Molecular Weight Characterization of Poly(Acrylamide-co-Sodium Acrylate). I. Viscometry

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SYNOPSIS

Mark–Houwink constants for polyacrylamide and poly(acrylamide-co-sodium acrylate) in $0.2M$ Na_2SO_4 were measured using eight fractionated samples of polyacrylamide and 26 hydrolyzed polyacrylamide samples. The dependence of K and a on the copolymer compositions was found for the range of acrylate content 6 ~ 40 mol %. A relationship between intrinsic viscosity and acrylate content in the form of square root law was found. Molecular weights of copolymer samples with various compositions were estimated using viscometry with Mark–Houwink equations established in this work. The molecular weights of narrow MWD copolymer samples could be measured with an error of ±5%, whereas those of broad MWD copolymer samples with an error of ±8%.

INTRODUCTION

The molecular weight characterization of polyelectrolytes is relatively difficult, since variations in copolymer composition alter the electrostatic environment and, hence, the size of even structure of the polymer chain. Hydrolyzed polyacrylamide (HPAM) is therefore often used for methods development since it has a random distribution of charged groups along the backbone, provided alkaline hydrolysis is performed under mild conditions[1-3] and the molecular weights of the parent PAM can be estimated by conventional techniques. Many studies have been reported on the solution properties and the molecular weight characterization of HPAM,[4-14] but only one study was done using fractionated polyacrylamide (PAM) with narrow molecular weight distributions (MWD). In their investigation, Schwartz and Francois[14] used fractionated PAM to estimate the Mark–Houwink constant at two levels of hydrolysis. These data are, however, insufficient to develop methodology for the molecular weight characterization of poly(acrylamide-co-sodium acrylate) over a wide range of compositions.

The objective of this study was to find valid methods for the molecular weight characterization of HPAM or poly(acrylamide-co-sodium acrylate) over the composition range of commerical interest. We have hydrolyzed a series of fractionated and well-characterized PAM samples under mild alkaline conditions. The intrinsic viscosities and weight average molecular weights were measured. In anticipation that the results of these studies could be applied to GPC calibration, we employed aqueous Na_2SO_4 solution as a solvent for polymers in these measurements and chose the M_w range of PAM fractions from 1.2×10^6 to 1.4×10^4 Daltons. Since most commercial HPAMs are of hydrolysis degree (HD), 10%–30%, we have mainly used HPAM samples with the HD in this range.

EXPERIMENTAL

Polymer Preparation

Nonionic polyacrylamides with broad MWD used for fractionation were synthesized on a pilot scale in our laboratory, except for the sample of M_w = 62,000, which was provided by ALCHEM INC. (Burlington, Ontario, Canada). The polymerizations were carried out in aqueous solution at 50–

60°C with $K_2S_2O_8$ as initiator and ethanol mercaptan as the chain transfer agent.

Fractionation

Precipitational fractionation was performed at room temperature using water as a solvent and acetone and methanol as nonsolvents.

Gel Permeation Chromatography

The MWD of PAM fractions was measured in $0.2 M$ Na_2SO_4 with a 5000 liquid chromatograph (Varian Canada Inc.) equipped with TSK PW 3 K, 5 K, 6 K columns (Toya Soda). Molecular weight calibration was done using universal calibration with seven narrow polyethyleneoxide standards (Toya Soda Manufacturing Co., Ltd.) and two broad MWD PAM samples. Peak broadening correction was performed using standard methods.[15,16]

Hydrolysis

PAM in aqueous solution was weighed into a three-neck flask of 500 mL and kept in a 30°C water bath

for at least 1 h. Amounts of $4N$ NaOH and deionized water (making the concentration of PAM 4 wt %and NaOH $0.5N$) were added to the flask under vigorous agitation. After the addition, gentle stirring was applied to prevent degradation of the polymer. Samples were withdrawn at predetermined times and poured into excess methanol (70–100 times the volume). The precipitated HPAM was purified by repeated washing with methanol. For low molecular weight samples, centrifugation at 5,000 rpm for 1/2 h was performed to recover the fine particles of HPAM. The solid HPAM was dried in a vacuum oven at about 60°C for at least 16 h and weighed for analysis immediately after being cooled to room temperature and withdrawn from the oven.

Analysis of Hydrolysis Degree

Elemental C, N, and H measurements were done by Guelph Chemical Lab. Ltd. (Ontario, Canada). The amount of Na was determined using atomic absorption spectroscopy (Perkin-Elmer 2380). Carboxyl groups were measured by conductometeric and potentiometric titration with $0.01N$ NaOH as titrant.
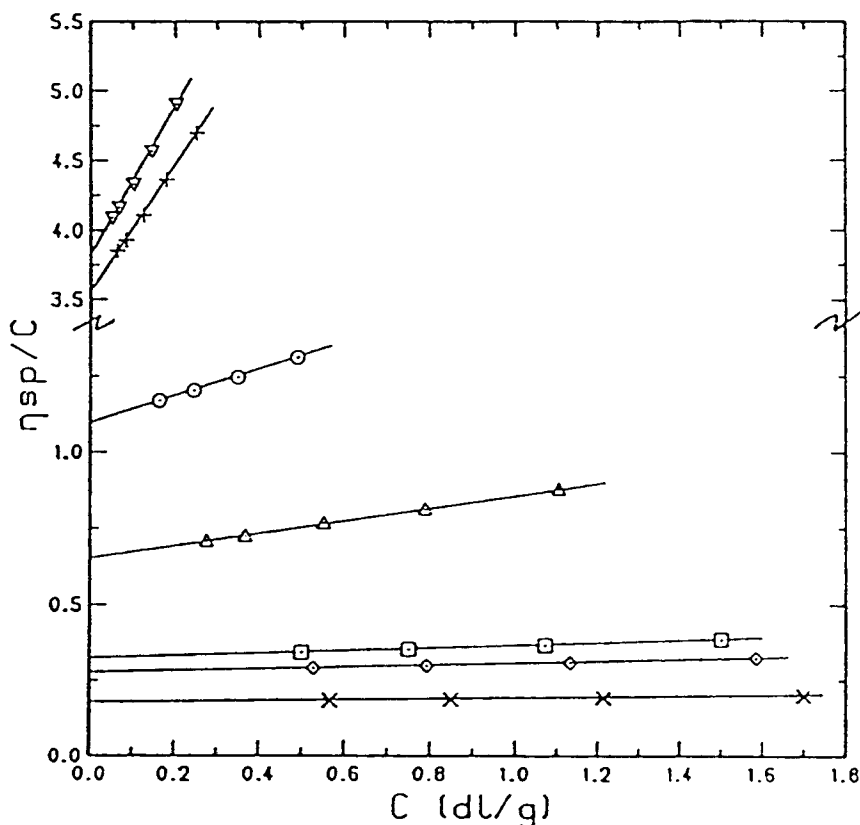
Figure 1   Plot of reduced specific viscosity vs. concentration of PAM: (✕) M_w = 13,900; (◇) M_w = 26,900; (□) M_w = 36,000; (△) M_w = 99,000; (○) M_w = 201,000; (+) M_w = 990,000; (▽) M_w = 1,244,000.

