

A NEW TYPE LOW SHEAR RATE VISCOMETER FOR HIGH MOLECULAR WEIGHT POLYMER*

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ABSTRACT

In this paper, the effects of shear rate on the intrinsic viscosity measurement of partially Hydrolysed Polyacrylamide (HPAM) in salt solution were studied with homemade multi-bulb viscometer and low shear rate rheometer. The critical shear rate of HPAM in salt solution for high molecular weight HPAM was determined. A low shear rate capillary viscometer was designed in which the $[\eta]$ approached to value at zero shear rate can be obtained for HPAM-salt system. The effect of molecular weight on shear rate dependence of viscosity was also studied.

INTRODUCTION

Common Ubbelohde viscometer is generally regarded as high shear rate viscometer^[1]. The shear rate varies from 300 to 600 s⁻¹ when the concentration of polyacrylamide sample changes from 5.0×10^{-3} to 1.0×10^{-2} g/ml^[2]. This kind of viscometer is only suitable for Newtonian fluid and some non-Newtonian fluids with low or moderate molecular weight. When the molecular weight of polymer is beyond certain critical value, the viscosity may exhibit strong shear rate dependence. Therefore, the intrinsic viscosity measured by such viscometer may have discrepancies from normal value. Kulicke^[3] found that the Mark-Houwink equation coefficients reported by different authors varied to some degree. It was believed that shear rate dependence of viscosity was one of the reasons. Many studies were involved in searching for the method in which the effect of shear rate can be eliminated. The method of extrapolating viscosity to zero shear rate used to be predominant in the period of times^[4,5], but it was argued by some authors latterly. The horizontal capillary viscometer by which the zero shear rate can be obtained was reported by Xu^[6]. However, it was difficult to be applied in common laboratory due to complicated systems of pressure supply, control and monitoring required.

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The limitation of conventional Ubbelohde viscometer is its high shear rate, which is around $3 \times 10^2 \text{ s}^{-1}$. Some studies showed that the critical shear rate in Newtonian region for partially hydrolyzed polyacrylamide ($\overline{M}_w = 1 \times 10^7$) in pure water was $1 \times 10^{-1} \text{ s}^{-1}$ at concentration of $1.0 \times 10^{-2} \text{ g/ml}$ ^[3]. Therefore, the suitability of using pure water as a solvent for viscosity measurement for HPAM is questionable. Since the intrinsic viscosity of polyelectrolytes could generally be lowered by high salt concentration due to the suppression of the electrostatic repulsion between the charged groups, a salt solvent was used in our determination of intrinsic viscosity. In this paper, the effects of shear rate on the intrinsic viscosity measurement of HPAM in a salt system were studied with low shear rate viscometer and rheometer. The critical shear rate in salt solution for high molecular weight HPAM was determined. A low shear rate capillary viscometer was designed in which the $[\eta]$ at zero shear rate can be approached for HPAM-salt system.

EXPERIMENTAL

1. Polymer samples

Partially hydrolyzed polyacrylamide HPAM 430 (Cyanamide Co, Japan), HPAM 1155 (Allied Colloid, Great Britain), and polyacrylamide PAM synthesized in our laboratory were selected. PAM sample was fractionated by precipitation method in methanol-H₂O system to get the samples with narrow molecular weight distribution. The details are listed in Table 1.

Table 1 The properties of HPAM and PAM samples

Sample	Polydispersity	$[\eta]^*$ (ml/g)	H.D.** %	$\overline{M}_w \times 10^{-6}$
HPAM 430	unfractionated	1412	30.0	10.0
HPAM 1155	unfractionated	1200	25.2	6.80
PAM p1/8	fractionated	745	< 2.0	3.65
PAM p2/8	fractionated	565	< 2.0	2.88
PAM p3/8	fractionated	465	< 2.0	2.20

*: Measured in 1 mol/L NaCl system at $3.0 \pm 0.05^\circ\text{C}$

**: Degree of hydrolysis

2. Intrinsic viscosity measurement

The intrinsic viscosities of HPAM in 1 mol/L NaCl were measured by Ubbelohde viscometer, multi-bulbs viscometer, and Low Shear-30 Rheometer in parallel. The multibulbs viscometer is illustrated in Fig. 1, and the parameters are listed in Table 2. The efflux time of solvent in Ubbelohde viscometer was controlled above 120 s to eliminate the effect of kinetic energy correction. The measuring temperature was

controlled within $30 \pm 0.05^\circ\text{C}$, and the samples were dissolved for 24h and filtered with sintered-glass filter before measurement.

