High Shear Rheology and Shear Degradation of Aqueous Polymer Solutions

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Synopsis

We have investigated the possibility of replacing hydraulic oils with aqueous polymer solutions having the same rheological properties. We measured the low and high shear rate viscosities of polymer solutions at several moderate concentrations and compared the results to the predictions of a molecular model. We found that viscosities measured at shear rates near 1 million reciprocal seconds are in good agreement with those calculated using the model of Mochimaru.[6] Shear degradation studies were also conducted using higher molecular weight versions of some of the polymers. Exposure of these to very high shear rate caused a permanent decrease in viscosity and a corresponding change in the molecular weight and molecular weight distribution. Taken together, these results show that very low molecular weight polymers at moderate concentrations are necessary to formulate an aqueous hydraulic fluid with approximately Newtonian behavior at shear rates near 1 million reciprocal seconds, and without long-term polymer degradation.

INTRODUCTION

The rising cost of petroleum in the last decade caused us to investigate the possibility of replacing the hydraulic fluids used in large industrial plants with aqueous polymer solutions at low polymer concentrations. An ideal substitute fluid would have the same, or very similar properties, as the hydraulic oil. This ideal fluid would thus have a viscosity of approximately 40 m · Pa · s · (centiPoise) at 313 K, and an approximately Newtonian response over a shear rate range of 0–1 million reciprocal seconds. In addition, the fluid properties must be constant for long times to avoid costly equipment down time. Therefore, mechanical or shear degradation of the polymer must be avoided.

The high shear rheology and shear degradation behavior of polymers has been previously studied using water-insoluble polymers,[1] and water-soluble polymers of very high molecular weight in dilute solution.[2] We have therefore studied the rheological and degradation behavior of aqueous solutions of intermediate molecular weight polymers at moderate concentrations, in an attempt to define limits for the design and use of polymers for such applications.

EXPERIMENTAL

Polymer Solutions

The various water-soluble polymers used in this study are given in Table I. Solutions were prepared by carefully, but rapidly, adding a weighed amount of powdered polymer to the desired solvent being rapidly stirred with a

TABLE I
Polymers Used in This Study

NLPolymer type	Identification	Source	Molecular weight	Virial coefficient	Water content	dn/dc (mL/g)	Solvent
Polyacrylamide	SEPARAN[a] PG-2	Dow	1,460,000	2.4×10^{-4}	8.8%	0.163	0.1M NaH$_2$PO$_4$ pH = 7
Poly(acrylamide-co sodium acrylate)	PUSHER[a] 700E	Dow	14,070,000	—	—	—	—
"	R641-41	Dow	141,000	—	—	0.147	0.3M NaCl
Poly(ethylene oxide)	PEOPO-A	Dow	52,700	1.07×10^{-3}	—	0.156	Methanol
	Polyox[b] WSRN-10	UCC	157,000	1.00×10^{-3}	0	0.134	Phosphate buffer
Poly(vinyl alcohol)	Vinol[c] 107	Air Prod.	35,300	4.77×10^{-4}	5.2	0.153	Water
	Vinol[c] 325	Air Prod.	98,600	4.47×10^{-4}	5.6	0.153	Water
Poly(ethyl oxazoline)	PETOX-A	Dow	198,000	2.21×10^{-4}	4.4	0.175	Phosphate buffer
"	PETOX-B	Dow	384,000	4.27×10^{-4}	3.2	0.175	Phosphate buffer

[a] Trademarks of The Dow Chemical Company.
[b] Trademarks of Union Carbide Corp.
[c] Trademarks of Air Products Corp.

magnetic stirrer. After the polymer was thus dispersed, the jar was securely capped and shaken for several hours using a platform-type shaker. For poly(vinylalcohol) samples it was necessary to heat the dispersions to 363°K with stirring to obtain clear solutions. These viscous solutions were then transferred quantitatively to volumetric flasks, diluted nearly to the mark, then held overnight at 298°K in a water bath before being diluted accurately to the mark. Each solution was filtered through a 100 mesh nylon screen before use; the solutions were all found to be essentially free of undissolved material. The concentrations were corrected for the moisture content of the polymers. These were determined on a Cenco Moisture Balance.

