

Studies on Determination of Molecular Weight for Ultrahigh Molecular Weight Partially Hydrolyzed Polyacrylamide

MEILING YE,* DONG HAN, and LIANGHE SHI

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, China

SYNOPSIS

The molecular weight characterization of partially hydrolyzed polyacrylamide (HPAM) for enhanced oil recovery use is rather difficult because of its ultrahigh molecular weight copolymer and polyelectrolyte behaviors in solution. In this work the effects of aqueous NaCl solution concentration and degree of hydrolysis of polymer on molecular dimension were studied. A simple and precise method for determining molecular weight of HPAM is presented. The molecular weight of HPAM with any degree of hydrolysis can be calculated from the $[\eta] - M_w$ equation of unhydrolyzed PAM in an H₂O system by measuring $[\eta]_{c \rightarrow \infty}$ of HPAM obtained in aqueous NaCl solutions by extrapolating salt concentration to infinity. Because the values of $[\eta]_{c \rightarrow \infty}$ of HPAM of different degrees of hydrolysis are all equal to the corresponding $[\eta]$ value of the unhydrolyzed PAM of the same degree of polymerization, the molecular weight of HPAM of any degree of hydrolysis can thus be calculated from the $[\eta] - M_w$ equation for PAM homopolymer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylamide (PAM) and its copolymers are the most widely used and technically important water soluble polymers. They gain their utility from their large macromolecule size, ionic substitution, and expanded configuration in aqueous solution. Partially hydrolyzed PAM (HPAM) is widely used as a pushing fluid in enhanced oil recovery from underground reservoirs. Because of its ultrahigh molecular weight copolymer and polyelectrolyte behavior in solution, the molecular weight of HPAM is rather difficult to characterize precisely. The difficulties encountered in viscometry were the intrinsic viscosity exhibits strong dependence of shear rate,¹ the dimensions of HPAM molecules change with the salt concentration,² and Mark-Houwink constants vary with the degree of hydrolysis of the polymer.³⁻⁵ Therefore, it is necessary to know beforehand the degree of hydrolysis. Because the determination of molecular weight for copolymer and polyelectrolyte was difficult, the result calculated from the Mark-Houwink equa-

tion of HPAM has a larger error. In this article a new and different approach is described and a simple and precise method for determining molecular weight of HPAM is presented.

EXPERIMENTAL

Viscometer

A conventional Ubbelohde viscometer was used to study the effect of salt concentration and degree of hydrolysis on the intrinsic viscosity and to compare the value of $[\eta]$ from the single point method and the dilute method. Viscometry measurements were carried out in NaCl solutions at $30 \pm 0.05^\circ\text{C}$.

A low shear rate viscometer with a long horizontal capillary of 500 mm was designed by our laboratory (see Fig. 1). This viscometer gave zero shear rate intrinsic viscosity, $[\eta]_0$, when applied to HPAM with high molecular weight (for details see Ye et al.⁶ and Han⁷). The efflux time of water was measured at $25 \pm 0.05^\circ\text{C}$ to yield a value of 227.1 s; the kinetic energy correction could be neglected.

* To whom correspondence should be addressed.

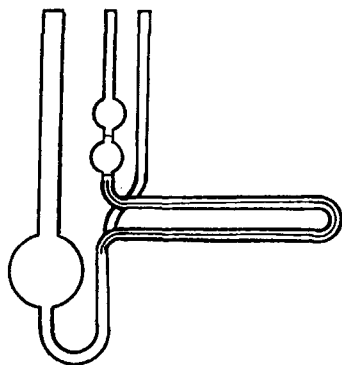


Figure 1 The low shear rate capillary viscometer.

Samples

A commercial sample of HPAM 430 (Japanese Cyanamide Co.) had a M_w of 1×10^7 and degree of hydrolysis of 25%. Its weight average molecular weight was determined with a low angle laser light scattering photometer (Chromatix KMX-6) in 0.5M NaCl solution at room temperature. Refractive index increment, dn/dc , measurement was carried out with the Chromatix KMX-16 laser light differential refractometer in the same solvent at $25 \pm 0.05^\circ\text{C}$.