Table 2 The specific parameters of multi-bulbs viscometer*

No. of Bulb	Diam. (cm)	Height (cm)	t_0 (s)**
1	1.42	2.0	227.1
2	1.60	4.3	199.8
3	1.65	7.3	199.8
4	1.85	9.4	202.1
5	1.95	12.2	191.0

* The length of capillary: 50cm, radius of capillary: 0.035 cm

** Measured in 1 mol/L NaCl system at $30 \pm 0.05^\circ\text{C}$

3. The rheological curve of HPAM measurement

The rheological curve of HPAM-1 mol/L NaCl system were measured by Low Shear-30 Rheometer (Contraves) at the range of shear rate from 0.07 s^{-1} to 128 s^{-1} under temperature of $30 \pm 0.1^\circ\text{C}$.

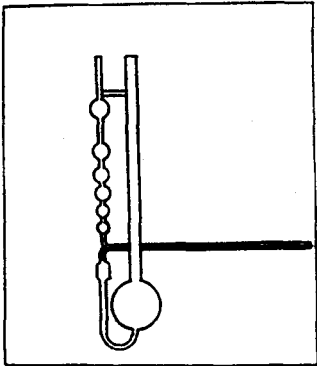


Fig. 1 The multi-bulbs capillary viscometer

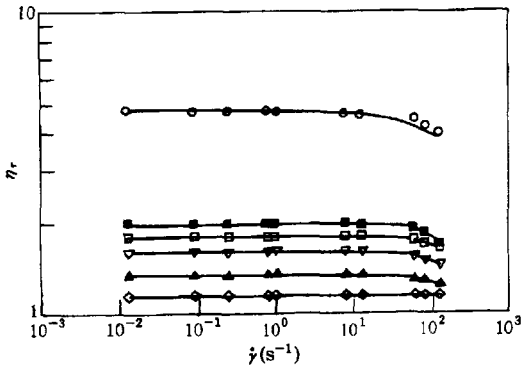


Fig. 2 Rheological curves of HPAM 430-1 mol/L NaCl system

○ $1.0 \times 10^{-3} \text{ g/ml}$; □ $3.33 \times 10^{-4} \text{ g/ml}$; ▲ $1.70 \times 10^{-4} \text{ g/ml}$; ■ $5.0 \times 10^{-4} \text{ g/ml}$; ▽ $2.50 \times 10^{-4} \text{ g/ml}$; ◇ $1.25 \times 10^{-4} \text{ g/ml}$

4. Weight average molecular weight determination

The weight average molecular weights of PAM fractions were determined by light scattering method. The refractive index increment dn/dc measurements were performed with KMX-16 (Chromatix) laser differential refractometer at 632.8 nm and $30 \pm 0.1^\circ\text{C}$. The intensities of light scattering for polymer solutions were determined by KMX-6 (Chromatix) low angle laser light scattering photometer. The $\overline{M}_w$ were calculated from those two parameters, for more see reference [7].

RESULTS AND DISCUSSION

1. Polymer solution behaviors

The rheological behaviors of HPAM 430 in 1 mol/L NaCl were studied in a shear rate range of 0.07 s^{-1} to 128 s^{-1} by Low Shear-30 Rheometer, and the rheological curves are shown in Fig. 2. These curves indicate that the high molecular weight polymer solutions behave as a typical non-Newtonian fluid, and the degree of shear thinning increases with increasing polymer concentration. The onset points at which shear thinning behavior commences are found to be in the range of $5 \times 10^1 - 1 \times 10^2 \text{ s}^{-1}$ for HPAM 430 - 1 mol/L NaCl system.

