

# Mark-Houwink-Sakurada Constants and Dilute Solution Behavior of Heterodisperse Poly(acrylamide-co-sodium acrylate) in 0.5M and 1M NaCl

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## Synopsis

Mark Houwink coefficients and molecular size parameters are presented for 31 unfractionated samples of polyacrylamide and hydrolyzed polyacrylamide in 0.5M and 1M aqueous NaCl. Polymers investigated include polyacrylamide, plus 10, 20, 50, 70, and 100 mol % poly(sodium acrylate). Their solution characteristics were studied by gel permeation chromatography, intrinsic viscosity, and light scattering techniques. A density function and heterodispersity index was assigned to each polymer sample due to the polydispersity of the molecular weight distributions. This technique improves the intrinsic viscosity-molecular weight correlation for heterodisperse commercially synthesized polymer systems. The intrinsic viscosity of these commercial compounds will yield useful estimates of their molecular weight, in spite of their obvious heterogeneity.

## INTRODUCTION

The poly(acrylamide-co-sodium acrylate) class of compounds continues to experience increased use in drilling fluids,<sup>1</sup> paper filler retention aids,<sup>2</sup> enhanced oil recovery,<sup>3</sup> and many effluent water clarification processes such as primary flocculants,<sup>4</sup> air flotation aids, and sludge dewatering.<sup>5,6</sup> In addition to polymer charge density, molecular weight is one of the single most important parameters in determining a polymer's field performance. Consequently, it is necessary to more fully characterize the solution behavior and viscosity-molecular weight relations for this commercially important class of polymers. This paper presents the Mark-Houwink constants and molecular dimensions of polyacrylamide, plus 10, 20, 50, 70, and 100 mol % poly(sodium acrylate) in 0.5M and 1M aqueous NaCl from gel permeation chromatography, light scattering, and intrinsic viscosity techniques.

There are numerous studies reported in the literature<sup>7-16</sup> describing the solution behavior and Mark-Houwink constants for polyacrylamide and hydrolyzed polyacrylamide. Rarely are heterodispersed polymer systems investigated. Most of the polymer samples exhibited very broad molecular weight distributions and thus required statistical corrections in correlating the findings from experimental viscosity-molecular weight measurements. The success of the Poddar and Forsman method<sup>17</sup> in assigning a heterodispersity index to the polymer sample depends on identification of a particular distribution density function for the molecular weight distribution chromatogram. In

most cases, there was little problem in characterizing the distributions from GPC data.

## EXPERIMENTAL

### Sample Polymerization

Electrophoretic grade acrylamide and reagent grade acrylic acid were polymerized by free radical initiation in distilled water at 60°C. 2,2'-Azo-bis(amidino propane) HCl served as the water soluble initiator. Polymerization times varied between 60 and 150 min. Molecular weight variations were produced by altering the concentrations of monomer and initiator, and occasionally adding very small amounts (less than 0.2 wt %) of 2-mercaptoethanol as a chain transfer agent. Monomer concentrations rarely exceeded 15 wt % in order to avoid "runaway" reactions and the production of insoluble microgel particles. The acrylic acid was neutralized with dilute sodium hydroxide to pH 7.80 prior to copolymerization. This synthesis pH is more conducive to block copolymerization due to the higher reactivity ratio for acrylamide at pH = 7.80 units. The reactivity ratio of acrylic acid decreases with increasing pH, while the reactivity ratio of acrylamide increases with increasing pH.<sup>18</sup> This block copolymerization will be most evident at the higher charge densities. To insure an oxygen free reaction environment, a nitrogen stream was bubbled into the comonomer solution for 15 min and then a nitrogen blanket was passed over the solution for the duration of the polymerization.

### Polymer Purification

After completion of the polymerization process, the polymer solutions were dialyzed in Spectrapor membrane tubing with a molecular weight cut off of 6000-8000 for 24 h. The samples were then rotary evaporated and freeze dried. Each polymer was analyzed for % water by the Karl Fischer method and examined with a Carlo Erba Total Nitrogen Analyzer for determination of the actual comonomer ratio or charge density. Since we were interested in the effects of varied and broad molecular weight distributions on polymer solution properties, no attempt was made to fractionate the whole polymer. Minimal branching by grafting should have occurred at the reaction temperatures and low initiator concentrations employed, as reported by earlier investigators.<sup>19</sup>

### Gel Permeation Chromatography

GPC or size exclusion chromatography was used to determine the polymer molecular weight distributions. It was not used to determine the absolute polymer molecular weights due to insufficient calibrations of the employed column set for many of the comonomer ratios. The average molecular weight calculations were made relative to polyacrylic acid standards for poly(sodium acrylate), and the comonomer ratios of 70 and 50 mol % sodium acrylate. Polyacrylamide standards were used for polyacrylamide and the comonomer ratios of 20 and 10 mol % sodium acrylate. Three different solvent-column conditions were used in the determinations. Each showed good reproducibility

in the molecular weight distributions and usually agreed quite well with the light scattering weight average molecular weight. The column and solvent of choice for polyacrylamide and the low charge density compounds is  $\mu$ Bondagel (E-High + E-linear + 500A) in 0.05M sodium sulfate. For the poly(sodium acrylate) and the high charge density compounds like the 50 and 70 mol % sodium acrylate species, a  $\mu$ Bondagel (E-High + E-linear + 500A) in 0.05M ammonium acetate worked nicely. A TSK (5000 PW + 6000 PW) column with a pH = 7.0 phosphate buffer also worked well for both the high and low density compounds and agreed quite well with the distributions from the other two solvent-column conditions. The samples were run at 50°C, with a flow rate of 0.7 mL/min, and an injection volume of 50  $\mu$ L of 0.125% w/v. The detector was a Knauer DRI at 4  $\times$  with a SICA 7000S data module.

