqueous Salt Solutions. With the exception of TBA–PAMS in TBA–Br ($C_\infty = 23$), the characteristic ratios for these systems in aqueous salt solutions are around 11–12 (Table I) and practically indistinguishable among salts with different counterions. Although differences in chain conformation should be expected when a given polyion is bound by counterions with different binding strengths, these differences were not detectable within the present experimental accuracy.

The effect of counterion binding strength on C_∞ is evident, however, when the difference in the extent of counterion binding is great. This is demonstrated by the value of C_∞ obtained for TBA–PAMS in TBA–Br. The bulky and diffusely bound TBA$^+$ ions[28] give rise to a less flexible conformation for the PAMS backbone and, hence, a larger value of C_∞ (23) is observed. In the presence of stronger binding Na$^+$ ions, such as in the systems TBA–PAMS + NaCl and Na–PAMS + TBA–Br, most of the binding sites are occupied by Na$^+$ ions, and smaller C_∞ values (11 and 12, respectively) than that for TBA–PAMS + TBA–Br were obtained.

Application of the Wormlike-Chain Model. The Kratky–Porod wormlike-chain model[2] was chosen to study chain conformation of polyelectrolytes. The polymers are characterized as a series of stiff threads with a stiffness parameter, the "persistence length", q. When q is large, the polymer is rodlike; when q is small, the polymer is coillike. From several theories for the intrinsic viscosity of wormlike coils,[4,29,30] we have adopted the method of Yamakawa and Fujii.[4] The intrinsic viscosity (in units of mL/g) is expressed as

$$[\eta] = 10^{-2}\Phi L_r^{3/2}/\lambda^3 M \tag{3}$$

Here, λ^{-1} is the Kuhn statistical length and is equal to two times the persistence length ($2q$). L_r is the reduced contour length or the total number of Kuhn's segments and is related to the contour length L or molecular weight M by

$$L_r = \lambda L = \lambda M/M_L \tag{4}$$

where M_L is the mass per unit chain length. Substituting eq 4 into eq 3, we obtain

$$[\eta] = 10^{-2}\Phi(L_r,d_r)M^{1/2}/(\lambda M_L)^{3/2} \tag{5}$$

where Φ is the Flory viscosity constant and is a function of L_r and the reduced hydrodynamic diameter d_r. The latter is related to the hydrodynamic diameter d by

$$d_r = \lambda d \tag{6}$$

Tables for $\Phi(L_r,d_r)$ were presented in ref 4.

Since the above theory was formulated without the consideration of excluded volume effects, the derived q and d_r values for the present systems should be called the "apparent" q and d_r, respectively.

By successive approximation, values of q were chosen in order to obtain the best fit of viscosity data (as presented in Figure 3a–e of the previous publication[1]). The estimated parameter q and the corresponding calculated L_r, M_L, and d_r according to eq 4 and 6 and the contour length, bond length, M_0, and coil diameter for the present systems are listed in Table II. These values were used to calculate $[\eta]$ according to eq 5. The solid curves shown in Figure 3a–e of ref 1 are the theoretical results. The values of q and L_r for the highest molecular weight fraction F_1 (with the weight-average degree of polymerization $\overline{N}_w = 3800$) and the lowest molecular weight fraction F_4 ($\overline{N}_w = 960$) or F_5 ($\overline{N}_w = 610$) are shown in Table II.

While the value of persistence length reflects a relative measure of chain flexibility, the total number of Kuhn's statistical segments (L_r) gives a more direct criterion for assuming the rodlike or coillike nature of a chain molecule. In general, a chain molecule containing 30–50 statistical segments or more is expected to display Gaussian coil behavior,[17] i.e., the characteristic ratio, $C_n = \langle r_0^2\rangle/nl^2$ approaches an asymptotic value when $n = 30$–50. The values of L listed in Table II for fractions F_1, F_4, and F_5 suggest that with the exception of F_5 all the fractions studied here are Gaussian coils. These results are also consistent with the results of $\langle s^2\rangle_z/\overline{N}_z$ vs. $\overline{M}_w$ presented in Figure 7 of part 1,[1] where $\langle s^2\rangle_z$ is the mean-square z-average radius of gyration and $\overline{N}_z$ is the z-average degree of polymerization. The conclusion that our present systems are coillike here clearly justifies the use of the Stockmayer–Fisman extrapolations adopted earlier for obtaining the unperturbed dimensions.

The correct estimates of persistence lengths may also be established by an independent determination from light-scattering data[5] or by comparing the calculated values of $\langle s^2\rangle_z$ (from eq 9 below) with the experimentally observed $\langle s^2\rangle_z$. The latter method was chosen here because it enables corrections to be made for the polydispersity of the present systems.