The comparison tests were also made with the home-made multi-bulbs capillary viscometer. The shear rate with different geometric size of viscometer can be calculated by using the following equation:

$$\dot{\gamma} = \frac{Rh g \rho}{2l \eta} \quad (1)$$

where: R and l are radius and length of the capillary respectively, h is the average height between the upper and lower etched lines, g is the acceleration of gravity, ρ is the liquid density, η is the absolute viscosity which can be obtained either by experiment or by the following equation:

$$\eta = \frac{\pi h g \rho R^4 t}{8lV} - \frac{mV\rho}{8\pi t l} = A\rho t - B\frac{\rho}{t} \quad (2)$$

where t is the efflux time of solution, and m is an instrument constant with a value around one. The relative viscosity of polymer solution measured with the multi-bulbs capillary viscometer and the shear rate calculated by the above equation are listed in Table 3, and plotted in Fig. 3:

It can be seen that the viscosities of HPAM exhibit strong shear rate dependence in this shear rate range. As the shear rate increases with increasing of the height level of liquid, the measured results tend to be varied. While the intrinsic viscosity measured from the lowest bulb of the multi-bulbs capillary viscometer is 1931, the intrinsic viscosity measured from that of the highest bulb is 1725, and the relative error exceeds 10%. Moreover, the error becomes more pronounced and reached 23.8% when the results obtained from Ubbelohde viscometer are compared with that of the lowest bulb's of multi-bulb viscometer. It is obvious that the magnitude of the intrinsic viscosity would be strongly dependent on the shear rate of the instrument used, and the ordinary Ubbelohde viscometer is not suitable for the polymer with

molecular weight over 1×10^7 . The low shear rate viscometer should be used for intrinsic viscosity determination of polymer with high molecular weight.

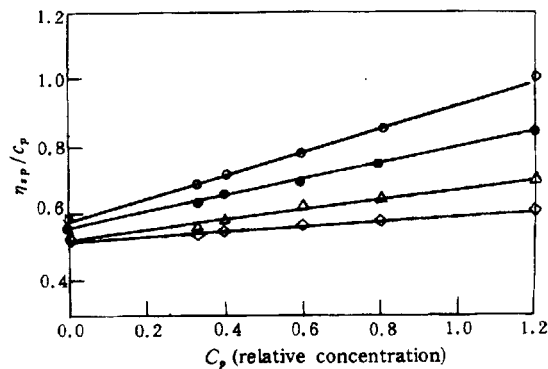


Fig. 3 $\eta_{sp}/C_p - C_p$ relation curves at different shear rate conditions
○ 260.4 s^{-1} ; ● 200.7 s^{-1} ; △ 155.8 s^{-1} ; ◇ 42.7 s^{-1}
Initial concentration $C_0 = 3.33 \times 10^{-4} \text{ g/ml}$

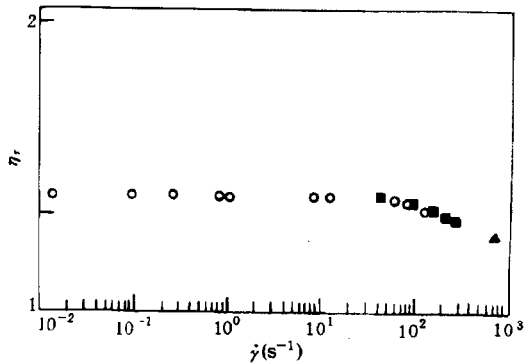


Fig. 4 Comparison of the results obtained from two kinds of viscometers
■ Multi-bulbs viscometer $3.3 \times 10^{-4} \text{ g/ml}$; ▲ Ubbelohde viscometer $3.3 \times 10^{-4} \text{ g/ml}$;
○ Low shear-30 rheometer $3.3 \times 10^{-4} \text{ g/ml}$