### Viscosity, Refractive Index Increment, and Light Scattering Measurements

Solvents and polymer solutions were filtered through 0.45–0.80  $\mu$ m cellulose acetate and cellulose nitrate membranes (Millipore). A 400 mL ultrafiltration cell (Amicon) served as the standard filtration system. For calibration of the photometer with benzene, a stainless steel cylindrical pressure holder was used with a 0.22  $\mu$ m Millipore teflon filter. All Millipore filters were rinsed with 600 mL of distilled water before use in order to remove the glycerol which acts as a preserving agent for the membrane. Aqueous salt solutions were prepared with distilled water and analytical grade salts.

Viscosity measurements were made at  $25 \pm 0.05^\circ\text{C}$  in a constant temperature water bath with a #75 Cannon-Fenske Viscometer. Intrinsic or limiting viscosities were determined in 0.5M and 1M aqueous NaCl at pH =  $9.0 \pm 0.15$  units. Intrinsic viscosities were extrapolated from the linear plots of reduced viscosity vs. concentration (Huggins Plot). The dilute polymer solutions behaved in a near-Newtonian manner at the shear rates employed; consequently, no account of the shear dependence correction term was made. Cannon Fenske pipets, nos. 50, 75 and 200, with various flow characteristics were applied to the diluted polymer solutions for testing of the shear dependence and its Newtonian behavior. There was less than 2% variation in the viscosity readings at the shear rates employed, indicating the viscosity was essentially a constant independent of the magnitude of the shear by stress ( $\tau$ ) or shear rate ( $\dot{\gamma}$ ). A  $\tau$  vs.  $\dot{\gamma}$  plot showed the dilute polymer solutions to behave in a linear Newtonian manner with the shear stress and shear rate proportional over the tested range. The maximum shear rate in the viscometer used in the intrinsic viscosity testing was  $853 \text{ s}^{-1}$ . In addition, none of the viscosity readings included a kinetic energy correction factor which was found to be negligible.

The specific refractive index increment measurements were made with a Brice-Phoenix differential refractometer in 1M aqueous NaCl, pH = 9.0 units, and at ambient temperature. The instrument was calibrated with distilled water solutions of potassium chloride. Many references<sup>8,15</sup> state the necessity of dialysis against the reference solvent in order to get an accurate assessment of the refractive index increment. It is important that the reference solvent and the polymer solution be at the same chemical potential. For this reason

the polymer was dialyzed against 1M NaCl for 48 h, and the solvent saved and later added to the reference compartment of the differential cell. Dialysis equilibrium is normally achieved within 20 h. The polyacrylamide concentration after dialysis was determined by a turbidimetric procedure using 5N acetic acid, sodium hypochlorite, and a spectrophotometer at 450 nm. The poly(sodium acrylate) polymers were titrated with 0.1M NaOH to pH end point for calculation of their after dialysis concentrations. Refractive index increment measurements were made with and without equilibrium dialysis.

Light scattering measurements were also carried out in 1M aqueous NaCl, pH = 9.0 units, and at ambient temperature with a Brice-Phoenix universal light scattering photometer and blue unpolarized light of 4361 Å (in vacuo). Scattering angles investigated were 30°, 45°, 60°, 75°, 90°, 105°, 120°, and 135°. The photometer was calibrated using benzene as a standard. The literature value<sup>20</sup> of  $48.5 \times 10^{-6} \text{ cm}^{-1}$  for the benzene Rayleigh ratio  $R(90^\circ)$  at 436 nm was used as a calibration standard for the photometer. A fluorescein sodium salt solution was used to calculate the angular correction terms over the scattering angles 135–30° due to distortions in the light intensity scattering envelope. The values of the weight average molecular weight  $\bar{M}_w$ , second virial coefficient  $A_2$ , and mean square radius of gyration  $\langle \bar{S}^2 \rangle$  were obtained from Zimm plot extrapolations.

## RESULTS AND DISCUSSION

The experimental values for the refractive index increments are listed in Table I. Values are given for those measurements taken before equilibrium dialysis at constant molality  $(dn/dc)_m$  and after dialysis at constant chemical potential  $(dn/dc)_\mu$ . The after dialysis values were consistently smaller (7%). These findings further illustrate the importance of equilibrium dialysis before investigating refractive index increments. Constant chemical potential refractive index increments were used in all molecular weight distributions.

Kulkarni and Gundiah reported<sup>16</sup> a  $dn/dc$  value of 0.179 for polyacrylamide in 0.12M aqueous NaCl which is in good agreement with our value. Similar findings were reported by Klein and Conrad<sup>8</sup> for the acrylamide-co-sodium acrylate system in 0.5M NaCl and 25°C. Their after-dialysis values of 0.174 for 10 mol % NaAc, 0.167 for 30 mol % NaAc, and 0.162 for 50 mol % NaAc verify our findings. However, some discrepancy arises from their 0.159

TABLE I  
Refractive Index Increments at Constant Molality and Constant Chemical Potential for Poly(acrylamide-co-sodium acrylate) in 1M Aqueous NaCl at Ambient Temperature

Polymer	$(dn/dc)_m$ (mL/g)	$(dn/dc)_\mu$ (mL/g)
Polyacrylamide	0.189	0.177
Poly(10 mol % sodium acrylate–90 mol % acrylamide)	0.191	0.174
Poly(20 mol % sodium acrylate–80 mol % acrylamide)	0.190	0.171
Poly(50 mol % sodium acrylate–50 mol % acrylamide)	0.183	0.164
Poly(70 mol % sodium acrylate–30 mol % acrylamide)	0.184	0.169
Poly(sodium acrylate)	0.189	0.179