Commercial sample PAM-33 (DKS, Japan) was an unhydrolyzed polymer with the degree of hydrolysis less than 3%. PAM-33 was hydrolyzed to HPAM-1 and HPAM-2 by adding different amounts of NaOH solution (7M) at 50°C to the degree of hydrolysis of 14.2 and 26.1%, respectively. To avoid degradation of the polymer, stabilizer and gentle stirring were applied during hydrolysis. The degree of hydrolysis was measured by potentiometric titration with the automatic titrator (AQUASTAR, C2000).

RESULTS AND DISCUSSION

Effect of Salt Concentration on Molecular Size of HPAM

HPAM is an anionic polymer with a large number of charges along the polymer chains. Owing to the electrostatic repulsion between charges, the molecular chain size of HPAM in water is expanded. The reduction in solution viscosity can be achieved by varying the solvent environment such as the addition of salt.² In this work, the effect of salt concentration on intrinsic viscosity of HPAM 430 in salt solution was studied by adding different amounts of NaCl. Our results show that intrinsic viscosity de-

creases with increasing salt concentration C_s (see Table I). The plot of $[\eta]$ against $C_s^{-1/2}$ is linear. This relationship agrees with the Rice equation⁸:

$$[\eta] = [\eta]_{C_s \rightarrow \infty} + BC_s^{-1/2}$$

where C_s is the salt concentration and $[\eta]_{C_s \rightarrow \infty}$ is the $[\eta]$ without the electrostatic repulsion effect.

Single Point Method of Determination of $[\eta]$

Usually, the intrinsic viscosity $[\eta]$ of polymer solution is determined from the extrapolation to zero concentration by using the following equations, the Huggins equation, eq. (1), and the Kraemer equation, eq. (2):

$$\frac{\eta_{sp}}{C_p} = [\eta] + k'[\eta]^2 C_p \quad (1)$$

$$\frac{\ln \eta_r}{C_p} = [\eta] - \beta[\eta] C_p \quad (2)$$

The experimental procedure of determining the intrinsic viscosity is time consuming. Several works^{8,9} have suggested alternative methods for calculating $[\eta]$ using the single point viscosity measurement. However, it is necessary to have some condition, such as the sum of parameter k' and β being 0.5. From Table I it can be seen that the sum of parameter k' and β is approximately equal to 0.5. Therefore, it is possible to use the single point method instead of the dilution method. We compared the values of $[\eta]$ obtained by using the two above methods (see Table II). The single point method of $[\eta]$ was calculated using eq. (3) by Cheng⁹:

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} / C_p \quad (3)$$

Table I Viscosity Data of HPAM 430–NaCl System (30°C)

Salt Concn (M)	$[\eta] \times 10^{-3}$ mL/g	k'^a	β^*	$C_s^{-1/2}$
0.2	1.886	0.48	0.11	2.24
0.5	1.630	0.36	0.11	1.41
0.6	1.560	0.46	0.11	1.29
0.8	1.360	0.40	0.12	1.12
1.0	1.410	0.46	0.08	1.00
1.3	1.410	0.38	0.13	0.88
1.5	1.360	0.50	0.04	0.82

^a k' is the Huggins constant and β is the Kraemer constant.

Table II Comparison of Data Obtained from Two Methods

Method	$C_p \times 10^4$ (g/mL)	η_r	η_{sp}	$[\eta] \times 10^{-3}$ (mL/g)	Error (%)
Dilute method				1.458	
Single point method ^a	1.624	1.259	0.259	1.483	1.7
	2.436	1.407	0.407	1.480	1.5
	3.248	1.570	0.570	1.490	2.2

^a Equation (3).

The results in Table II indicate that the relative error is less than 2.2%. Thus the single point method can be used for the viscosity measurement of the HPAM–NaCl system.