Viscosity Determinations

Equipment

Haake Rotovisco RV21. The viscosity of some of the polymer solutions, at relatively low shear rates, was determined using the NV cup and rotor system. The accuracy was occasionally checked by using Newtonian reference oils. At one point it became inoperable and measurements were then conducted using a Brookfield model LVT viscometer.

Brookfield LVT. The low shear viscosity of some of the solutions was determined in the small sample adapter, model SC4-18/13. This instrument was also calibrated with Newtonian reference oils before use.

Savant Model 500 High Shear Viscometer. The viscosity of the polymer solutions at shear rates near 1 million reciprocal seconds was determined using the recently developed Savant Model 500 viscometer (also known as the Tapered Bearing Simulator/Viscometer). Because of the relative newness, and custom construction, a thorough study of its operating characteristics was done before use, so that accurate viscosity values were obtained. A brief description and discussion of its operation is given below.

An overall description of the viscometer has been given recently by Selby.[3] The viscometer is essentially a concentric cylinder device, with the inner cylinder rotated by means of a constant speed motor. The retarding force due to viscosity is measured using a load cell, which is pressed upon by an arm extending from the motor/rotor assembly (see Fig. 1). The key innovation is that both the rotor and cup actually possess very small, and equal, tapers from top to bottom. This allows for a continuously variable gap between the rotor and cup, as the motor/rotor assembly is raised or lowered relative to the cup [see Fig. 2(a)]. By knowing the actual geometry of the rotor/cup assembly, the rotational speed, and the load cell response characteristics (obtained through calibration), one can in principle determine the shear rate and shear stress, and therefore calculate the viscosity. The derivation of the appropriate operating equations for viscosity, using such a "tapered cylinder" device, begins with standard equations for shear stress and shear rate[4]

$$\text{shear stress} = \frac{M}{2\pi r^2 h} \tag{1}$$

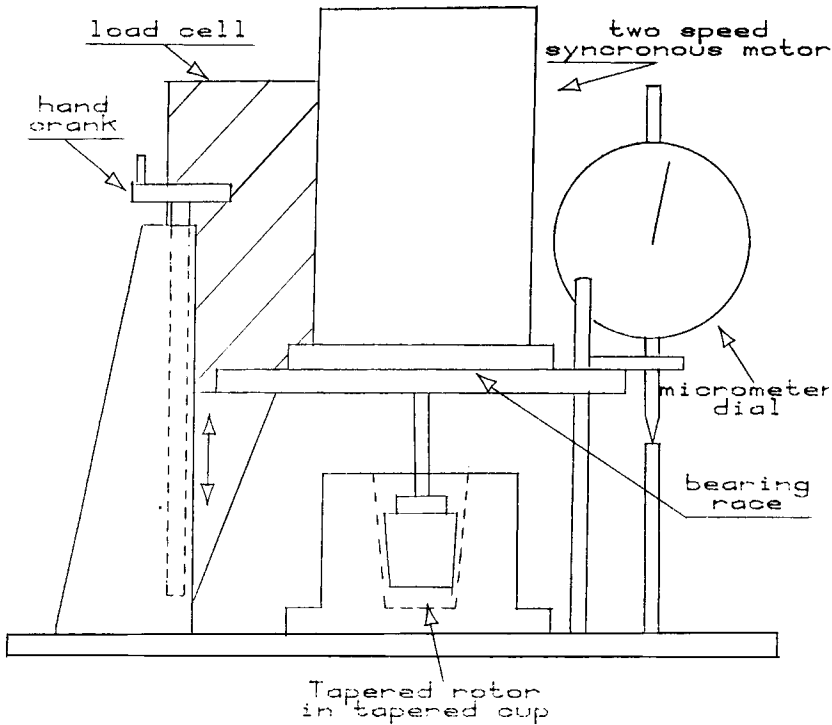$$\text{shear rate} = \frac{r\Omega}{\Delta r} \tag{2}$$