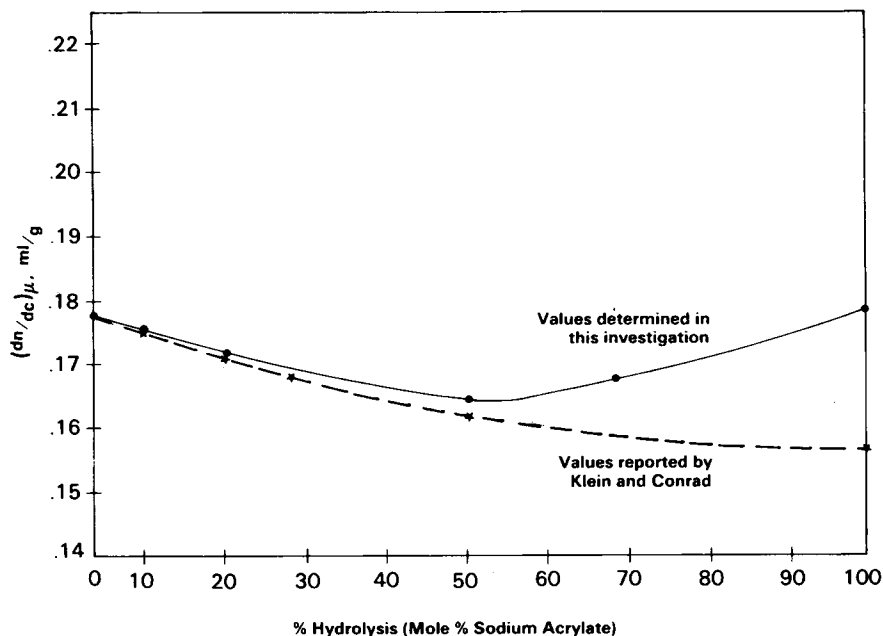


Fig. 1. Plot of constant chemical potential refractive index increment vs. % hydrolysis.

for 70 mol % NaAc and 0.157 for poly sodium acrylate. Figure 1 illustrates the contrast. Since the molar refraction is an additive and compositional property of a polymer-solvent system, it is not surprising that the refractive index increment is altered by variations in the comonomer ratios. However, it is difficult to predict or rationalize the magnitude and direction of the effect as the optical characteristics of the polymer segments change. The refractive index increments values reported in this paper are largest for the homopolymers polyacrylamide and poly(sodium acrylate), and decrease from these maximums as the other comonomer is increased. Consequently, a minimum is achieved at 50 mol % sodium acrylate. Klein's data indicates a minimum at 100 mol % sodium acrylate. It is difficult to resolve these differences, but one possibility is the pH or degree of ionization of the acrylic acid units. Orofino and Flory reported<sup>21</sup> a progressive increase in the refractive index increment with increasing degree of neutralization of the acrylic acid. In 1M aqueous NaCl at 30°C and near 100% neutralization, they reported a  $dn/dc$  value of 0.253, which although much higher than our value (0.179) and Klein's (0.157), is closer to the one reported in our study. Evidently pH and degree of neutralization could account for these differences between Klein, Orofino, and Flory, and our reported  $dn/dc$  values for poly(sodium acrylate). Klein never specified a pH for his studies, while we used a pH of 9.0 units. A low degree of neutralization may explain Klein's lower  $dn/dc$  value and minimum for poly(sodium acrylate).

Light scattering is still the principal method of determining the weight-average molecular weight ( $\bar{M}_w$ ) of polymers. The accuracy of the weight average molecular weights from light scattering was found to be 3-11% from measured molecular weight standards. Experimental light scattering data

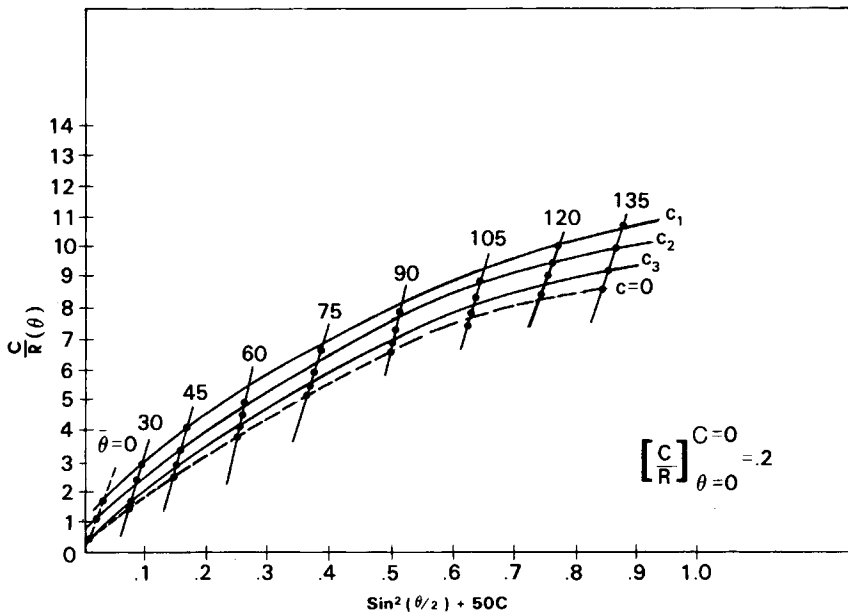


Fig. 2. Zimm plot with concentration curvature: poly(20 mol % acrylate-80 mol % acrylamide).

were examined according to the Zimm plot procedure,<sup>22</sup> where double extrapolation of polymer concentration and scattering angle to zero should give a common intercept. According to Huglin,<sup>23</sup> a general feature of polydispersity is that it makes the concentration curves (angular dependences) bend downward at the higher angles. Even though many of our polymer samples were