Effect of Degree of Hydrolysis on Intrinsic Viscosity

The Mark–Houwink constants k and α of HPAM were shown to exhibit strong dependence on the degree of hydrolysis.^{3,4} Therefore, it is very difficult to precisely measure the molecular weight for HPAM with an unknown degree of hydrolysis. To overcome these difficulties we studied further the effect of salt concentration and degree of hydrolysis on intrinsic viscosity. In this work, commercial sample PAM-33 was hydrolyzed to different degrees of hydrolysis by adding different amounts of NaOH under mild conditions at 50°C. Muller et al.¹¹ studied the hydrolysis reaction of PAM at 63°C and determined the weight average molecular weight, M_w , by light scattering of hydrolyzed products. The experimental results indicated that no degradation occurred during hydrolysis of the unhydrolyzed commercial PAM. According to this result, the degree of polymerization of two hydrolyzed PAM samples is equal to those of unhydrolyzed parent PAM-33. The effect of salt concentration and degree of hydrolysis on intrinsic viscosity was investigated by using these hydrolyzed and unhydrolyzed parent PAM samples. The intrinsic viscosities of our samples were determined at different NaCl salt concentrations. It was found that intrinsic viscosity increases with increasing degree of hydrolysis (see Fig. 2). The plots of $[\eta]$ versus $C_s^{-1/2}$ are linear, and all of the straight lines have the same intercept giving the value of $[\eta]_{C_s \rightarrow \infty}$, which means the value free from electrostatic repulsion effect. Chen and Wang¹² also obtained the same results for HPAM with degree of hydrolysis 0–50% in the NaNO₃ solution system.

Figure 2 clearly demonstrates that the $[\eta]_{C_s \rightarrow \infty}$ ob-

tained is independent of degree of hydrolysis of the polymer. That means the intrinsic viscosity of hydrolyzed PAM is equal to that of unhydrolyzed parent polymer. According to the above results we propose that the intrinsic viscosity for HPAM is determined by the single point method with a low shear rate viscometer or conventional Ubbelohde viscometer. The value of $[\eta]_{C_s \rightarrow \infty}$ is obtained by dilution with aqueous NaCl and extrapolating salt concentration C_s to infinity. Detail procedures follow.

The efflux time of the starting solution with HPAM–0.2M aqueous NaCl of 10 mL was determined at $25 \pm 0.05^\circ\text{C}$ and 5M aqueous NaCl was selected as the dilution solvent. Four polymer concentrations and NaCl salt concentrations were obtained by adding dilution solvent of 1, 1, 2, 2, and 6 mL to the starting polymer solution in the viscometer, respectively. The intrinsic viscosity $[\eta]$ of each polymer concentration and salt concentration was measured by the single point method. All of the data are listed in Table III. The plot of $[\eta]$ against $C_s^{-1/2}$ exhibited linearity and the intercept was $[\eta]_{C_s \rightarrow \infty}$ (see Fig. 3). In this way, $[\eta]_{C_s \rightarrow \infty}$ was obtained only by a single experiment in the viscometer, and the $[\eta]_{C_s \rightarrow \infty}$ obtained was independent of the degree of hydrolysis.

Calculation of Molecular Weight for HPAM

In the literature, the molecular weight for HPAM with different degrees of hydrolysis is calculated by the Mark–Houwink equation corresponding to the same degree of hydrolysis. However, a precise determination of the degree of hydrolysis is usually difficult. In this work, $[\eta]_{C_s \rightarrow \infty}$ obtained for HPAM is independent of the degree of hydrolysis. As a result, the molecular weight of HPAM can be calculated by using the $[\eta] - M_w$ equation of unhydrolyzed PAM. Many $[\eta] - M_w$ equations for PAM were published in the literature.¹³ Our equation¹⁴ is as follows:

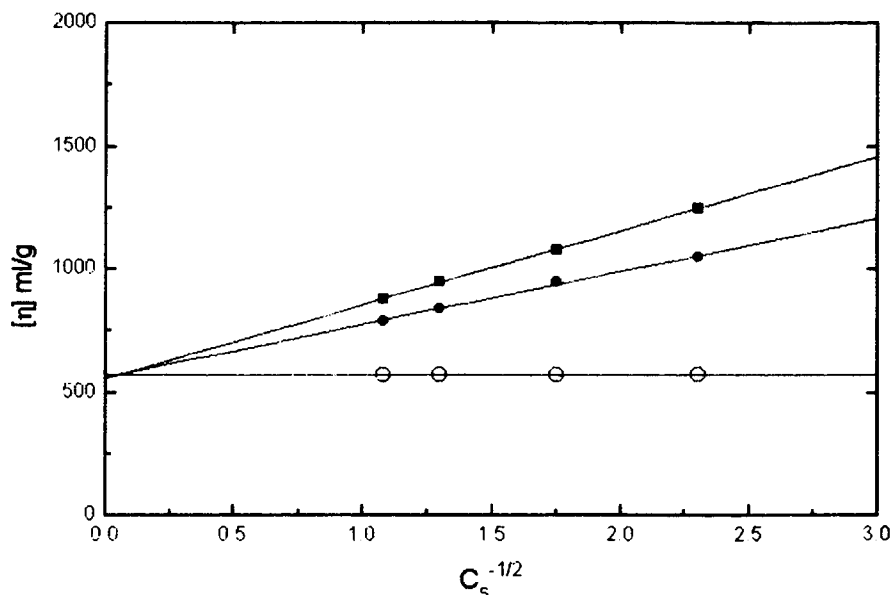
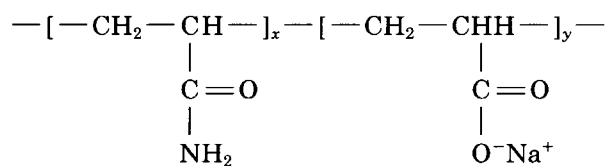