Table 3 Rheological parameters of HPAM 430-1 mol/L NaCl in capillary viscometer

Bulb height (cm)	t_0 (s)	$\dot{\gamma}$ (s^{-1})	η_r	$[\eta]$ (ml/g)	error*
16.5**	121.0	685.8	1.325	1425	23.8
12.2	191.0	260.4	1.410	1725	9.83
9.4	202.1	200.7	1.432	1755	8.26
7.3	199.8	155.8	1.468	1800	5.91
4.3	199.8	91.8	1.500	1825	4.60
2.0	227.1	42.7	1.536	1931	0.00

* $[\eta]_{h2.0} - [\eta]_h / [\eta]_{2.0\%}$, $[\eta]_{h2.0}$ and $[\eta]_h$ were measured from different bulb height

** : Ordinary Ubbelohde viscometer

The both results obtained from multi-bulbs capillary viscometer and rheometer

were plotted together in Fig. 4. It is interesting to find that not only these two curves match well, but also the shear rate corresponding to the lowest bulb are located in the Newtonian region in the rheological curve and the shear rates corresponding to the other four bulbs are in the region of shear thinning. This means that $[\eta]$ at the zero shear rate of high molecular weight of polymer can be approached in capillary viscometer by adjusting the length and the radius of capillary. According to this result, a simple low shear rate capillary viscometer was designed, as shown in Fig. 5 The parameters of the viscometer are listed in Table. 4.

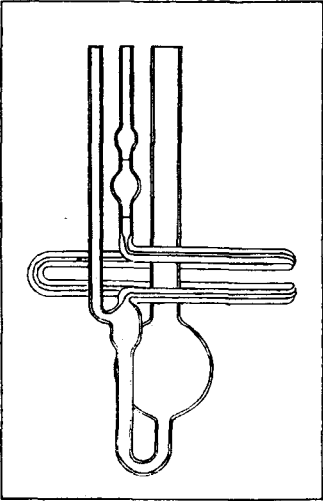


Fig. 5 The low shear rate capillary viscometer

Table 4 The parameters of low shear rate viscometer

Length of capillary (cm)	Radius of capillary (cm)	Average height of bulb (cm)	Diameter of bulb (cm)	t_0 (s) in H ₂ O
50.0	0.035	2.0	1.40	221

2. Effect of molecular weight on the shear rate dependence of viscosity

The intrinsic viscosities of HPAM with different molecular weights in 1 mol/L NaCl system were measured by low shear rate capillary viscometer and Ubbelohde viscometer. The weight average molecular weight of HPAM were also measured by light scattering method, shown in Table. 5.

These data clearly show that the effect of shear rate on the intrinsic viscosity becomes more pronounced for high molecular weight polymer. When the molecular weight of HPAM is 2.88×10^6 , the relative error is 6.0%, but reaches 23.8% when the molecular weight is 1×10^7 . For HPAM-1 mol/L NaCl system, the molecular weight of 2.88×10^6 with 6.0% relative error may be regarded as a critical value where the

effect of shear rate on viscosity may not be ignored. The problem can be solved by using the low shear rate viscometer.

Table 5 Comparison of results from different viscometers

Polymer	$\bar{M}_w \times 10^{-6}$	$^*[\eta]_u$	$^*[\eta]_0$	Error %
HPAM 430	10.0	1458.0	1913.0	23.8
PAM 1/8	3.65	745.4	825.0	9.7
PAM 2/8	2.88	598.5	636.6	6.0
PAM 3/8	2.20	512.2	525.8	2.6

* $[\eta]_u$ and $[\eta]_0$ were measured by Ubbelohde viscometer and the low shear rate capillary viscometer, respectively.

CONCLUSIONS

1. The shear rate dependence of viscosity of high molecular weight HPAM in Ubbelohde viscometer was found to be significant. The error may reach 23.8% as it is compared with zero shear rate viscosity.

2. The magnitude of shear rate dependence viscosity increases with increasing of molecular weight for HPAM-1 mol/L NaCl system. The effect of shear rate on viscosity can not be ignored when the molecular weight exceeds 2.88×10^6 .

3. A new type low shear rate viscometer was designed, in which $[\eta]$ at zero shear rate of polymer can be approached.

Keywords:

Viscometer; Intrinsic viscosity; Molecular weight; Polyelectrolyte; Polyacrylamide; Capillary viscometer

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