Molecular Weight Characterization of Polyacrylamide-CO-Sodium Acrylate. II. Light Scattering

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SYNOPSIS

The first large-scale fractionation method for polyacrylamides is reported. This has been optimized to prepare a series of narrowly distributed polymer standards with molecular weights between 10,000 and 1,000,000. These were subsequently hydrolyzed to between 5 and 35% sodium acrylate content through a saponification reaction. It has been found that the classical light-scattering theory, derived for nonionic scattering bodies, can be applied to polyelectrolytes provided the specific refractive index increment $(\partial n/\partial c)$ is evaluated at constant electrochemical potential (μ). This is obtained by dialyzing the polymer solution against the dialysate $(0.2M\ Na_2SO_4$ for polyacrylamide-co-sodium acrylate) for a predetermined equilibrium period, specific to the pore size of the membrane used. From such measurements at various copolymer compositions (F), the following empirical relationship is established:

$$\left(\frac{\partial n}{\partial c}\right)_{\mu,\text{PAM-NaAc}} = \left(\frac{\partial n}{\partial c}\right)_{\text{PAM}} (F_{\text{NaAc}})^a$$

where a was found to be -0.076. The validity of the specific refractive index increment at constant chemical potential is established through light-scattering measurements of the weight-average chain length of the hydrolyzed polyacrylamides. These were then compared with the chain lengths of the parent nonionic polymers from which they were derived. Excellent agreement is observed, implying the polyelectrolyte characterization method developed, and specifically the $(\partial n/\partial c)_\mu$'s, are accurate and reliable.

INTRODUCTION

Copolymers of acrylamide and sodium acrylate are used in aqueous solutions as drag reduction agents, flocculants, and thickeners. They are also employed in tertiary oil recovery as thixotropic aqueous polymer emulsions. These solutions are pseudoplastics and exhibit typical polyelectrolyte behavior with respect to salinity. The polymers can be prepared by direct copolymerization or derivatization from polyacrylamides. When the ionogenic monomer is introduced through a free radical addition mechanism, long acrylate and amide sequences form, with the microstructure conforming to Bernouillian statistics.[1,2] By comparison, polymers produced through alkaline saponification of the amide side chain are atactic.[3] This provides a relatively uniform charge density distribution that maximizes the viscosity increase for a given molecular weight and improves the polymer's performance.[4] The hydrolysis substitution reaction is, however, limited to approximately 65% conversion. [Kurenkov[5-8] has found the limiting extent of hydrolysis decreased as the polymer synthesis temperature or monomer concentration was increased. Preliminary investigations by Hunkeler[9] have supported these results, concluding that the limiting degree of hydrolysis decreases slightly as molecular weight rises.] This has been explained by a neighboring group catalysis model.[10] Upon attack by a hydroxyl ion the NH_2 group is

pushed aside and simultaneously attracted by the adjacent amide. Although this reaction is usually interpreted by second-order retardation kinetics, a more valid approach is to treat an acrylamide dyad as the reactive species. Troung[1] has shown that near the limits of hydrolysis the acrylamide dyad and triad concentrations become negligible. These are replaced by an abundance of AMA triads which, under the proposed mechanism, would be unreactive. The intramolecular catalysis or "joint-site" mechanism seems plausible since for an atactic polymer the concentration of MM dyads reaches zero at two-thirds acrylamide content, in excellent agreement with experimental findings.[1]

Complete hydroxy substitution can be obtained in acidic media at high temperatures. However, intramolecular imidization,[11] degradation,[12] and a Bernouillian sequence length distribution[13] limit the polymers' utility.

The modeling of the hydrolysis kinetics over the complete range of pH has recently been attempted by Kheradmond et al.[14] The model seems to have good predictive power and is consistent with experimental data.