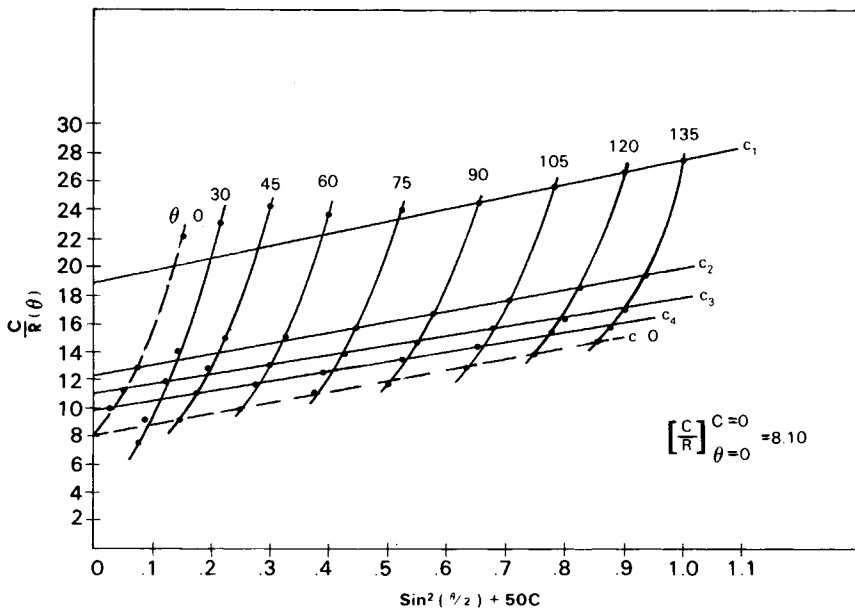


Fig. 3. Zimm plot with angular curvature: poly(70 mol % sodium acrylate-30 mol % acrylamide).

TABLE II  
Weight Average Molecular Weight, Second Virial Coefficient, Root-Mean-Square Radius of Gyration, and Root-Mean-Square End to End Distance from Light Scattering-Zimm Plot in 1M NaCl

Sample	$\bar{M}_w \times 10^{-5}$ (daltons)	$A_2 \times 10^5$ (mol cm <sup>3</sup> g <sup>-2</sup> )	$\langle \bar{s}^2 \rangle^{1/2}$ (Å)	$\langle \bar{r}^2 \rangle^{1/2}$ (Å)
Poly(sodium acrylate)				
1	2.39	1.26	324	793
2	2.78	1.77	392	959
3	2.95	1.73	380	930
4	4.76	1.40	528	1292
5	7.40	1.39	611	1496
Poly(70 mol % sodium acrylate-30 mol % acrylamide)				
6	2.40	9.21 <sup>a</sup>	531	1301
7	2.64	1.73 <sup>a</sup>	430	1053
8	3.40	2.32 <sup>a</sup>	662	1622
9	3.75	2.25	462	1131
10	4.70	1.78	564	1381
11	8.38	1.54 <sup>a</sup>	872	2135
Poly(50 mol % sodium acrylate-50 mol % acrylamide)				
12	3.14	2.23	418	1025
13	6.31	2.02	627	1535
14	8.62	1.93	807	1976
15	10.79	1.36 <sup>a</sup>	880	2154
16	14.59	1.93	1004	2459
Poly(20 mol % sodium acrylate-80 mol % acrylamide)				
17	1.15	1.66	232	569
18	2.27	14.79	845	2070
19	3.39	1.50	450	1103
20	8.78	1.25	781	1913
21	30.04	0.95	1396	3421
Poly(10 mol % sodium acrylate-90 mol % acrylamide)				
22	2.49	1.69	315	771
23	6.57	1.34	652	1597
24	7.79	1.24	846	2072
25	10.10	1.09	791	1937
26	24.86	1.02	1358	3327
Polyacrylamide				
27	0.91	1.86	270	661
28	2.64	1.30	292	714
29	10.24	1.47	694	1701
30	15.49	1.08	765	1873
31	32.43	0.98	1192	2918

<sup>a</sup>Denotes curvature in the  $\theta = 0$  curve.

very polydispersed, curvature at the higher angles was not that pronounced. Figure 2 illustrates one of the exceptions where polydispersity seemed to exaggerate the angular dependence of the downward curvature. Four of the six polymers of the poly(70NaAc-30AAm) series exhibited concentration dependence over the entire scattering angle range, but was most apparent at the more dilute polymer concentrations. Figure 3 is a representative example.

Table II summarizes the light scattering experimental data. The slope of the  $\theta = 0$  curves yields the second virial coefficient  $A_2$ . The initial slope of the  $C = 0$  curve was instrumental in the calculation of polymer dimensional

TABLE III  
Weight Average, Viscosity Average, and Number Average Molecular Weights  
from GPC and Light Scattering Techniques

Sample	$\bar{M}_w \times 10^{-5}$	Polydispersity	Distribution curve	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$
Poly(sodium acrylate)					
1	2.39	3.76	Schulz-Flory	2.32	0.64
2	2.78	5.42	Log Normal	2.55	0.51
3	2.95	4.91	Log Normal	2.72	0.60
4	4.76	2.66	Log Normal	4.53	1.79
5	7.40	3.40	Schulz-Flory	7.17	2.18
Poly(70 mol % sodium acrylate-30 mol % acrylamide)					
6	2.40	2.42	Schulz-Flory	2.31	0.99
7	2.64	8.97	Log Normal	2.22	0.29
8	3.40	2.01	Schulz-Flory	3.30	1.69
9	3.75	5.52	Schulz-Flory	3.57	0.68
10	4.70	5.70	Schulz-Flory	4.52	0.82
11	8.38	2.49	Log Normal	7.89	3.36
Poly(50 mol % sodium acrylate-50 mol % acrylamide)					
12	3.14	8.78	Log Normal	2.46	0.36
13	6.31	5.00	Schulz-Flory	5.79	1.26
14	8.62	5.30	Schulz-Flory	7.91	1.63
15	10.79	1.23	Log Normal	10.54	8.77
16	14.59	2.18	Schulz-Flory	13.76	6.69
Poly(20 mol % sodium acrylate-80 mol % acrylamide)					
17	1.15	6.00	Log Normal	0.98	0.19
18	2.27	1.89	Log Normal	2.15	1.20
19	3.39	5.80	Schulz-Flory	3.17	0.58
20	8.78	1.51	Log Normal	8.47	5.81
21	30.03	19.1	Log Normal	23.22	1.57
Poly(10 mol % sodium acrylate-90 mol % acrylamide)					
22	2.49	7.70	Log Normal	2.10	0.32
23	6.57	4.40	Log Normal	5.81	1.49
24	7.79	1.11	Schulz-Flory	7.72	7.02
25	10.10	3.20	Schulz-Flory	9.58	3.16
26	24.86	1.12	Schulz-Flory	24.64	22.20
Polyacrylamide					
27	0.91	2.70	Schulz-Flory	0.86	0.34
28	2.64	3.85	Log Normal	2.32	0.69
29	10.24	1.49	Log Normal	9.86	6.87
30	15.49	1.94	Schulz-Flory	14.82	7.98
31	32.43	3.44	Log Normal	28.85	9.43