Table I M_w, **PDI, and [η] of PAM Fractions**

	Sample							
	F1	F2	F3	F4	F5	F6	F7	F8
M_w	1.244E6	9.90E5	4.01E5	2.01E5	9.90E4	3.60E4	2.69E4	1.39E4
PDI	1.8	2.0	1.8	1.7	1.6	1.5	1.3	1.2
[η]dL/g	3.804	3.555	1.733	1.096	.6502	.3220	.2741	.1754

Viscometry

The intrinsic viscosities of polymers in $0.2M$ Na_2SO_4 were obtained from the quandratic form as well as from the conventional form of the Huggins equation by the least-squares technique.[17,18] The efflux time was measured with #75 Cannon-Ubbelohde semi-micro dilution viscometer at $25 \pm 0.05°C$.

Light Scattering

The refractive index increment dn/dc measurements were performed with Chromatrix KMX-16 laser differential refractometer at 632.8 nm and 23°C. For HPAM, dialysis in the same solvent was

applied. The weight-average molecular weights determined with a low-angle laser light-scattering photometer (Chromatix KMX-6) in $0.02M$ (for PAM) and $0.2M$ Na_2SO_4 (for HPAM) at room temperature. All the HPAM samples were dialyzed for 120 h before measurement. The details are provided in Ref. 19.

RESULTS AND DISCUSSION

Characterization of Polyacrylamide

Eight PAM fractions with polydispersity indices 1.2 ~ 2.0 were obtained by fractionation. Their reduced
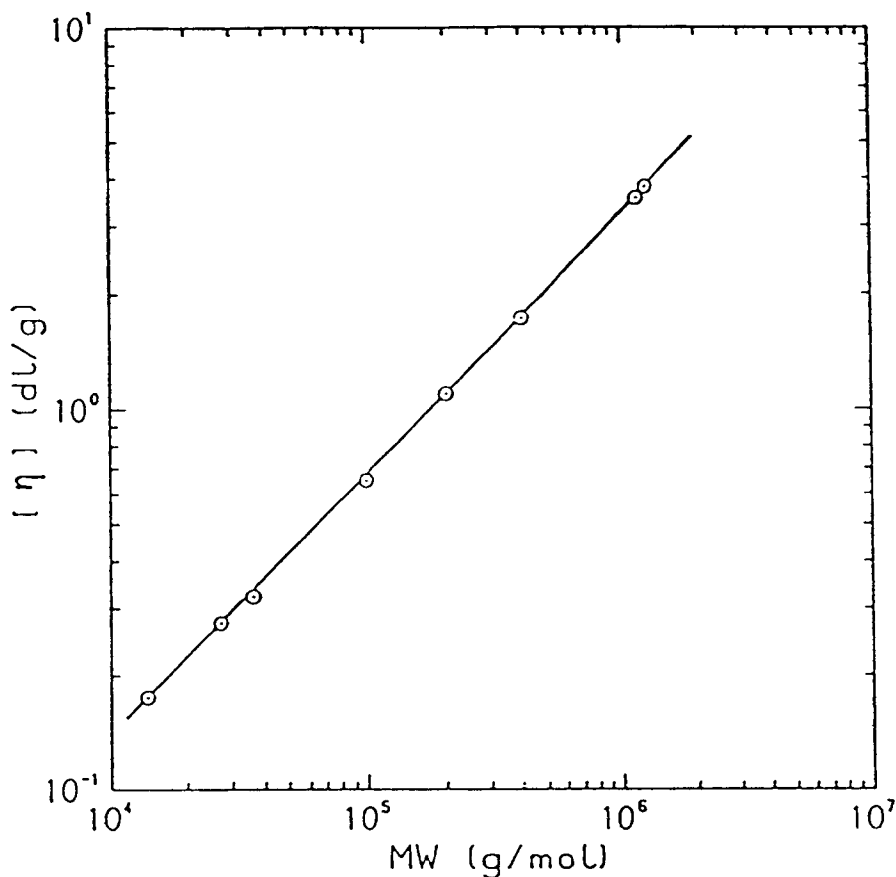
Figure 2   Plot of log[η] vs. log M_w for PAM in $0.2M$ Na_2SO_4 at 25°C.

specific viscosities $\eta sp/c$ when plotted vs. concentrations gave straight lines with regression coefficients of 0.999 ~ 0.9999 (see Fig. 1). The intrinsic viscosities from the quadratic equation were slightly different from those from the conventional equation with an average deviation of 0.46% (see Table I).

The Mark–Houwink constants K and a were estimated by the error-in-variables method,[20,21] in which the variances of log M_w were evaluated from Hunkeler and Hamielec's data,[22] whereas those of log[η] were calculated from our data using Chee's equation[17] ignoring the variance in concentrations. Then, the Mark–Houwink equation was established for PAM in 0.2M Na$_2$SO$_4$ at 25 ± 0.05°C:

$$[\eta] = 2.43E\text{-}4\ M_w^{0.69} \tag{1}$$

The 95% confidence intervals for parameters K and a are K = 2.43E-4 ± 0.36E-4 and a = 0.69 ± 0.014. The double logarithm plot of [η] vs. M_w is given in Figure 2. The "a" value is consistent with that obtained by Kulicke and Bose[23] in 0.1M Na$_2$SO$_4$, which was 0.7.