Typical of polyelectrolytes, the solution behavior of polyacrylamide-co-sodium acrylate has several peculiarities. For example, the intrinsic viscosity, radius of gyration, and second virial coefficient all show maximums at 50–70% acrylate levels.[12,15] This is due to a combination of electrostatic repulsion and intramolecular hydrogen bonding. [This has been confirmed by observing downward shifts in the wave number of the $\delta(NH_2)$ absorption.[12]] The latter diminishes as the amide groups are hydrolyzed. The viscosity also reaches a limit at a degree of neutralization of approximately 60%. Above this level counterion shielding has been postulated to reduce the electrostatic repulsion.[16]

The purpose of this research is to develop a valid characterization method for weight-average molecular weights of copolymers of acrylamide and sodium acrylate. Initially a series of polyacrylamides will be synthesized and fractionated to yield narrow molecular weight distributions. These will first be measured in their nonionic form where light scattering is more reliable and accurate than for ion-containing polymers. These will then be hydrolyzed to various degrees and analyzed in their ionic form. The measured weight-average chain length will be used to evaluate the absolute accuracy of the polyelectrolyte characterization method. Such an error estimate is impossible without an a priori knowledge of the polymer's molecular weight. Therefore, polyelectrolyte methods development must be proceeded by de-

rivatization from nonionic species. Nagai and Osishi[17] have reached the same conclusion studying cationic polyelectrolytes.

EXPERIMENTAL

Polymer Preparation

Polyacrylamides were synthesized by aqueous free radical polymerizations using potassium persulfate (BDH, 99% purity) as an initiator and ethanol mercaptan (BDH) as a chain transfer agent. The polymers were heterodisperse in molecular weight, with polydispersities between 2.0 and 2.5 as measured by size exclusion chromatography (SEC). SEC chromatograms were measured with a Varian 5000 liquid chromatograph, using Toya Soda columns (TSK 3000, 5000, 6000 PW) and an aqueous mobil phase [$0.02 M$ Na_2SO_4 (BDH), 0.1 wt % sodium azide (Aldrich) and 0.01 wt % tergitol NPX (Union Carbide Corp.)]. The spectrum were recorded on a Varian CDS 401 Data Station.

The synthesis conditions did not lead to preliminary hydrolysis as was determined by the ^{13}C NMR spectra. The spectra was recorded for a 10 wt % D_2O solution at 125.76 MHz and 70.9°C in the Fourier transform mode with inverse gate decoupling. The pulse width was 6.8 ms with an acquisition time of 0.557 s.

Fractionation

Polymer fractionation can be performed by a variety of techniques based on differential solubility, sedimentation, diffusion, and chromatographic exclusion. For the large-scale fractionation of high molecular weight polyacrylamide fractional precipitation is preferred since it provides good separation efficiency and high yields, without requiring excessively dilute solutions. Previous investigations on polyacrylamide fractionation have used several nonsolvents including methanol,[18–20] isopropanol,[21] acetone, dioxane, and THF.[22] Wu[23,24] found acetone to have the highest solvent power by the solvent–precipitation–fractionation (SPF) method. She also observed the narrowest polydispersity for fractions separated with mixtures of water and acetone as a nonsolvent. However, at high molecular weights, methanol performed better, providing a more uniform polymer distribution between the lean and rich phases. A summary of the fractionation conditions and procedures used in this research is given in Table I. This method is the first large-scale procedure to

Table I   Fractionation Conditions

Solvent	Distilled deionized water
Nonsolvent	Acetone, methanol (BDH, reagent grade)
Temperature	$23 \pm 2°C$
Polymer concentration	1–8 wt % of initial solution[a]
Reservoir	Polyethylene: 20 L, 50 L
Agitation	1/8 hp heavy-duty lab stirrer with torque limiting controller (Series H, G.K. Heller Corp. Floral Pk., NY)
Nonsolvent addition	Dropwise
Length of nonsolvent addition	2–48 h[b]
Settling time	2–7 days
Method of phase separation	Supernatant layer was siphoned off and refractionated

[a] Polymer concentration was reduced for higher molecular weight samples to maintain low viscosities and high fractionation efficiencies.

[b] Larger amounts of nonsolvent were needed to separate lower molecular weight polymers and refractionated samples.

be applied to polyacrylamide, although large-scale apparatus have been used before.[25] Figure 1 illustrates the magnitude in the reduction in polydispersity due to fractionation.