parameters such as the root mean square radius of gyration  $\langle \bar{s}^2 \rangle^{1/2}$  and root mean square end to end distance  $\langle \bar{r}^2 \rangle^{1/2}$ . As expected, there was the general tendency of the second virial coefficient to decrease with increasing molecular weight within any one copolymer system.

Results from gel permeation chromatography are described in Table III. This includes a density function representation (i.e., log normal or Schulz-Flory), the polydispersity index, and polymolecularity corrections to the light scattering weight average molecular weight  $\bar{M}_w$  to give a viscosity average value  $\bar{M}_v$ . The number average molecular weight was not determined directly, but calculated from the relation, polydispersity index =  $\bar{M}_w/\bar{M}_n$ . The polymolecularity corrections were derived from the distribution functions



TABLE IV  
Proportionality Constant and Slope from Double Logarithmic Plot of the Root-Mean-Square Radius of Gyration vs. the Weight Average and Viscosity Average Molecular Weight from the Relationship  $\langle \bar{s}^2 \rangle^{1/2} \propto M^{\text{slope}}$  in 1M Aqueous NaCl

System	Weight Average $\bar{M}_w$		Viscosity Average $\bar{M}_v$	
	Slope	Proportionality constant	Slope	Proportionality constant
Polyacrylamide	0.56	0.298	0.56	0.298
Poly(10 NaAc-90AAm)	0.63	0.138	0.59	0.234
Poly(20 NaAc-80AAm)	0.55	0.406	0.57	0.330
Poly(50 NaAc-50AAm)	0.59	0.256	0.52	0.677
Poly(70 NaAc-30AAm)	0.61	0.203	0.44	2.06
Poly(sodium acrylate)	0.54	0.417	0.53	0.53

listed in the *Polymer Handbook*.<sup>24</sup> A computer program was developed to determine the corrections which were generally achieved in five iterations or less.

The radius of gyration dimension was examined through the relationship  $\langle \bar{s}^2 \rangle^{1/2} \propto M^{\text{slope}}$ , where the exponent is the slope of the double logarithmic plot of the root-mean-square radius of gyration vs. the average molecular weight. Heterodispersity corrections were applied so the plot is based on viscosity average molecular weights rather than weight average. Table IV lists the slopes and the proportionality constants under viscosity and weight average conditions for each polymer type in 1M aqueous NaCl.

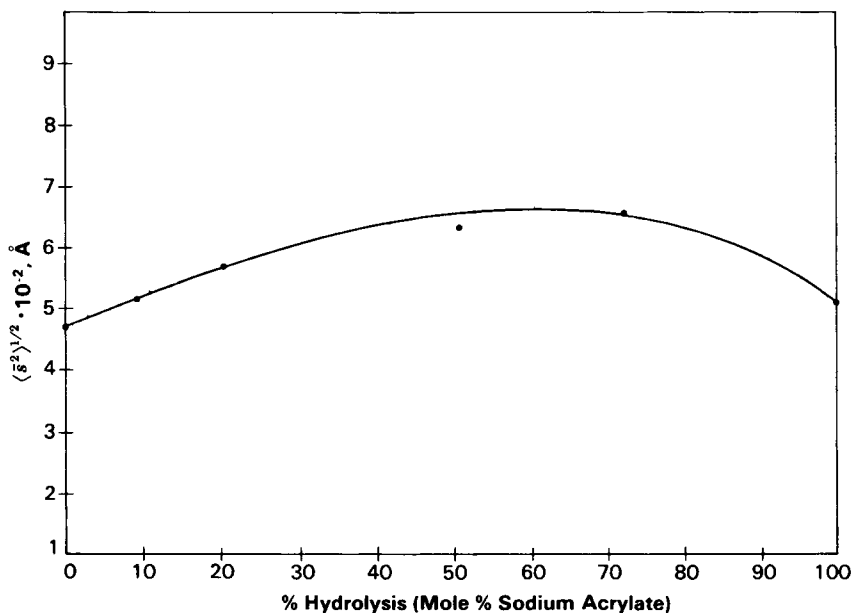


Fig. 4. Variation of root-mean-square radius of gyration vs. change in charge density (% hydrolysis): Calculation for  $\bar{M}_v = 5 \times 10^5$  daltons (dimensions in 1M NaCl).