CHARACTERIZATION OF HYDROLYZED POLYACRYLAMIDE

Analysis of Hydrolysis Degree

The hydrolysis degree estimated using Na content measured by atomic absorption spectroscopy is relatively lower than those found by titration. This might infer the loss of Na$^+$ from HPAM during washing with methanol. A test of Na content in one sample before immersing and after immersing supported this hypothesis. However, a comparison of internal and external standard methods revealed the influence of the viscosity of the polymer solution on the flow rate and therefore on the analysis result.

In contrast to atomic absorption spectroscopy, the titration methods are insensitive to the carboxyl forms, either in the H$^+$ form or in the Na$^+$ form, as well as insensitive to the viscosity of solution. Hence, they are more reliable in analyzing the hydrolysis degree of HPAM. Conductometery is, however, preferred to potentiometry because of its better repro-
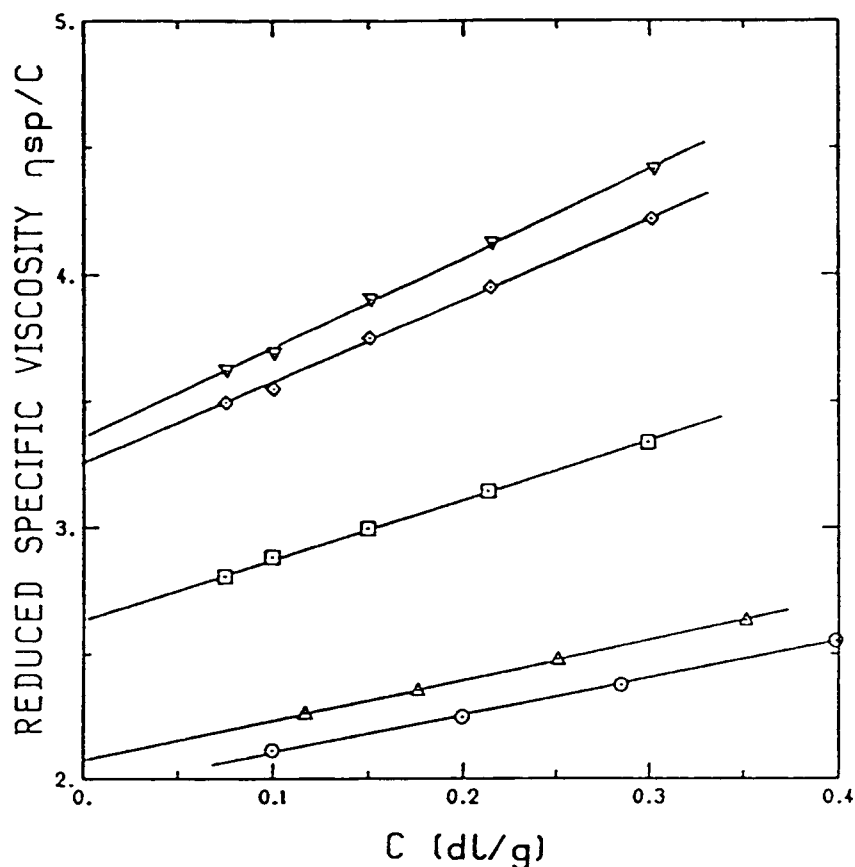
Figure 3 Reduced specific viscosity vs. concentration of F3HY in 0.2M Na$_2$SO$_4$: (⊙) HD = 6.4%; (△) HD = 9.5%; (□) HD = 14.9%; (◇) HD = 23.0%; (▽) HD = 26.0%.

ducibility or smaller standard deviation: 0.4 ~ 2.0%, compared to 1.0 ~ 4.0% for the latter.[24]

Viscosity and the Square Root Law

As shown by the straight lines of $\eta sp/c$ vs. concentration c in Figure 3, HPAM in 0.2M Na$_2$SO$_4$ behaves like a nonionic polymer. However, the intrinsic viscosity of polyelectrolytes with different compositions should be a function of M_w, composition of polymer, x, and concentration of added salt, C_s:

$$[\eta] = f(M_w, x, C_s)$$

In our case, x = hydrolysis degree (HD), and C_s is constant, so

$$[\eta] = f(M_w, HD)$$

For an HPAM sample of given M_w, $[\eta]$ will change with HD only.

The experimental work has supported the preceding analysis.[4-9,11,25] The plots of $[\eta]$ vs. HD are bell-shaped with a maximum $[\eta]$ at about HD = 40% ~ 50%. Kulkarni and Gundiah[5] plotted $[\eta]$ vs. $HD^{1/2}$ and obtained straight lines in the HD range of 10% ~ 35%.

From our own data (Fig. 4), a square root law has been found:

$$[\eta] = A \times HD^{1/2} + B \qquad (2)$$

where A and B are slope and intercept of plot $[\eta]$ vs. $HD^{1/2}$, respectively. Although they are constant for a series of HPAM samples from the same parent PAM, and A and B will vary with the M_w of parent PAM as shown in Table II.
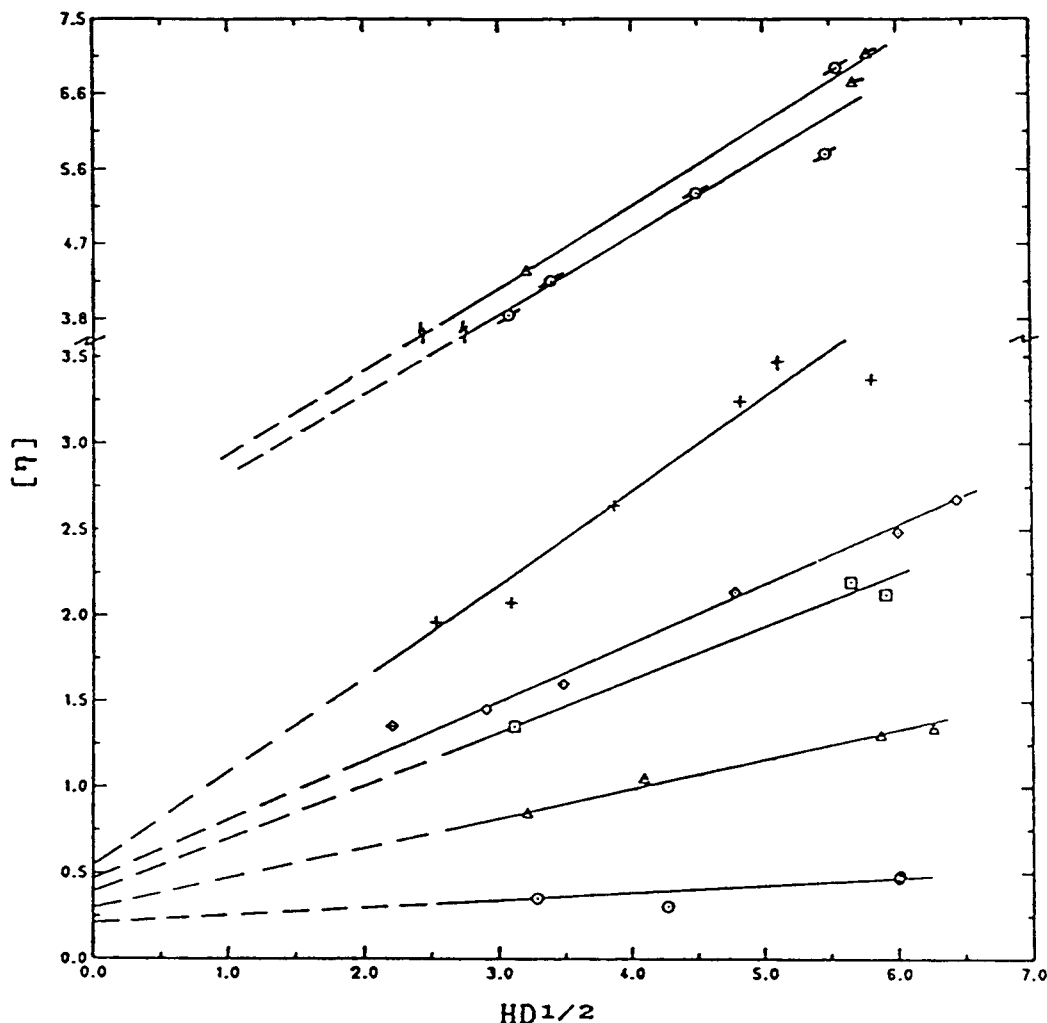
Figure 4   Dependence intrinsic viscosity of HPAM on the square root of hydrolysis degree: (⊙) F7HY; (△) F5HY; (□) F4HY; (◇) HY2; (+) F3HY; (⊘) HY5; (△) F2HY.

Table II   Parameters A and B in eq. (2) for HPAM from the PAM with Various Molecular Weights

Sample	$[\eta]_0$	A	B
F7HY	0.2741	0.0462 ± 0.011	0.201 ± 0.056
F5HY	0.6502	0.159 ± 0.027	0.363 ± 0.137
F4HY	1.096	0.300 ± 0.098	0.428 ± 0.495
HY2[a]	1.257	0.348 ± 0.026	0.428 ± 0.128
F3HY	1.733	0.507 ± 0.085	0.634 ± 0.375
F2HY	3.555	1.010 ± 0.173	1.109 ± 0.872

[a] M_{w0} = 246,900; PDI = 1.8.

Obviously, both A and B are functions of the molecular weight of the parent PAM (M_{w0}) and, therefore, functions of the intrinsic viscosity of the parent PAM ($[\eta]_0$). The plots in Figures 5 and 6 reveal fairly good linear relationships between A, B, and $[\eta]_0$. The data calculated from Kulkarni's results are also plotted in the figures. The same trends have been observed.
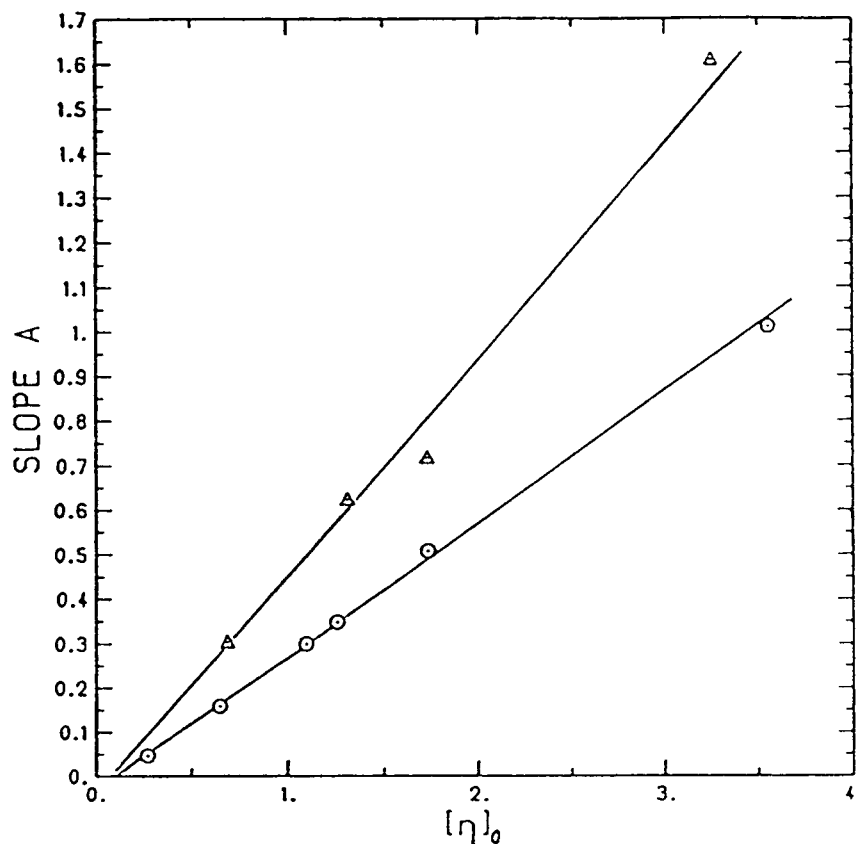
Using linear regression, equations for A and B have been found as