Benoit and Doty[3] derived an expression for the radius of gyration of a wormlike-chain molecule as

$$\langle s^2\rangle = q^2\left\{\frac{x}{3} - 1 + \frac{2}{x} - \frac{2}{x^2}[1 - e^{-x}]\right\} \tag{7}$$

Table II
The Parameters for the Wormlike-Coil Model Estimated from Intrinsic Viscosity–Molecular Weight Data

Polymer	Solvent	q, Å		L_r		M_L, g/Å	d_r	
		(F$_1$)	(F$_5$)	(F$_1$)	(F$_5$)		(F$_1$)	(F$_5$)
Na–PAMS	0.01 N NaCl	152.5	122.5	31.7	6.4	90	0.02	0.02
	0.05 N NaCl	81	67.5	60	11.5	90	0.03	0.03
	0.1 N NaCl	71.5	56	64	13.2	95	0.03	0.045
	0.5 N NaCl	45	37	102	20.0	95	0.06	0.06
	1.0 N NaCl	40.5	34.5	107	20.3	100	0.06	0.08
	5.0 N NaCl	30	28.5	145	25	100	0.08	0.10
	0.5 N TBA–Br	39	28.5	117	25.8	95	0.06	0.09
	1.0 N CsCl	44	36	104	20.5	95	0.06	0.06
		q, Å		L_r		M_L, g/Å	d_r	
		(F$_1$)	(F$_5$)	(F$_1$)	(F$_5$)		(F$_1$)	(F$_5$)
H–PAMS	5.0 N NaCl	32	25	136	28	90	0.08	0.10
		q, Å		L_r		M_L, g/Å	d_r	
		(F$_1$)	(F$_4$)	(F$_1$)	(F$_4$)		(F$_1$)	(F$_4$)
Cs–PAMS	1.0 N CsCl	37.5	27	132	46	130	0.10	0.15
	1.0 N NaCl	33.5	26.5	148	47	130	0.10	0.10
		q, Å		L_r		M_L, g/Å	d_r	
		(F$_1$)	(F$_5$)	(F$_1$)	(F$_5$)		(F$_1$)	(F$_5$)
TBA–PAMS	1.0 N NaCl	35.5	24	150	36	160	0.08	0.15
	5.0 N NaCl	26	18	204	47.5	160	0.10	0.15
	0.5 N TBA–Br	52.5	41	101	21	160	0.10	0.125
	i-BuOH + 0.001 N TBA–Br	97.5	75	55	11	160	0.045	0.045
	$C_2H_4Cl_2$ + 0.001 N TBA–Br	41.5	31.5	128	27	160	0.10	0.15
	Acetone + 0.02 N TBA–Br	30	30	177	28.5	160	0.10	0.10
	Acetone + 0.1 N TBA–Br	27.5	27.5	193	31	160	0.10	0.10

Table III
Comparison of the Radii of Gyration Observed by Light Scattering and Calculated from the Persistence Length Using Eq 9

Polymer	Solvent	b, Å	$\langle s^2\rangle_z^{1/2}$, Å (F$_1$)		$\langle s^2\rangle_z^{1/2}$, Å (F$_4$)		$\langle s^2\rangle_z^{1/2}$, Å (F$_5$)	
			Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
Na–PAMS	0.05 N NaCl	2.54	520	560			21_5	210
	0.5 N NaCl		430	408			15_5	153
TBA–PAMS	$C_2H_4Cl_2$ + 0.001 N TBA–Br	2.8	400	423	190	188		
	Acetone + 0.02 N TBA–Br	2.8	360	360	190	183		
	Acetone + 0.1 N TBA–Br	2.8	350	345	190	175		

where $x = L/q$. When $x > 6$, $e^{-x} \rightarrow 0$ and

$$\langle s^2\rangle \simeq q^2 \left\{\frac{x}{3} - 1 + \frac{2}{x}\left[1 - \frac{1}{x}\right]\right\} \tag{8}$$

By incorporating corrections for polydispersity into eq 8, Flory and co-workers[31] derived

$$\langle s^2\rangle_z \simeq q^2 \left[\frac{\overline{N}_z b}{3q} - 1 + \frac{2q}{\overline{N}_w b}\left(1 - q/\overline{N}_n b\right)\right] \tag{9}$$

where $\overline{N}_z$, $\overline{N}_w$, and $\overline{N}_n$ are the z, weight, and number-average degrees of polymerization, respectively, and b is the monomeric projection length.

The values of $\langle s^2\rangle_z^{1/2}$ calculated by use of estimated values for b and q and measured $\overline{N}_z$, $\overline{N}_w$, and $\overline{N}_n$ (see eq 4 and 5 in ref 1) are shown in Table III for three fractions F_1, F_4, and F_5 in aqueous NaCl and in organic media. Also shown for comparison are the corresponding values of $\langle s^2\rangle_z^{1/2}$ as measured by light scattering.[1] Despite the fact that the Yamakawa–Fujii theory cannot strictly be applied to the present systems with excluded volume, and the "apparent" q and d_r values (Table II) do indeed depend on molecular weight, particularly at low C_s, the agreement between the calculated and the observed $\langle s^2\rangle_z^{1/2}$ values is remarkable. This may indicate that the high values of the Mark–Houwink exponent ν reflect, in good part, incomplete hydrodynamic shielding for the rather bulky chain.