The exponent 0.56 that we report for polyacrylamide compares to 0.55 as reported by Gundiah and Kulkarni<sup>16</sup> in 0.12*M* aqueous NaCl, to 0.64 as reported by Francois et al.<sup>14</sup> in 0.1*M* aqueous NaCl, and to 0.59 as reported by Klein and Conrad<sup>9</sup> in water. Figure 4 illustrates the variation of  $\langle \bar{s}^2 \rangle^{1/2}$  with % hydrolysis for  $5 \times 10^5$  molecular weight sample. The maximum polymer dimensions for a fixed molecular weight compound occurs in the 60–70 mol % sodium acrylate range. Variations in the refractive index increment as seen in Figure 1 are not solely accountable for this behavior. The actual data points indicate a minimum in the refractive index increment at 50 mol % sodium acrylate, while a maximum experimental value for the radius of gyration occurs at 70 mol %. A subsequent paper will discuss other solution

TABLE V  
Intrinsic Viscosity Data in 0.5*M* and 1*M* Aqueous NaCl Solutions at 25°C  
and pH = 9.0 Units (dL g<sup>-1</sup>)

Sample	$[\eta]_{0.5M}$	$[\eta]_{1.0M}$
	Poly(sodium acrylate)	
1	1.388	0.956
2	1.588	1.264
3	1.521	1.198
4	2.774	2.187
5	3.665	2.912
	Poly(70 mol % sodium acrylate–30 mol % acrylamide)	
6	2.220	1.633
7	2.390	1.657
8	2.815	2.422
9	2.973	2.649
10	3.994	3.345
11	6.029	—
	Poly(50 mol % sodium acrylate–50 mol % acrylamide)	
12	1.947	1.596
13	3.433	3.210
14	4.496	4.228
15	4.947	4.360
16	6.022	5.230
	Poly(20 mol % sodium acrylate–80 mol % acrylamide)	
17	0.864	0.681
18	1.127	—
19	2.378	2.282
20	4.509	4.207
21	9.007	8.087
	Poly(10 mol % sodium acrylate–90 mol % acrylamide)	
22	1.304	1.216
23	2.960	3.025
24	3.064	3.096
25	4.731	4.691
26	9.010	9.708
	Poly acrylamide	
27	0.561	0.645
28	1.291	1.369
29	3.341	—
30	5.050	—
31	7.923	8.166

properties of these polymers and suggest an explanation for this behavior in terms of expansion coefficients and steric factors.

### VISCOSITY-MOLECULAR WEIGHT RELATION

The Mark-Houwink-Sakurada equation gives the relation between the intrinsic viscosity of a polymer and its weight average or viscosity molecular weight. Table V lists the intrinsic viscosity data in 0.5M and 1M NaCl solutions at 25°C and pH = 9.0 units. The coefficients  $K$  and  $a$  for each copolymer were determined in these solvents. Intrinsic viscosity units are dL g<sup>-1</sup>. Due to the heterodispersity of the samples studied, polymolecularity corrections were applied to the double logarithmic plots. Figure 5 shows the viscosity-molecular weight relationships with and without the corrections for 0.5M NaCl. The slope and intercept of those lines yield the following equations:

**For 0.5M Aqueous NaCl.**

*Without heterodispersity corrections*

*With heterodispersity corrections*

*Polyacrylamide:*

$$(1a) [\eta] = 1.14 \times 10^{-4} M_w^{0.746}$$

$$(1b) [\eta] = 1.21 \times 10^{-4} M_v^{0.746}$$

*Poly(10 mol % sodium acrylate-90 mol % acrylamide):*

$$(2a) [\eta] = 2.69 \times 10^{-5} M_w^{0.858}$$

$$(2b) [\eta] = 8.10 \times 10^{-5} M_v^{0.789}$$

*Poly(20 mol % sodium acrylate-80 mol % acrylamide):*

$$(3a) [\eta] = 1.398 \times 10^{-4} M_w^{0.749}$$

$$(3b) [\eta] = 1.09 \times 10^{-4} M_v^{0.775}$$

*Poly(50 mol % sodium acrylate-50 mol % acrylamide):*

$$(4a) [\eta] = 1.672 \times 10^{-4} M_w^{0.742}$$

$$(4b) [\eta] = 5.78 \times 10^{-4} M_v^{0.655}$$

*Poly(70 mol % sodium acrylate-30 mol % acrylamide):*

$$(5a) [\eta] = 7.06 \times 10^{-5} M_w^{0.834}$$

$$(5b) [\eta] = 6.38 \times 10^{-5} M_v^{0.844}$$

*Poly(sodium acrylate):*

$$(6a) [\eta] = 1.750 \times 10^{-5} M_w^{0.909}$$

$$(6b) [\eta] = 2.44 \times 10^{-5} M_v^{0.887}$$

A deficiency of supporting viscosity measurements in 1M aqueous NaCl for polyacrylamide and the 20 mol % hydrolyzed product leaves some question as to the validity of the Mark-Houwink-Sakurada expressions in 1M NaCl for these two copolymers. The data that were collected, however, was fairly precise and, consequently, still gives reasonable values. Below are the polymolecularity corrected and uncorrected Mark-Houwink-Sakurada equations in 1M NaCl from linear regression analysis.