The molecular weight of each fraction was measured using a Chromatix KMX-6 LALLS photometer, with a cell length of 15 mm and a field stop of 0.2. This corresponded to an average scattering angle of 4.8°. A 0.45-μm cellulose–acetate–nitrate filter (Millipore) was used for polymer solutions. A 0.22-μm filter of the same type was used to clarify the solvent. Distilled ionized water with $0.02 M$ Na$_2$SO$_4$ (BDH, analytical grade) was used as solvent. The results are given in Table II.

The refractive index increment of the solvent was determined using a Chromatix KMX-16 laser dif-

ferential refractometer at 25°C and a wavelength of 632.8 nm. The dn/dc was found to be 0.1869 for acrylamide homopolymers.

Polymer Hydrolysis

The fractionated polyacrylamides were hydrolyzed in an aqueous solution containing 4 wt % polymer. The reaction was performed in a three-neck 250-mL round bottom Pyrex flask. The center opening was tightly fit with a glass agitator equipped with two, 1-in. Teflon blades. The agitator was connected to an external motor (Type RZRI-66, Caframo). The two side necks housed a thermometer and were available for sample withdrawals, respectively. The
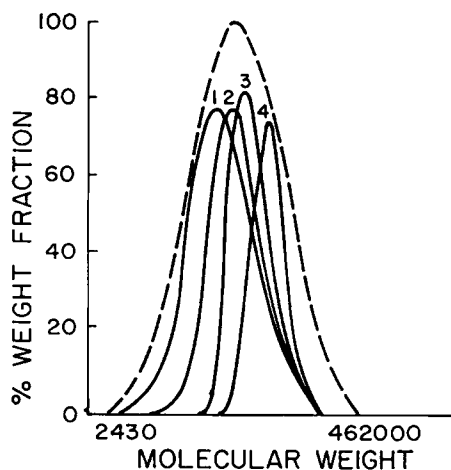

Figure 1   Unnormalized SEC chromatograms showing the reduction in polydispersity upon fractionation. Dashed line: original polymer. Solid lines: Fractions 1–4.

Table II   Weight-Average Molecular Weight and Second Virial Coefficients for Polyacrylamide Fractions

Sample	$M_w \times 10^{-3}$ (g/mol)	$A_2 \times 10^4$ (mL mol/g^2)
FA-1R	1240	5.718
S2	1220	5.600
LFA2-1	1140	5.930
S7	984	4.048
LFA4-1	466	7.695
S8	286	8.194
LFA2-2	233	8.605
LFB1-1D	119	12.060
AL-1	72.6	14.126
LFB1-2	64.4	20.833(?)
LFA4-2	48.2	7.528(?)
LFB1-1U	40.0	16.508
LFB1-3	26.9	17.195
LFB1-4	13.0	12.102

flask was immersed in a constant temperature bath, operating at 30 ± 0.5°C. Distilled deionized water with 0.5 M NaOH (BDH) was used as the reaction medium. Experiments were carried out for 6 h in duration, with aliquots withdrawn periodically at approximately 15-min intervals.

Hydrolysis was performed on five nonionic fractions with nominal molecular weights of 30,000, 120,000, 200,000, 400,000, and 1,000,000 daltons. At each molecular weight a range of polymer compositions from 0 to 35% sodium acrylate was obtained. These polymers were precipitated in methanol, an ideal solvent since it solubilizes the unreacted sodium hydroxide, and dried *in vacuo* to constant weight. The samples were subsequently stored in a sealed glass desiccator over silica gel.