Fig. 1. A schematic drawing of the Savant Model 500 High Shear Viscometer.

where M is the output torque of the instrument, r is the rotor radius, h is the rotor height, Ω is the angular velocity of the rotor, and Δr is the gap between rotor and cup. The output torque of the instrument, M, is given as a voltage from the load cell. This displayed voltage is calibrated by suspending various standard masses, m, from the instrument *via* a pulley system. Knowing the magnifying torque arm, d, of the instrument, the torque is

$$M = mgh \tag{3}$$

where g is the acceleration due to gravity.

The gap, Δr, between rotor and cup is continuously variable by means of a multiturn screw. The relative vertical distance between rotor and cup is precisely measured by means of a dial-type micrometer. The actual gap between rotor and cup at any vertical position P_i is

$$\Delta r = \frac{P_i - P_o}{T_p} \tag{4}$$

where P_o is the relative vertical position where the rotor will contact the cup, and T_p is the magnitude of the taper machined into the viscometer. Combining equations 1, 2, and 4 to yield viscosity gives

$$\eta = \frac{M}{2\pi r_a^2 h} \left[\frac{\Omega r_a}{(P_i - P_o)/T_p} \right]^{-1} \tag{5}$$
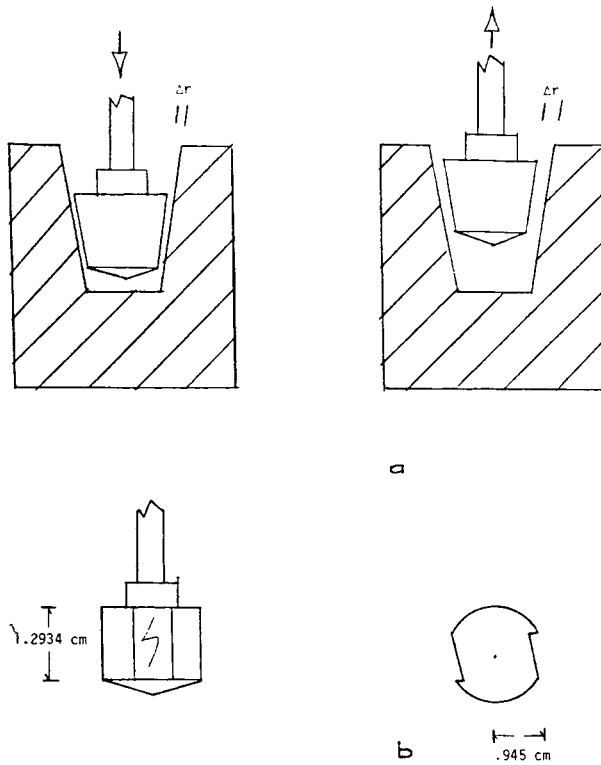
Fig. 2. Details of the cup/rotor assembly of the Savant Viscometer. (a) The gap is increased or decreased by raising or lowering the rotor in the cup. (b) Dimensions of the rotor.
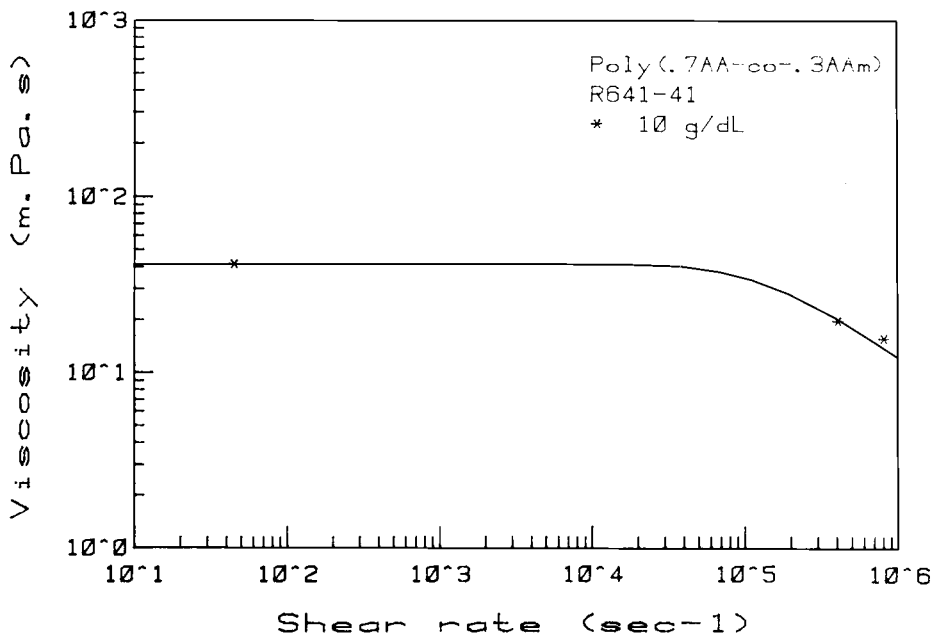