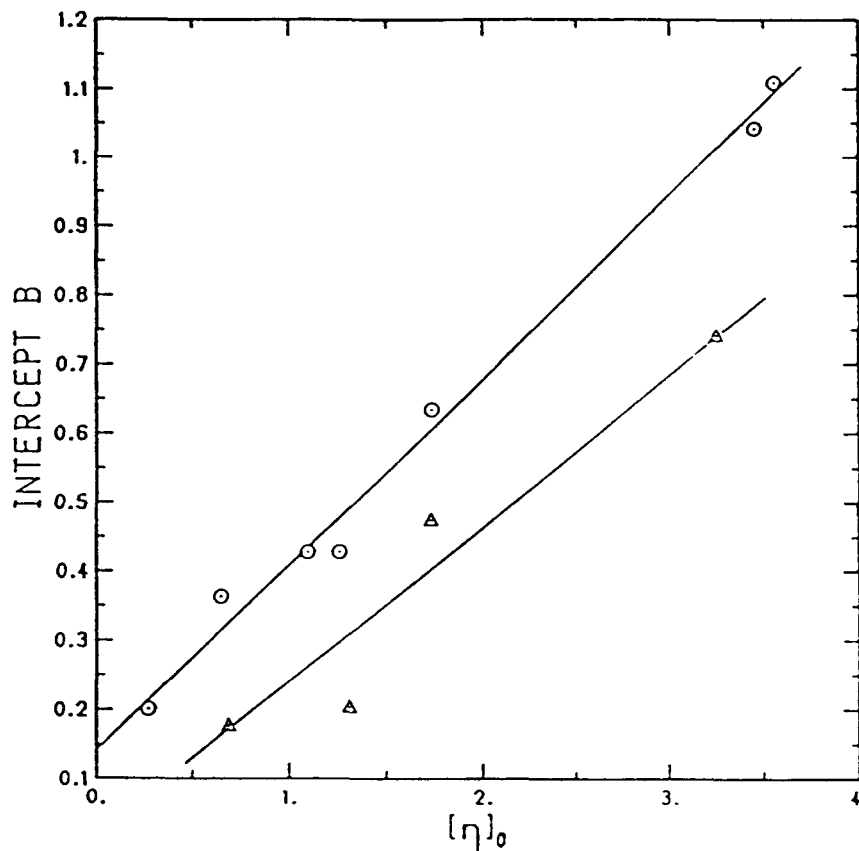$$A = f([\eta]_0) = 0.294[\eta]_0 - 0.0246 \qquad (3)$$

$$B = f([\eta]_0) = 0.266[\eta]_0 + 0.144 \qquad (4)$$

Hence, an emprical equation of $[\eta]$ as a function of $[\eta]_0$ and HD can be obtained for HPAM in $0.2M$ Na_2SO_4 at $25.0 \pm 0.05°C$:

$$[\eta] = (0.266 + 0.294HD^{1/2})[\eta]_0$$
$$+ 0.144 - 0.0246HD^{1/2} \qquad (5)$$

Figure 5   Slope of ($[\eta] - HD^{1/2}$ plot) for HPAM vs. $[\eta]$ of the parent PAM: (⊙) this work; (△) Kulkarni and Gundiah's work.[5]

Figure 6   Intercept of ($[\eta] - HD^{1/2}$ plot) for HPAM vs. $[\eta]$ of the parent PAM: (⊙) this work; (△) Kulkarni and Gundiah's work.[5]

From this equation, one can readily estimate the intrinsic viscosity of HPAM of any composition in the range of 6 ∼ 40% if the $[\eta]_0$ and HD are known.

Mark–Houwink Equations for HPAM

In the Mark–Houwink equation

$$[\eta] = KM_w^a \tag{6}$$

the parameters K and a are constant only if the polymer composition, solvent, and temperature are unchanged. For HPAM under the given conditions, K and a are functions of hydrolysis degree. Klein and Conrad[8] observed a maximum value of exponent a at about 40% HD and a minimum value of K at about 20% HD. McCarthy et al.[7] showed some changes in the values of K and a with HD but did not show definite trends.

Since the intrinsic viscosities of HPAM, especially those for high molecular weight samples, strongly depend on HD, it is necessary to choose the HPAM samples with exactly the same HD to determine the parameters K and a. Because of the difficulties in preparing HPAM samples with the exactly desired HD, interpolation from equations, such as the square root law, will be very useful.

Using the square root law [eq. (2)] for various molecular weights, the intrinsic viscosities of HPAM at HD = 6, 10, 15, 20, 25, 30, 35, and 40% were obtained. Assuming that all the hydrolyzed acrylamide groups are in Na form, the molecular weights of HPAM were calculated from the stoichiometric equation

$$M_{ws} = M_{wPAM}/71.08[94.04x + 71.08(1 - x)] \tag{7}$$

where x is the mole fraction of hydrolyzed groups and $x = HD/100\%$. Correlating the intrinsic viscosities and the molecular weights, a set of Mark–Houwink constants has been determined and are listed in Table III. Some examples of log-log plots of $[\eta]$ and M_w are given in Figure 7 for HPAM with various compositions.

Using polynomials to regress the above data, two empirical equations were obtained for HPAM. The

Table III   Mark–Houwink Constants K and a for HPAM with Various HD

HD (mol %)	a	K (10^{-4})	Regression coefficient
6	0.669	3.31	0.9982
10	0.694	2.85	0.9991
15	0.712	2.57	0.9995
20	0.725	2.41	0.9997
25	0.734	2.30	0.9997
30	0.742	2.22	0.9998
35	0.748	2.16	0.9997
40	0.753	2.12	0.9997

equations, parameters, and 95% confidence intervals are summarized below:

$$a = C_0 + C_1 HD + C_2 (HD^2) + C_3 (HD^3)$$

where $C_0 = 0.625 \pm 0.007$, $C_1 = 8.86E\text{-}3 \pm 1.27E\text{-}3$, $C_2 = -2.40_5 E\text{-}4 \pm 0.617E\text{-}4$, $C_3 = 2.48E\text{-}6 \pm 0.89$

$E\text{-}6$, and $\log K = d_0 + d_1 HD + d_2 (HD^2) + d_3 (HD^3)$, where $d_0 = -3.36 + 0.024$, $d_1 = -2.39E\text{-}2 + 0.42$ $E\text{-}2$, $d_2 = 6.96E\text{-}4 + 2.05E\text{-}4$, and $d_3 = -7.37E\text{-}6 + 2.95E\text{-}6$.

The regressed curve plotted with K, a datum in Figure 8, showed a good fit with the polynomials. One can calculate the values of "K" and "a" precisely at any polymer composition of interest, over the range 6 ~ 40% acrylate, from these polynomials.