Figure 2 Plot of $[\eta]$ vs. $C_s^{-1/2}$ for the Polymer with the same DP.

$$[\eta]_{\text{H}_2\text{O}} = 3.66 \times 10^{-2} M_w^{0.66} \quad (4)$$

In this $[\eta] - M_w$ relation, intrinsic viscosities of all of the fractionated samples were measured in water with a low shear rate viscometer at $25 \pm 0.05^\circ\text{C}$ and the range of molecular weight was from 1.6×10^5 to 3.8×10^6 . Because HPAM is a copolymer of acrylamide and sodium acrylate, its chemical structure is as follows:



The molecular weight of acrylamide monomer is 71 and the molecular weight of sodium acrylate is 94. For PAM and HPAM of the same degree of polymerization, the molecular weight of HPAM in-

creases with increasing the degree of hydrolysis. Therefore, when the molecular weight of HPAM is calculated by the $[\eta] - M_w$ equation of PAM, the value should be corrected for the incorporation of sodium acrylate molecules. Because the degree of polymerization (DP) is not changed during hydrolysis, the $[\eta] - M_w$ relation of eq. (4) could be converted to $[\eta] - \text{DP}$ relation:

$$[\eta]_{\text{H}_2\text{O}} = 3.66 \times 10^{-2} (m\text{DP})^{0.66} \quad (5)$$

where m is the molecular weight of the acrylamide unit. From eq. (5) we can calculate the DP of HPAM. Then the viscosity average molecular weight (M_η) of HPAM is calculated by using the following equation:

$$M_\eta = \text{DP}[AX + m(1 - X)] \quad (6)$$

Table III Viscosity Data of HPAM 430 at Different Polymer and Salt Concentrations

No.		$C \times 10^4$ (g/mL)	t (s)	t_0 (s)	η_r	C_s (M)	$C_2^{-1/2}$	$[\eta] \times 10^{-3}$ (mL/g)
1	10-mL polymer solution (0.2M NaCl)	1.752	244.5	151.2	1.617	0.2	2.24	2.976
2	Add 1 mL 5M NaCl	1.591	213.5	154.1	1.385	0.64	1.25	2.157
3	Add 1 mL 5M NaCl	1.458	207.2	157.3	1.317	1.0	1.0	1.961
4	Add 2 mL 5M NaCl	1.250	205.3	163.3	1.257	1.57	0.8	1.819
5	Add 6 mL 5M NaCl	0.875	206.5	178.7	1.156	2.6	0.62	1.724