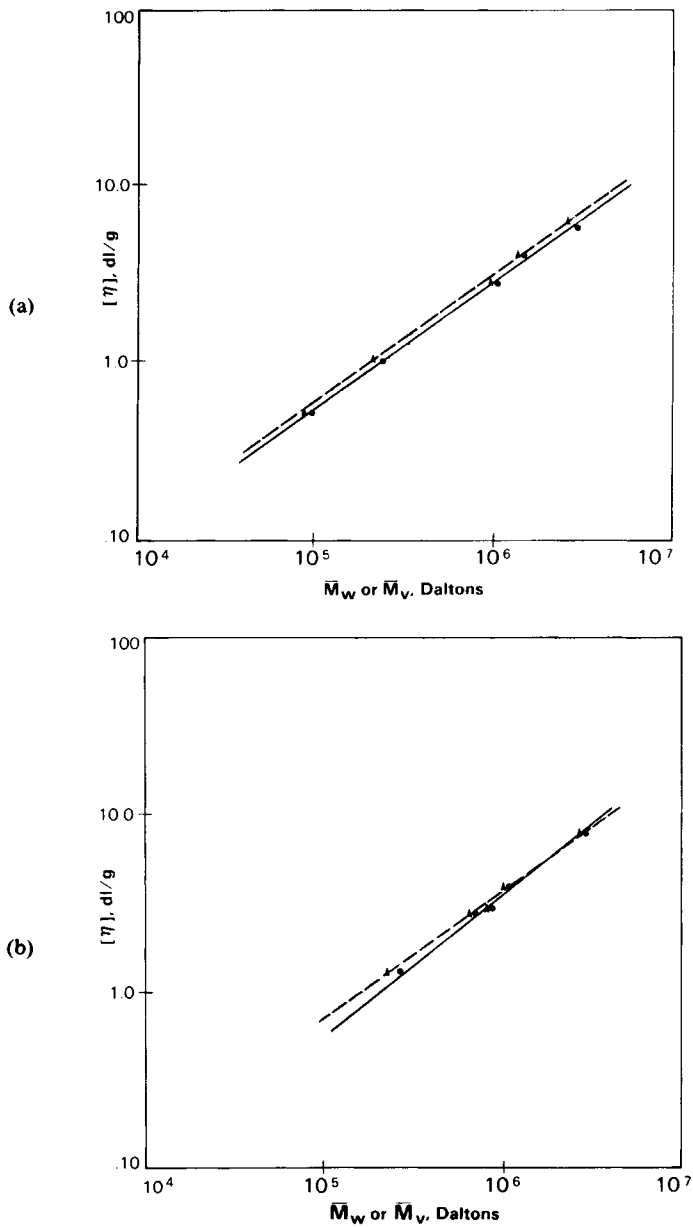


Fig. 5. Double logarithmic plot of intrinsic viscosity in 0.5M aqueous NaCl vs. weight average or viscosity average molecular weight: (---) heterodispersity correction; (—) no corrections ( $\bar{M}_w$ ). (a) Polyacrylamide; (b) poly(10 mol % sodium acrylate-90 mol % acrylamide); (c) poly(20 mol % sodium acrylate-80 mol % acrylamide); (d) poly(50 mol % sodium acrylate-50 mol % acrylamide); (e) poly(70 mol % sodium acrylate-30 mol % acrylamide); (f) poly(sodium acrylate).

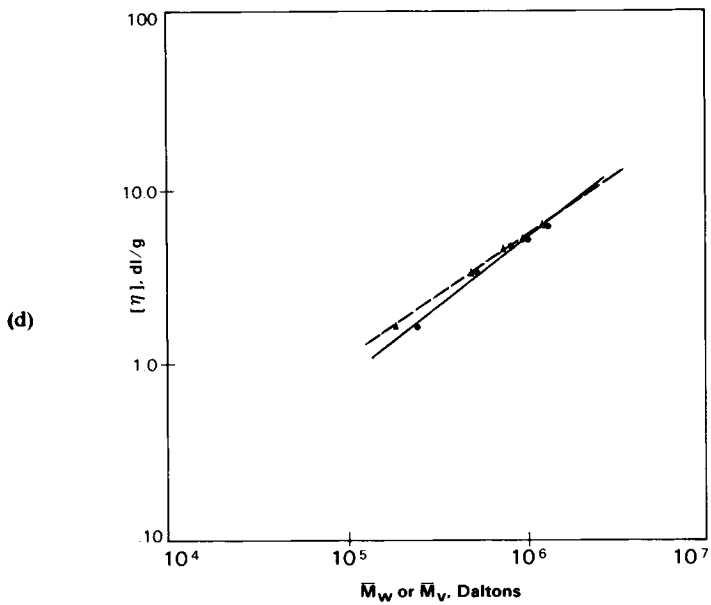
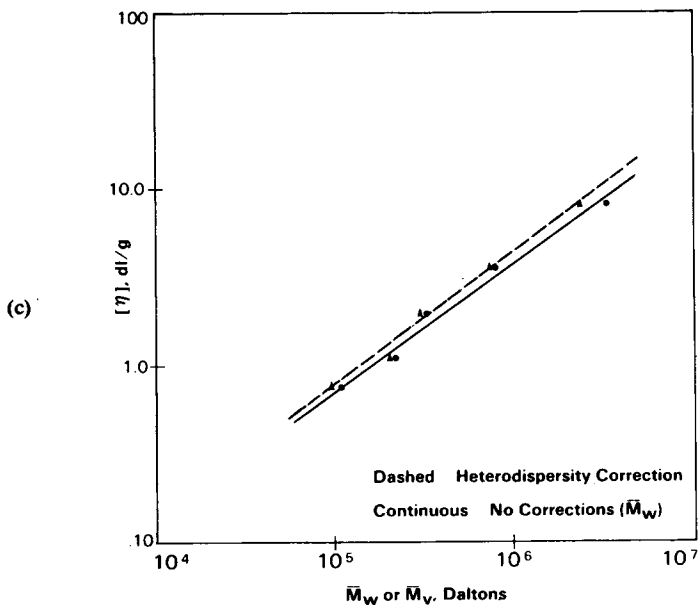


Fig. 5. (Continued from the previous page.)