Fig. 3. Rheological flow of poly(.7 sodium acrylate-co-.3 acrylamide), sample R641-41, including data points at 10 g/dL polymer concentration and prediction according to Eq. (7).

One additional feature of the rotor, necessary for proper centering of the rotor in the cup, is the presence of "flats" machined into the rotor surface [see Fig. 2(b)]. The presence of these flats would seem to decrease the rotor surface area from which the shear stress is calculated, but this has been shown not to be the case.[3]

Rearranging Eq. (5) gives the rotor positioning equation, where Ω has been replaced by $2\pi(\text{rpm})/60$

$$P_i = \left[\frac{4\pi^2}{60} r_a^3 h T_p(\text{rpm}) \eta \right] \frac{1}{M} + P_o \qquad (6)$$

To accurately position the rotor, one needs to measure the height, h, and radius, r, of the rotor, and the taper, T_p. For a fluid of known Newtonian viscosity η, one determines the torque, M, due to viscosity, at various rotor positions, P_i, near the contact position P_o. A linear least-squares analysis of the data as P_i versus $1/M$ gives the actual contact position, P_o as intercept and the quantity $S = 4\pi^2 r_a^3 h T_p(\text{rpm})\eta/60$ as the slope, from which one may determine the actual taper of the rotor assembly.

The dimensions of the rotor are given in Figure 2(b). Using Eq. (6) and the load-cell calibration data on several different Newtonian fluids, the actual taper of the rotor was determined to be 132:1 or 26 minutes of arc. The load-cell calibration was found to be described by the equation M = 75.15D − 46 (when a 50 g mass was added to the pulley system during operation to offset the springiness of the power wires). The calculated viscosity values are given in the appropriate figures that follow.
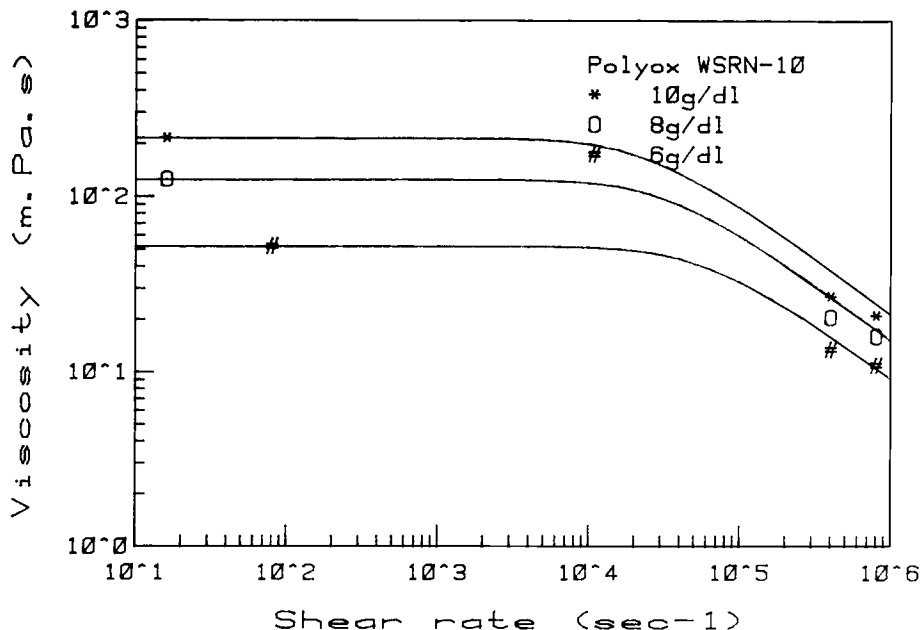