Molecular Weights of Hydrolyzed Polyacrylamide

The molecular weights of HPAM samples were calculated using the Mark–Houwink equations (as M_{wv}) established in this work as well as from the stoichiometric equation (as M_{ws}). In the former, the values of K and a applied were obtained from the polynomials and the $[\eta]$'s and HD's were from the experiments. The two kinds of molecular weights together with those measured by light scattering are listed in Table IV.
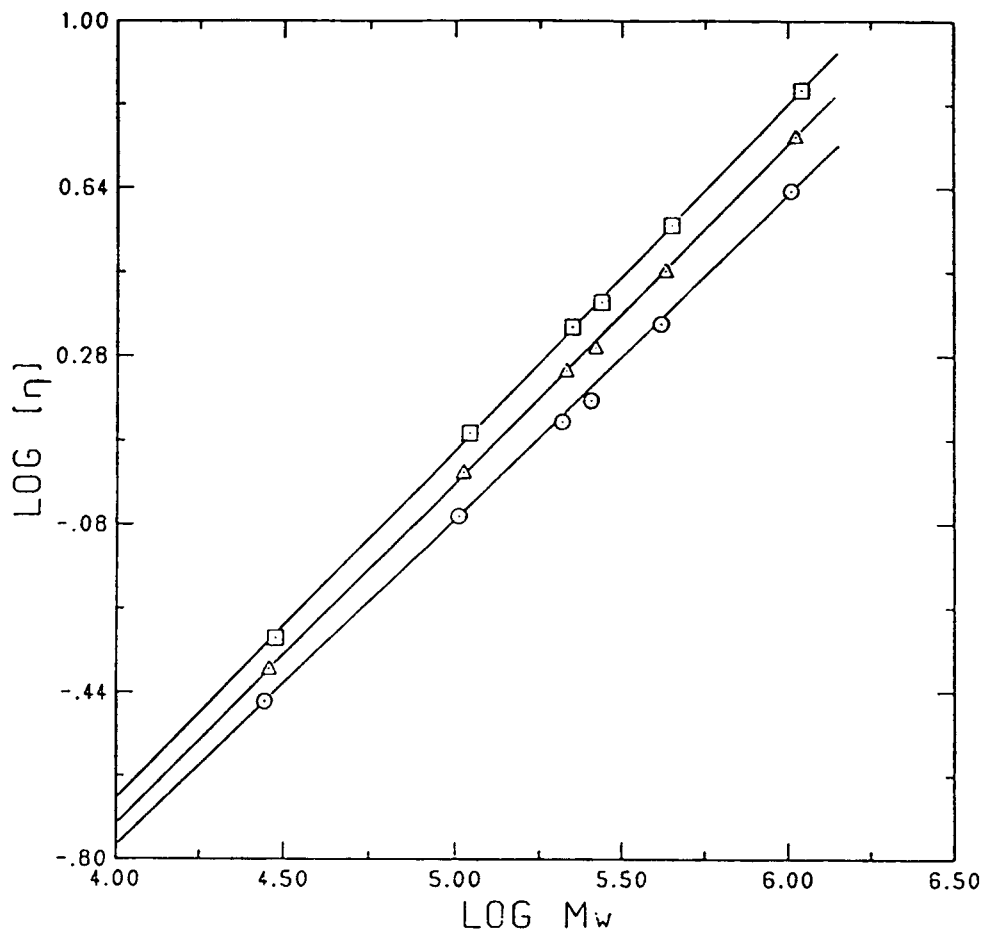
Figure 7   Plot of $\log[\eta]$ vs. $\log M_w$ for HPAM of various hydrolysis degrees: ($\odot$) HD = 10%; ($\triangle$) HD = 20%; ($\square$) HD = 35%.
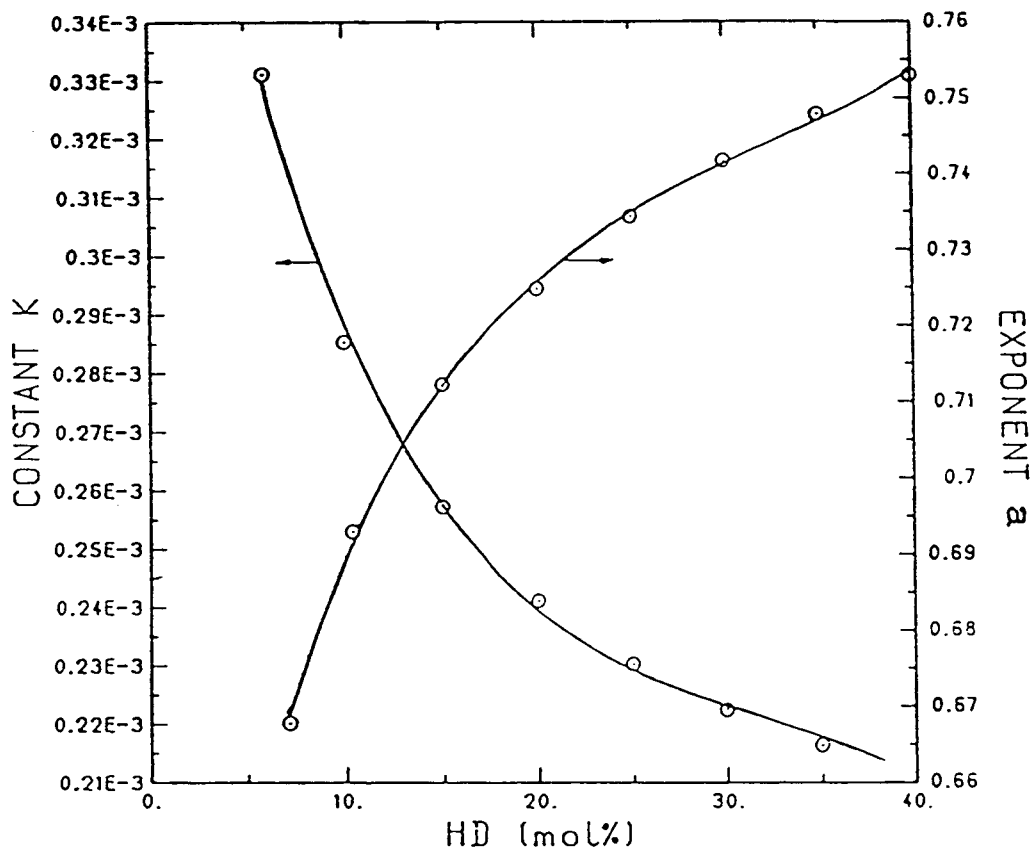
Figure 8 Mark–Houwink constants K and a for HPAM at various hydrolysis degrees: (—) from correlated polynomials; (⊙) data point.