The wormlike-coil parameters for several linear polyelectrolytes, estimated in the same manner as those listed in Table II, are shown in Table IV. Shown for comparison are the data for low ionic strength, where the coil is extended, and at the theta condition, where the polymer is coiled. The values of $[\eta]$ at the theta condition for sodium polyacrylate (Na–PA),[10] sodium poly(styrenesulfonate) (Na–PSS),[11] and the copolymer of ethylacrylate and sodium acrylate (mole ratio 3:1) (Na–EA–A)[13] were measured directly, whereas the value for the present polymer, Na–PAMS, was estimated from the Stockmayer–Fixman extrapolation as described earlier. The similarity in q values for Na–PA and Na–PAMS both in 0.01 N NaCl and theta solvents suggests a resemblance in chain flexibility for the two polymers. The smaller values for Na–PSS and Na–EA–A, particularly at theta condition, clearly indicate the more compact structure of these two polymers relative to Na–PA and Na–PAMS. This is attributed to the interactions among phenylene groups in Na–PSS and the hydrophobic interactions among the ester groups in Na–EA–A which cause the polymer coils to collapse.

Finally, the persistence lengths estimated according to the scheme of Yamakawa–Fujii are compared with those obtained by the limiting Benoit–Doty equation using light-scattering

Table IV
The Parameters for the Wormlike-Coil Model for Several Polyelectrolytes in Aqueous Salt Solutions

Polymer	Solvent	$\overline{M}_w \times 10^{-6}$	q (=$\lambda^{-1}/2$), Å	L_r	M_L	d_r
Na–PA	0.01 N NaBr	0.5	145	45	38	0.01
	1.5 N NaBr (Θ point)	0.5	12.5	500	40	0.15
Na–PAMS	0.01 N NaCl	1.7_0	152.5	32	90	0.02
	Θ aq media	1.7_0	12.0	360	100	0.15
Na–PSS	0.01 N NaCl	1.5_5	104	93	80	0.03
	4.17 N NaCl (Θ point)	1.5_5	7.8	1100	90	0.3
Na–(EA–A)	0.05 N NaCl	1.0_6	27	436	45	0.08
	1.2 N NaCl (Θ point)	1.0_6	5.5	2140	45	0.40

Table V
Comparison of the Persistence Lengths of PAMS Polymers Calculated from Viscosity and from Light Scattering According to Eq 10

		q, Å (viscosity)			q, Å
Solvent	b, Å	(F_1)	(F_4)	(F_5)	(light scattering)
0.05 N NaCl	2.5	81		67.5	67
0.5 N NaCl	2.4	45		37	51
$C_2H_4Cl_2$ + 0.001 N TBA–Br	2.8	41.5		31.5	36
Acetone + 0.02 N TBA–Br	2.8	30	30	30	32
Acetone + 0.1 N TBA–Br	2.8	27.5	27.5	27.5	28

data. In the limit of infinite chain length ($x \rightarrow \infty$), eq 9 is replaced by

$$\lim_{x \to \infty} \frac{\langle s^2 \rangle_z}{\overline{N}_z} = qb/3 \qquad (10)$$

Previously,[1] we found that $\langle s^2 \rangle_z / \overline{N}_z$ approaches asymptotic levels for the present polymers in aqueous as well as in organic media. By using these asymptotic values, we have calculated the persistence lengths using estimated b values according to eq 10. These values are listed in Table V. The fair agreement of these persistence lengths suggests that the polymers are coillike, except for the lowest molecular weight fraction F_5, and we conclude that use of eq 10 is a good approximation for estimating persistence lengths.

Conclusion

The unperturbed dimensions of several poly(2-acrylamido-2-methylpropanesulfonate) polymers were obtained by the Stockmayer–Fixman extrapolation technique. The calculated characteristic ratios, C_∞, are as follows: $C_\infty = 23$ for TBA–PAMS in aqueous TBA–Br, $C_\infty = 19$ for TBA–PAMS in organic media, and C_∞ = 11–12 for H–PAMS, Na–PAMS, Cs–PAMS, or TBA–PAMS in aqueous NaCl or CsCl.

The polymer is more extended when it is bound to the bulky and diffusely bound TBA^+ ion but more coiled when it is bound to the smaller but stronger binding ions, H^+, Na^+, or Cs^+. The unperturbed dimensions of TBA–PAMS in organic media are 1.3 times those in aqueous NaCl solutions, indicating that chain flexibility depends on the nature of the solvent.

The persistence lengths were compared for a number of polyelectrolyte–salt systems. The results suggest that the present polymer, particularly Na–PAMS in aqueous NaCl, is as coillike as a number of other linear polyelectrolytes.

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