Copolymer Characterization

The composition of copolymers of acrylamide with sodium acrylate can be measured using a variety of chromatographic, spectrometric, elemental, or titrative techniques. Early investigations into these copolymers measured the extent of hydrolysis by potentiometric[6,10,16,26-29] or conductiometric titrations.[11] Elemental analysis (C—H—N) is also common.[30,31] However, it is sensitive to trace residuals of water, which are difficult to completely remove. ^{13}C NMR techniques have been reported[1-3] and give excellent results for low to moderate molecular weight polymers, but require extensive data acquisition for chain lengths above approximately 1000. Infrared methods have been developed[12,32,33] and while they provide quick estimates of the composition, their reliability and reproducibility are poor.[34] Recently, Maurer and Klemann[35] have used ion chromatography and found it provided excellent agreement with atomic absorption spectroscopy (for Na^{+}). Indeed, the elemental analysis of Na^{+} directly is insensitive to residual water, but we have found it to underpredict the degree of ionization, likely because of incomplete neutralization. Elemental sodium methods are also susceptible to contamination by sodium ions, either from insufficient washing of NaOH or residual on the glassware. Therefore, although elemental methods have the best reproducibility, their absolute accuracy is insufficient.

In this work both potentiometric and conductiometric electrodes were placed in the titration reservoir. This was equipped with a flow through jacket to control temperature and sealed such that an inert nitrogen atmosphere could be maintained over the sample. Entrance holes for the probes and titrant were included. Homogenized aqueous solutions of polyacrylamide-co-sodium acrylate were titrated with 1.0 M HCl (BDH; reagent grade) and backtitrated with 0.1 M NaOH (BDH; reagent grade). The potentiometric and conductiometric calculation gave compositions within 1% of each other. Duplicate titrations were performed on a representative number on samples to estimate the reproducibility.

Light Scattering of Polyelectrolytes

When performing light scattering on polyelectrolyte samples, the effect of ionogenic monomers is manifested in an apparent second virial coefficient and refractive index increment. Nonetheless, the light-scattering equation derived for nonionic polymers[36-38] can be generalized for polyelectrolytes[39] provided the following criterion are met:

1. The local fluctuations in concentration, density, and refractive index are electrically neutral.[40]
2. The refractive index increment is obtained at constant electro-chemical potential of the counterions in the solution and the environment of the polymer coil.[41]

The second criterion is satisfied by dialyzing the polymer and aqueous salt solutions against each other. At Donnan equilibrium, the chemical potential of the counterion will be the same at all locations in the solution. Therefore, to correctly measure the molecular weights of polyelectrolytes we must first determine $(\delta n / \delta c)_\mu$ as a function of copolymer composition.

For characterization of dilute solution properties of polyacrylamide-co-sodium acrylate, Wu[24] has determined that polyelectrolyte interactions are suppressed for Na_2SO_4 concentrations of 0.2 mol/L. This was consequently selected as a solvent for the light-scattering characterization performed in this investigation.

Dialysis

A cellulose dialysis membrane (Spectra/Por 6) with a molecular weight cutoff of 1000 was purchased from Spectrum Medical Industries, Inc. (Los Angeles, CA). A small pore size was selected to prevent oligomers from diffusing into the dialysate. Prior to use the membranes were conditioned in the dialyzing buffer (0.2 M Na_2SO_4) for one hour, and rinsed with distilled deionized water.

Polymer solutions were prepared at a concentration suitable for light scattering.[42] One hundred mil-

liliters of these solutions were pipetted into the membrane, which was sealed at one end with a dialysis tubing enclosure. After the second end of the membrane was secured, it was submersed in 3 L of saline solution. This was housed in a 4-L polyethylene container, isolated from the atmosphere.

After a predetermined time the vessel was opened and the membrane removed. Several concentrations of the polymer were prepared by diluting the dialyzed solution with the dialysate. The samples were immediately analyzed by light scattering or differential refractometry.