An average error in molecular weight determination of 4.7% is relatively low as compared with light scattering, osmometry, and GPC. The agreement between viscometric method through $[\eta]-M_w$ correlation and stoichiometric method is good even for the samples of high polydispersities (e.g., HY5). For even broader samples ($M_w/M_n > 2.5$), polymolecularity correction might be necessary to reduce the error.[7,26–28]

DISCUSSION

Mark–Houwink Constants

As shown in Table III and Fig. 8, the value of K decreases exponentially with increase in hydrolysis degree. This is similar to Klein and Conrad's data.[8] As a measure of flexibility of polymer chains, K is portional to the viscosity constant Φ[28,29]

$$K \sim \Phi$$

where $\Phi = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)$ for nondraining polymer coils. Since Φ will become smaller when the

polymer chains become more rigid, it is reasonable for K to reduce when the concentration of charged groups increases.

The values of the exponent "a" obtained in this work is in the range 0.67–0.76. This is in agreement with the theoretical predictions[28] for unbranched, nonsolvent-draining coils with excluded volumes and implies that $0.2M$ Na_2SO_4 is not a good solvent for polyacrylamide or poly(acrylamide-*co*-sodium acrylate); therefore the conformation of the polymer chain is random coil in this solvent.

Constant K and exponent "a" are not independent parameters since from the theoretical derivation, "a" is also a function of "ϵ":

$$a = 0.5(1 + 3\epsilon)$$

Hence, K and a have a certain relation as summarized by Elias[28] for various coillike polymers:

$$\log K = C_1 - C_2 a$$

where C_1 and C_2 are positive constants. Our data show a similar relationship between K and a for the

Table IV   Molecular Weights of HPAM from Mark–Houwink Equations, Stoichiometric Equation (eq. 7), and from Light Scattering

HD (mol %)	$[\eta]$ (dL/g)	M_{WLS}	M_{WV}	M_{WS}	Err (%)[a]
F7HY					
10.77	0.3524	35,800	28,300	27,800	1.53
36.00	0.4692	31,700	28,800	30,000	−4.19
36.08	0.4872	—	30,200	30,000	0.64
F5HY					
10.30	0.8468	119,600	101,500	102,300	−0.80
16.70	1.049	—	112,300	104,300	7.61
34.42	1.303	—	114,700	110,000	4.30
39.20	1.342	135,500	112,900	111,500	1.22
F4HY					
9.68	1.353	247,000	205,000	207,300	−1.08
31.90	2.200	—	238,600	221,700	7.62
34.90	2.127	268,000	219,900	223,700	−1.67
HY2					
4.86	1.355	—	267,400	250,800	6.62
8.42	1.451	—	241,100	253,600	−4.92
12.10	1.601	—	235,800	256,600	−8.10
22.80	2.137	—	262,200	265,100	−1.11
36.00	2.486	—	267,300	275,600	−3.01
41.50	2.677	—	273,100	280,000	−2.46
F3HY					
6.40	1.961	—	421,400	409,300	2.97
9.53	2.075	468,000	383,800	413,300	−7.15
14.90	2.640	—	431,200	420,300	2.59
23.20	3.242	—	459,800	431,100	6.68
26.00	3.470	—	479,700	434,700	10.35
33.10	3.372	467,000	417,200	443,900	−6.00
HY5[b]					
9.46	3.979	—	925,500	1,061,500	−12.81
11.50	4.228	—	969,500	1,068,300	−9.25
20.15	5.329	—	974,700	1,097,000	−11.16
36.60	6.893	—	1,126,800	1,132,500	−0.51
F2HY					
10.30	4.354	1,014,000	1,076,500	1,022,900	5.24
32.20	6.709	—	1,064,500	1,093,000	−2.60
33.40	7.067	822,000	1,122,000	1,096,800	2.30
Average absolute error (%)					4.70

[a] Err (%) = $(M_{\mathrm{WV}} - M_{\mathrm{WS}})/M_{\mathrm{ws}} \times 100\%$.
[b] HY5 is from unfractionated PAM with PDI 2.5.

copolymer with various compositions as follows and in Figure 9:

$$\log K = -1.946 - 2.302a$$

(In our case, constant C_1 is negative.) The agreement again proves the coillike conformation of poly(acrylamide-co-sodium acrylate) in the salt solution.

Limitation of Square Root Law

A theoretical interpretation of the square root law will be attempted in a future paper, so the discussion here concerns only the limitations of the square root law.

It should be noted that in Table II and Figure 5 involving the square root law

$$[\eta] = A \times HD^{1/2} + B \tag{2}$$
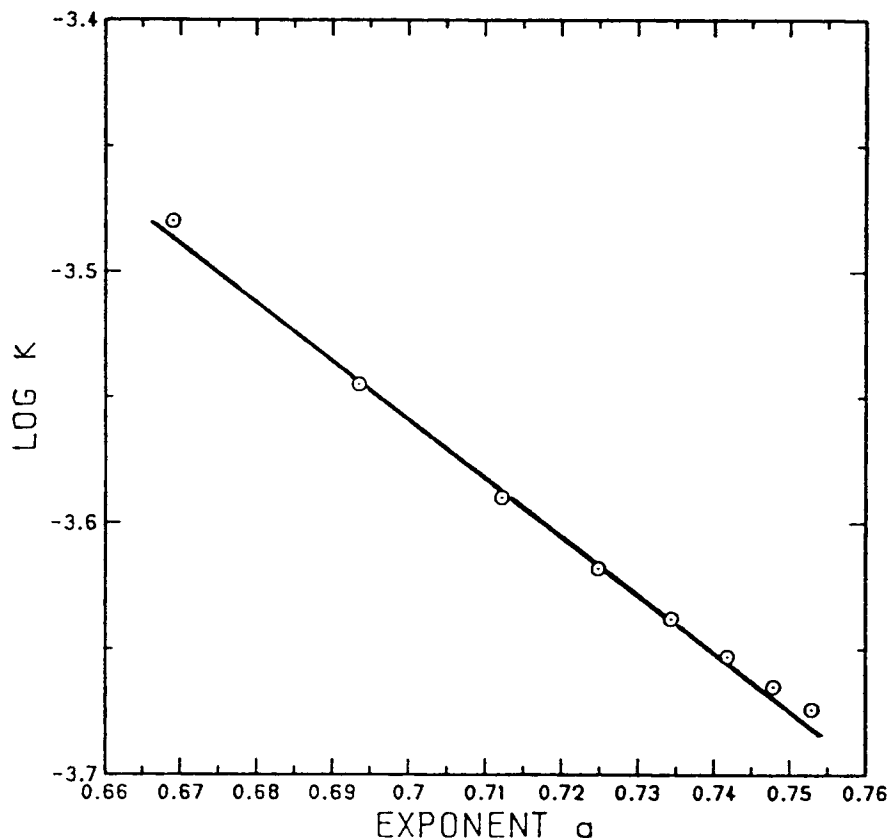
Figure 9   Log K vs. exponent a of HPAM at various hydrolysis degrees: from top left to bottom right, the data points are at HD = 6, 10, 15, 20, 25, 30, 35, 40%.