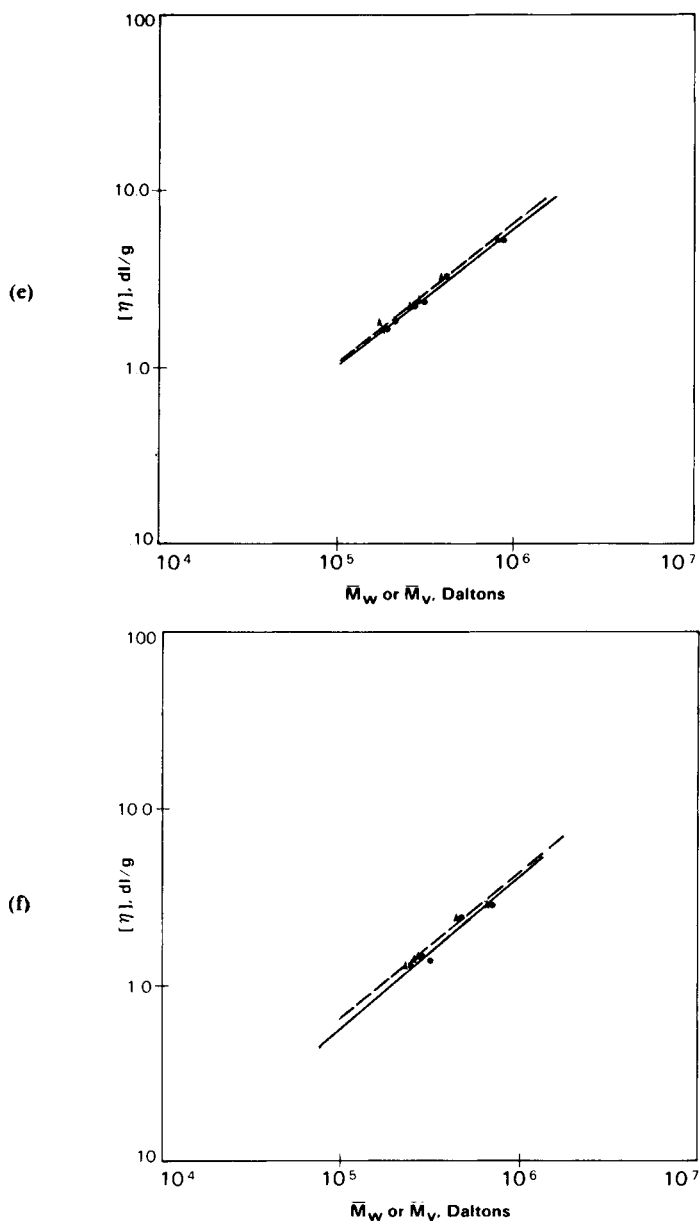


Fig. 5. (Continued from the previous page.)

## For 1M Aqueous NaCl.

Without heterodispersity corrections

With heterodispersity corrections

*Polyacrylamide:*

(1c)  $[\eta] = 1.912 \times 10^{-4} M_w^{0.711}$

(1d)  $[\eta] = 1.84 \times 10^{-4} M_v^{0.720}$

*Poly(10 mol % sodium acrylate-90 mol % acrylamide):*

(2c)  $[\eta] = 1.53 \times 10^{-5} M_w^{0.908}$

(2d)  $[\eta] = 3.07 \times 10^{-5} M_v^{0.860}$

*Poly(20 mol % sodium acrylate-80 mol % acrylamide):*

(3c)  $[\eta] = 1.413 \times 10^{-4} M_w^{0.744}$

(3d)  $[\eta] = 1.307 \times 10^{-4} M_v^{0.759}$

*Poly(50 mol % sodium acrylate-50 mol % acrylamide):*

(4c)  $[\eta] = 9.03 \times 10^{-5} M_w^{0.779}$

(4d)  $[\eta] = 2.98 \times 10^{-4} M_v^{0.695}$

*Poly(70 mol % sodium acrylate-30 mol % acrylamide):*

(5c)  $[\eta] = 1.10 \times 10^{-6} M_w^{1.142}$

(5d)  $[\eta] = 2.60 \times 10^{-6} M_v^{1.072}$

*Poly(sodium acrylate):*

(6c)  $[\eta] = 5.41 \times 10^{-6} M_w^{0.981}$

(6d)  $[\eta] = 6.0 \times 10^{-6} M_v^{0.974}$

Mark-Houwink constants from the literature for the acrylamide-co-sodium acrylate system are listed in Table VI. Any differences in the reference values for the constant ( $K$ ) and the exponent ( $a$ ) may be attributed to heterodispersity, the random or block arrangement of the comonomer units, the pH at

TABLE VI  
Mark-Houwink constants as Reported in the Literature for the Poly(acrylamide-co-Sodium Acrylate) Poly(AAm-NaAc) System in Similar Solvent<sup>a</sup>

Compound	Solvent	$K$	$a$	References
Polyacrylamide (PAAm)	0.12 NaCl water, 30°C	$5.31 \times 10^{-5}$	0.79	16
	0.5M NaCl water, 25°C	$7.19 \times 10^{-5}$	0.77	8
	0.2M NaCl water, 20°C	$30.2 \times 10^{-5}$	0.68	13
	0.1M NaCl water	$9.33 \times 10^{-5}$	0.75	14
	0.2M NaCl water	$6.31 \times 10^{-5}$	0.80	25
Poly(10NaAc-90AAM)	0.5M NaCl water, 25°C	$6.2 \times 10^{-5}$	0.81	8
Poly(20NaAc-80AAM)	0.5M NaCl water, 25°C	$6.3 \times 10^{-5}$	0.82	8
Poly(50NaAc-50AAM)	0.5M NaCl water, 25°C	$8.2 \times 10^{-5}$	0.82	8
Poly(70NaAc-30AAM)	0.5M NaCl water, 25°C	$1.1 \times 10^{-4}$	0.79	8
Poly(sodium acrylate) (PNaAc)	0.5M NaBr, 15°C	$5.4 \times 10^{-4}$	0.63	26

<sup>a</sup> Intrinsic viscosity in dL g<sup>-1</sup>.

which the intrinsic viscosity was run (usually not reported), and iminization or branching.

### CONCLUSIONS

Reliable values of the weight average molecular weight of commercial samples of poly(acrylamide-co-sodium acrylate) may be obtained from their intrinsic viscosities in 0.5M or 1.0M NaCl. These solutions remain good solvents for all of the polymers, ranging from polyacrylamide to poly(sodium acrylate). The constants for the Mark-Houwink-Sakurada equations presented here tend to give calculated molecular weights that fall in the same range as published results.

The data in this investigation will serve as a basis for a subsequent publication describing the unperturbed molecular dimensions, the expansion coefficients, and conformational properties of these heterodispersed poly(acrylamide-co-sodium acrylate) samples.

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