RESULTS AND DISCUSSION

Determination of the Refractive Index Increment at Constant Chemical Potential

In order to determine the time required for Donnan equilibrium of the sodium ion in this particular solvent–membrane combination, several parallel experiments were performed. A polyacrylamide-co-sodium acrylate (PAM-NaAc) with 30% ionic content and a nominal molecular weight of 400,000 daltons was selected as a representative sample. A 0.15 wt % polymer solution was prepared and was separated into six samples, which were dialyzed for 0, 24, 48, 72, 96 and 120 h, respectively. After these periods the solutions were diluted and their refractive index increments determined against the dialysate. A plot

Table III   Refractive Index Increments at Constant Chemical Potential for Various Compositions of Polyacrylamide-co-Sodium Acrylate

Acrylate Content in Copolymer (mol %)	$(\partial n/\partial c)_\mu$
0.0	0.1869
6.4	0.1624
9.6	0.1551
15.0	0.1503
33.0	0.1464

of the trend in the refractive index increment with dialysis time is shown in Figure 2. Clearly equilibrium is reached after 72 h, although for subsequent measurements a dialysis time of 120 h was used. The refractive index increment at constant chemical potential was determined as a function of the extent of hydrolysis (Table III and Figure 3). The observed decrease in $(\delta n/\delta c)_\mu$ with acrylate content, a manifestation of the negative selective sorption of sodium sulfate, has been reported previously.[12,29,34,43] Only Kulanari and Gundiah[44] have found a contradictory dependency. None of these authors have used the same solvent as in this work and therefore direct comparison of the magnitude of $\delta n/\delta c$ is not possible. Nonetheless, the validity of these measurements will be confirmed in the next section.
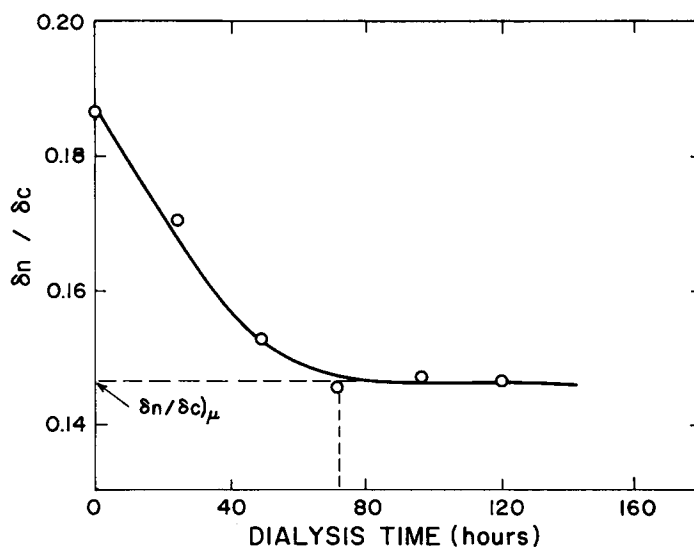

Figure 2   Refractive index increment $(\delta n/\delta c)$ as a function of dialysis time. Chemical potential equilibrium of the sodium counterion, between the polymer coil and bulk solution, is reached after 72 h. The corresponding refractive index increment at constant chemical potential $(\delta n/\delta c)_\mu$ is 0.1464.
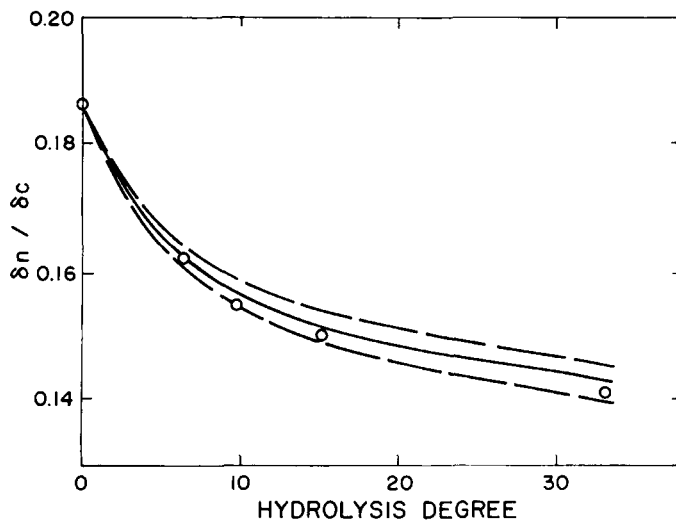
Figure 3 Refractive index increment at constant chemical potential as a function of the acrylate level in a polyacrylamide-co-sodium acrylate. Solid line is the regressed equation, dashed lines are the 95% confidence limits.