the intercept B is always smaller than is the intrinsic viscosity of the parent PAM ($[\eta]_0$). Therefore, eq. (5) will overpredict the intrinsic viscosity when HD approaches zero. The deviation of B from $[\eta]_0$ increases with an increase in the molecular weight of the parent PAM [Fig. 10 shows the dependence of the deviation ($[\eta]_0 - B$) on $[\eta]_0$]. This suggests that there should be a minimum value of HD or, say, a minimum distance between charged groups at which the intrinsic viscosity of HPAM equals that of the parent PAM. Above this charge density, electrostatic forces cause an expansion of the polymer chain and therefore the increase of the intrinsic viscosity. Below the minimum HD, the square root law is invalid.

To determine the applicable range of HD, the general square-root equation [eq. (5)] is divided by $[\eta]_0$; hence,

$$[\eta]/[\eta]_0 = 0.2664 + 0.2939 HD^{1/2}$$

$$+ (0.1435 - 0.02465 HD^{1/2})/[\eta]_0 \quad (8)$$

HD_{min} calculated using this equation at $[\eta]/[\eta]_0 = 1$ for various values of $[\eta]_0$ are listed in Table V. Ob-

viously, the HD_{min} values vary with the molecular weight of the parent PAM. This might infer that it is more reasonable for one to consider the charge density of coillike polyelectrolytes based on the coil volume than on the chain length.

When HD is higher than 40 $\sim$ 50%, slope A will change sign and the values of A and B may be different. This range of hydrolysis degree is not within the interest of this study, and therefore further discussion is not given.

One can conclude, however, that the square root law is valid for the molecular weight range of 10^4 $\sim$ 10^6 when HD is larger than 6% and smaller than 40%.

Potential Application for GPC Measurements

Since a set of Mark–Houwink parameters K and a have been determined for HPAM with various hydrolysis degrees, it is possible to evaluate universal calibration for GPC of HPAM or poly(acrylamide-*co*-sodium acrylate) if the latter is of narrow com-
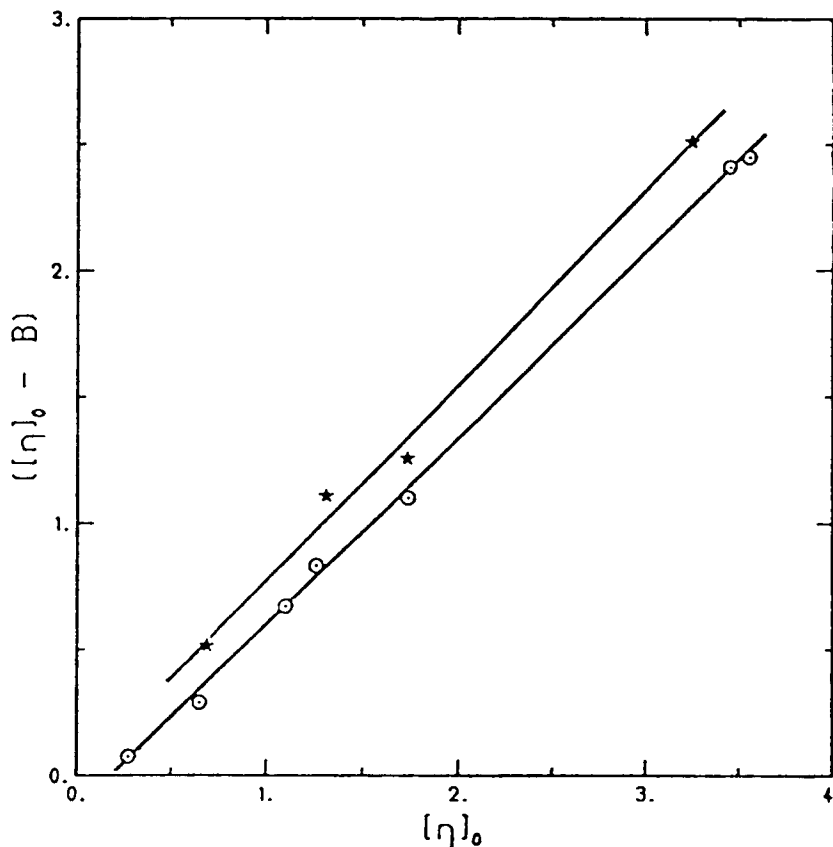
Figure 10 Dependence of $([\eta])_0 - B)$ of HPAM on $[\eta]$ of parent PAM: (⊙) this work; (★) Kulkarni and Gundiah's work.[5]

position distribution. This study is now in progress in our laboratory.

CONCLUSIONS

The measurement of intrinsic viscosity of hydrolyzed polyacrylamide in $0.2M$ Na_2SO_4 can be used to estimate weight average molecular weights given the appropriate Mark–Houwink constants for the ionic polymers. The relationship between the intrinsic viscosity and the composition of the copolymer can be expressed by a square root law from

which the intrinsic viscosity at any level of hydrolysis in the range 6–40% can be readily calculated. Mark–Houwink constants in this range can be found as functions of copolymer composition. Applying these constants, weight average molecular weights determined by viscometry for hydrolyzed PAM samples were accurate to within 5% for degrees of hydrolysis in the range 6–40% and molecular weights in the range 10^4 to 1.24×10^6.

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Table V Minimum Values of *HD* at Various $[\eta]_0$

$[\eta]_0$	HD_{min}
0.2741	1.66
0.500	3.65
1.000	4.69
1.500	5.01
2.000	5.16
3.000	5.31
4.000	5.39
5.000	5.43

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