Fig. 4.   Rheological flow of poly(ethyleneoxide), sample POLYOX WSRN-10, including data at three concentrations and predictions according to Eq. (7).

Viscosity Procedure

All viscosity measurements were done at $298 \pm 0.1°K$, using an automatically controlled heater/refrigerator with a water/ethylene glycol bath. Polymer solutions were equilibrated in the viscometers for five minutes before taking the reading. Viscosities and shear rates were then calculated using the equations and calibrations provided with, or appropriate to, each specific viscometer.

Molecular Weights

Weight average molecular weights were determined using a LDC/Milton Roy Chromatix KMX-6 Low Angle Laser Light Scattering (LALLS) photometer at 633 nm. A 6–7 degree annulus, 0.3 fieldstop, and 15 mm cell were employed. Differential refractive index increments (dn/dc) were determined on a LDC/Milton Roy Chromatix KMX-16 differential refractometer. For the nonionic polymers, dn/dc values were obtained using undialyzed solutions.

The molecular weights, virial coefficients, solvent systems, and refractive index increments are reported in Table I.

Initial attempts to use the phosphate buffer system as solvent for the poly(vinylalcohol) samples and the ethyleneoxide/propyleneoxide copolymer were thwarted by aggregation. This was evidenced by noisy and excessive scattering, especially at high polymer concentrations, and by curved and/or negatively sloped KC/R versus C plots. The use of deionized water for the poly(vinylalcohol) samples, and methanol for the polyglycol sample eliminated these problems.
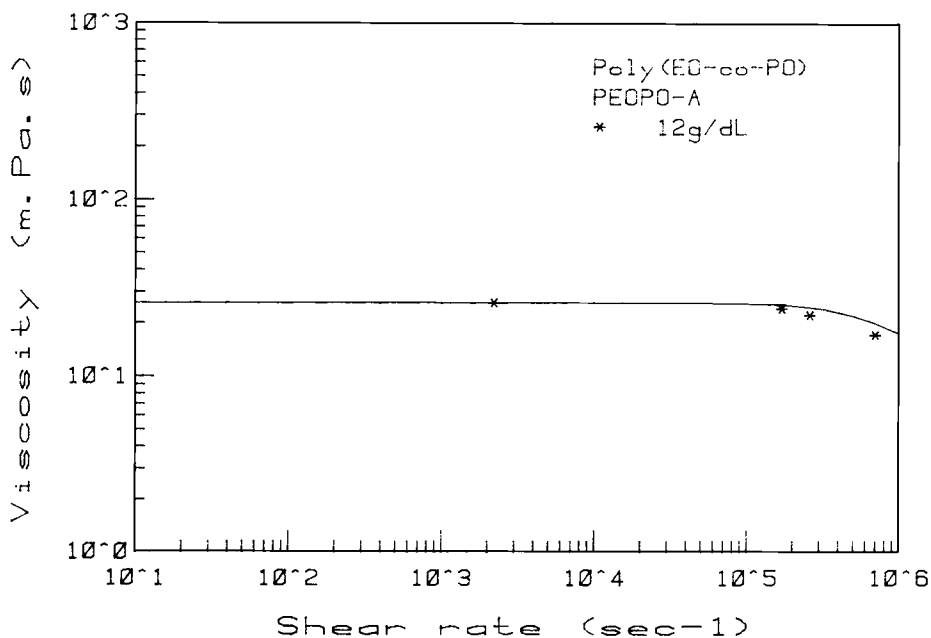