The equation

$$\left(\frac{\partial n}{\partial c}\right)_{\mu,\text{PAM-NaAc}} = 0.1869 \, (F_{\text{NaAc}})^{-0.076}$$

has been fit from this data so that the refractive index may be computed at any specific copolymer composition (F) between 0 and 33% sodium acrylate (NaAc).

Evaluation of the Molecular Weight Method for Polyacrylamide-co-Sodium Acrylate

Light-scattering measurements were made for each of the five narrow polymer standards. A typical result, showing the Rayleigh factor as a function of composition, is given in Figure 4. From these linear plots the weight-average molecular weights ($\bar{M}_w$) were regressed. These were normalized with respect to composition, with the corresponding chain
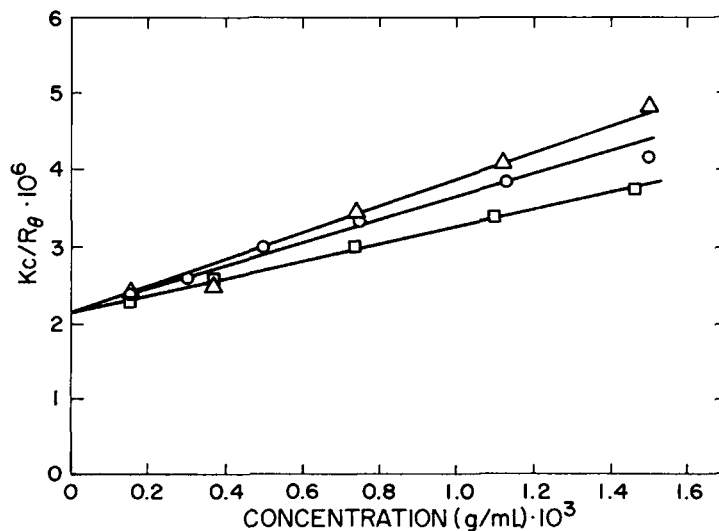

Figure 4 Light-scattering plots showing the equivalence of molecular weight determination for polyelectrolytes and the nonionic polymer from which they were derived. (O) polyacrylamide, (□) HPAM with 9.53% hydrolysis, (△) HPAM with 33.7% hydrolysis.

Table IV Comparison of the Polyelectrolyte and Nonionic Molecular Weight Characterization Procedures

Molecular Weight of Polyacrylamide Measured by the Nonionic Method	Molecular Weight Measured on Polyacrylamide-co-Sodium Acrylate by the Polyelectrolyte Method		Percent Deviation from Nonionic	
$\bar{r}_w$ (nonionic polyacrylamide)	$\bar{r}_w$ (10% hydrolysis)	$\bar{r}_w$ (30% hydrolysis)	10% Hydrolysis	30% Hydrolysis
379	482	402	21.4	5.7
1,676	1,633	1,702	2.6	1.5
3,282	3,413	3,439	3.8	4.6
6,563	6,412	5,959	2.4	10.1
13,859	13,845	10,446	0.1	24.6
			Average deviation 7.68%	

lengths summarized in Table IV, and the raw light-scattering data given in Table V. The polyelectrolyte chain lengths deviate on average by 7.68% from the original polyacrylamide homopolymer. Such an agreement is well within the random errors of aqueous light scattering ($\pm 10\%$).[42] We can conclude therefore that the measured molecular sizes of the ionic and nonionic polymers agree. It is worthwhile to note that without the correct refractive index increment, the estimation of the molecular weight of a 30% hydrolyzed polyacrylamide is 62% underpredicted! Therefore, the polyelectrolyte method, and the specific refractive index increments at constant chemical potential are accurate and reliable. Furthermore, it is sufficient to correct the optical constant for $(\delta n / \delta c)_\mu$, in order to obtain accurate molecular weights of polyelectrolytes.