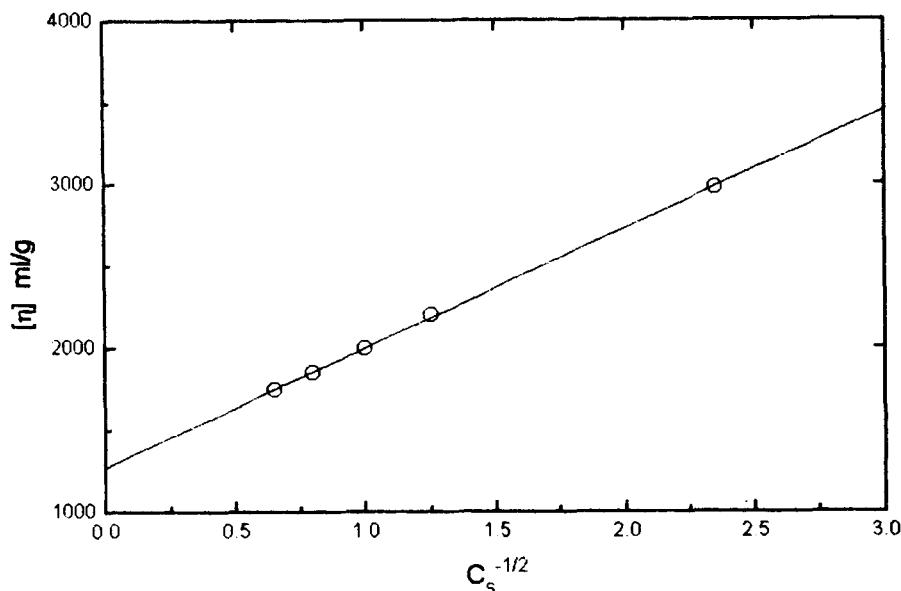


Figure 3 Plot of $[\eta]$ vs. $C_s^{-1/2}$ for HPAM 430-NaCl System.

where A is molecular weight of sodium acrylate, X is degree of hydrolysis, and m is the molecular weight of acrylamide.

Therefore, for HPAM with a known degree of hydrolysis, the $[\eta]_{C_s \rightarrow \infty}$ is measured first by our method. Then the degree of polymerization is calculated from eq. (5) and M_η can be obtained from eq. (6). Because commercial HPAM used in enhanced oil recovery has the degree of hydrolysis around 30%, an empirical formula can be applied to calculate the M_η :

$$M_\eta = 78 DP \quad (7)$$

Before determining the intrinsic viscosity it should be noted that a conventional Ubbelohde viscometer can only be applied for HPAM with low molecular weight ($M_w < 2 \times 10^6$). This is due to the fact that the conventional viscometer is a high shear rate instrument, and HPAM solution may exhibit strong shear rate dependence of viscosity. When the molecular weight is higher than 2×10^6 , it is necessary to use a low shear rate viscometer.⁷

CONCLUSIONS

1. $[\eta]_{C_s \rightarrow \infty}$ (intrinsic viscosity free from electrostatic repulsion effect) was measured by the dilution method in a single experiment.

2. $[\eta]_{C_s \rightarrow \infty}$ obtained is independent of degree of hydrolysis of the polymer, that is, $[\eta]_{C_s \rightarrow \infty}$ of HPAM equals that of unhydrolyzed parent PAM.
3. The molecular weights of HPAM with any degree of hydrolysis can be calculated from the $[\eta] - M_w$ equation of unhydrolyzed PAM in a water system by measuring $[\eta]_{C_s \rightarrow \infty}$ of HPAM in NaCl solution.

This work was supported by the National Natural Science Foundation of China and the Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica.

REFERENCES

1. K. C. Tam, *Polym. Int.*, **24**, 1 (1991).
2. K. C. Tam and C. Tiu, *Colloid Polym. Sci.*, **268**, 911 (1990).
3. K. J. McCarthy, C. W. Burkhardt, and D. P. Parazak, *J. Appl. Polym. Sci.*, **33**, 1699 (1987).
4. J. Klein and K. D. Conrad, *Makromol. Chem.*, **179**, 1635 (1978).
5. X. Y. Wu, D. Hunkeler, A. E. Hamielec, R. H. Pelton, and D. R. Woods, *J. Appl. Polym. Sci.*, **42**, 2081 (1991).
6. M. L. Ye, D. Han, and L. H. Shi, *YouTian HuaXue*, **11**, 348 (1994).
7. D. Han, M.S. Dissertation, Institute of Chemistry, Academia Sinica, 1993.

8. S. Rice, *Polyelectrolyte Solutions*, Academic Press, New York, 1961, p. 503.
9. K. S. Cheng, *Gaofenzi Tongbao*, **4**, 3159 (1960).
10. M. H. Rafi'ee Fanood and M. H. George, *Polymer*, **28**, 2244 (1987).
11. G. Muller, J. P. Laine, and J. C. Fenyo, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 659 (1979).
12. J. S. Chen and L. Wang, Proc. Symp. Macromol., 519 (1985).
13. P. Munk, T. Aminabhavi, P. Williams, D. Hoffman, and M. Chmelir, *Macromolecules*, **13**, 871 (1980).
14. S. H. Hu, M.S. Dissertation, Institute of Chemistry, Academia Sinica, 1985.

Received February 27, 1995

Accepted September 11, 1995