Fig. 5. Rheological flow of poly(ethyleneoxide-co-propyleneoxide), sample PEOPO-A, including data points at 12 g/dL and prediction according to Eq. (7).

Shear Degradation Experiments and Molecular Weight Distributions

Degradation Studies. After each polymer solution was sheared at the maximum shear rate used with the high shear viscometer, the viscometer was stopped and the solution was removed using a syringe with a wide bore needle. The viscosity was redetermined at low shear rate in the Brookfield viscometer with the small sample adapter. For most of the samples, this viscosity was within experimental error of the original viscosity measure at low shear rate. For two of the samples which showed obvious decreases in viscosity after shearing at high rate, molecular weight distributions were determined both before and after shearing.

Molecular Weight Distributions. The molecular weight distribution of the poly(0.7 sodium acrylate-co-0.3 acrylamide) sample was determined using size exclusion chromatography coupled with LALLS. The chromatographic method used was that described by Kato.[5a] The column set was a Toyo Soda TSK-6000PW, −5000PW, and −3000PW, each 30 cm in length. The eluent was 0.3 M NaCl with 0.05 weight percent sodium azide added to inhibit microbial growth. The flow rate was 1.0 mL/min. The eluting polymer concentration was monitored with a Waters R401 refractive index detector. The LALLS photometer was equipped with a 5 mm path length flow cell. A 6–7 degree annulus and 0.2 mm field stop were used.

The molecular weight distribution of the very high molecular weight partially hydrolyzed poly(acrylamide) (PUSHER* polymer) was determined using
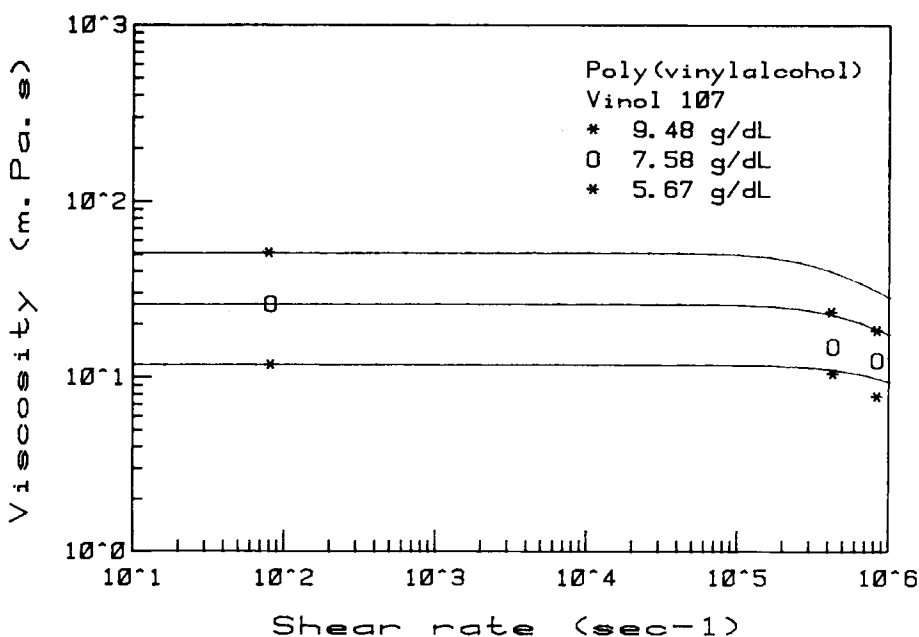

Fig. 6. Rheological flow of poly(vinylalcohol), sample VINOL 107, including data at three polymer concentrations and predictions according to Eq. (7).