The following procedure is recommended for the molecular weight characterization of polyacrylamide-co-sodium acrylate:

A dilute solution of the polyelectrolyte should be prepared at an appropriate concentration for light scattering[42] in a solvent of high ionic strength, for example, $0.2M$ Na_2SO_4. The polymer solution should subsequently be dialyzed against the saline solution for an equilibrium period in a membrane of small pore size. This will equilibrate the electrochemical potential of the Na^+ counterion between the bulk solution and the domain of the polymer coil. Several dilutions of the base polymer solution should then be prepared by combining the dialyzed solution and the dialysate. [These new polymer solutions will also be in electrochemical potential equilibrium with the dialysate since they are prepared from mixtures of two solutions with the same

activity of Na^+ ions.] The excess Rayleigh factors (R_θ) can then be measured by light scattering over the range of concentrations (c) prepared:

$$R_\theta = R_{\theta_c} - R_{\theta_{Dialysate}}$$

With an estimate of the copolymer composition (F), the specific refractive index increment at constant chemical potential, $(\partial n / \partial c)_\mu$, can be calculated and used to compute the optical constant (K):

$$K = \frac{2\pi^2 n^2}{\lambda^4 Na} \left(\frac{\partial n}{\partial c} \right)^2_\mu$$

where n is the refractive index of the solvent, Na is Avogadro's number, and λ is the wavelength of radiation. The weight-average molecular weight ($\bar{M}_w$) can subsequently be regressed from measurements of the excess Rayleigh factors, at several polymer concentrations, using the classical light-scattering equation, valid for low observation angles:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} + 2A_2c$$

where A_2 is the experimentally measured second virial coefficient, an estimate of the interaction potential between two polymer coils in a given solvent.

CONCLUSIONS

A polyelectrolyte characterization method has been developed for copolymers of acrylamide and sodium

Table V Raw Light-Scattering Data for Each Fraction

Nonionic Characterization (polyacrylamide)		Polyelectrolyte Characterization (polyacrylamide-co-sodium acrylate)			
Sample	Chain Length $(\bar{r}_w)$	Sample	Hydrolysis Degree (%)	Concentration (g/mL) $\times 10^3$	$K/R_\theta \times 10^2$ (mol mL/g^2)
LFB1-3	379	HY4-1	10.77	0.404	7.273
				1.010	2.695
				2.020	1.648
				3.030	1.195
				4.040	0.961
		HY4-3	36.0	0.4789	6.872
				1.1972	2.236
				2.3940	1.451
				3.5920	1.145
				4.7887	0.981
LFB1-1D	1,676	HY3-1	10.3	0.1548	5.610
				0.3871	2.396
				0.7743	1.302
				1.1614	0.935
				1.5485	0.744
		HY3-3	37.2	0.1531	5.071
				0.3827	2.137
				0.7654	1.207
				1.1480	0.891
				1.5307	0.792
LFA2-2	3,282	HY7-1	9.68	0.1527	2.797
				0.3816	1.238
				0.7633	0.681
				1.1449	0.503
				1.5265	0.410
		HY7-3	31.9	0.1393	2.864
				0.3483	1.120
				0.6965	0.710
				1.0448	0.542
				1.3930	0.461
LFA4-1	6,563	HY6-2	9.53	0.1470	1.567
				0.3674	0.706
				0.7348	0.410
				1.1020	0.309
				1.4695	0.259
		HY6-6	33.7	0.1494	1.614
				0.3736	0.674
				0.7471	0.460
				1.1207	0.367
				1.4942	0.325
S7	13,853	HY8-1	10.3	0.0231	4.401
				0.0578	1.810
				0.1155	0.977
				0.1733	0.706
				0.2310	0.559
		HY8-3	35.1	0.0259	4.823
				0.0647	2.078
				0.1295	1.082
				0.1942	0.778
				0.2589	0.566

acrylate containing between 0 and 35 mol % ionic groups. The precision of the procedure has been found to be quite high based on a comparison of the chain lengths measured by light scattering for the ionogenic polymers and the nonionic polymers from which they were derived. It is recommended for polyacrylamide-co-sodium acrylates prepared either by direct free radical synthesis or through hydrolysis.

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