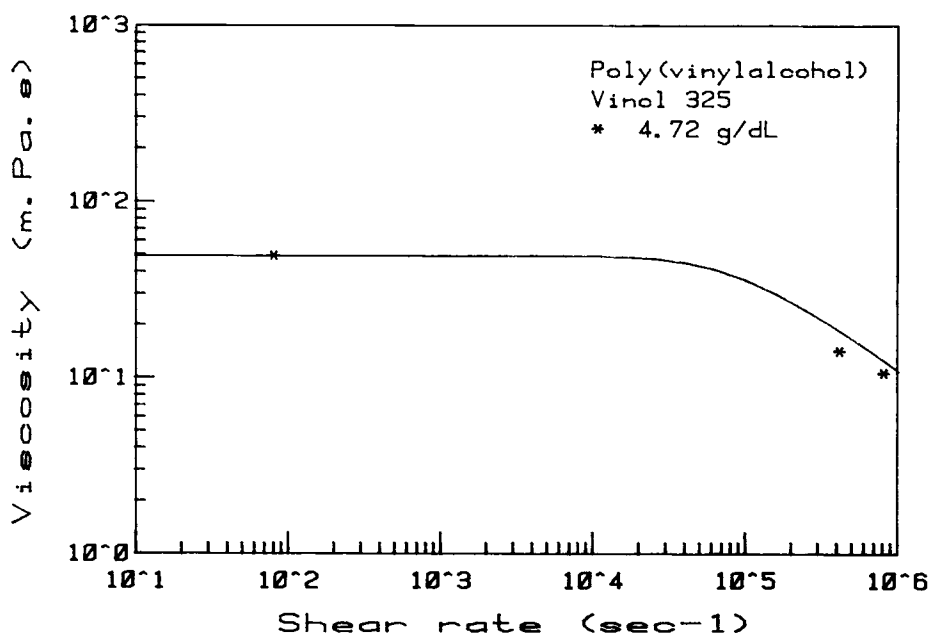*Trademark of The Dow Chemical Company.

Fig. 7.   Rheological flow of poly(vinylalcohol), sample VINOL 325 with data points at 5 g/dL and prediction according to Eq. (7).

the recently developed hydrodynamic chromatography (HDC) method for water-soluble polymers.[5b]

RESULTS AND DISCUSSION

The results of the viscosity measurements and calculations at both high and low shear rate are shown as data points in Figures 3–11. The curves on each graph represent the shear thinning (non-Newtonian) behavior of the polymer solutions as predicted using the molecular based model of Mochimaru[6]

$$\frac{\eta(\gamma) - \eta_s}{\eta_o - \eta_s} = \frac{6.3}{(\lambda\gamma)}\sinh\left[1/3\sinh^{-1}(0.475\lambda\gamma)\right] \qquad (7)$$

where $\eta(\gamma)$ is the viscosity at a shear rate γ, η_s is the solvent viscosity, η_o is the viscosity of the polymer solution at low shear rate, and λ is the Bueche relaxation time of the polymer solution, given as:

$$\lambda = \frac{12\eta_o M}{\pi^2 cRT} \qquad (8)$$

In this equation, M is the polymer molecular weight, c is the polymer concentration in g/mL, R is the gas constant, and T is the temperature.

The agreement between the calculated (predicted) shear thinning behavior and the high shear viscosities measured in the work is generally excellent. The exceptions are the results for poly(ethyloxazoline), when the predicted curves are constructed using the assumption of a linear, random coil polymer in
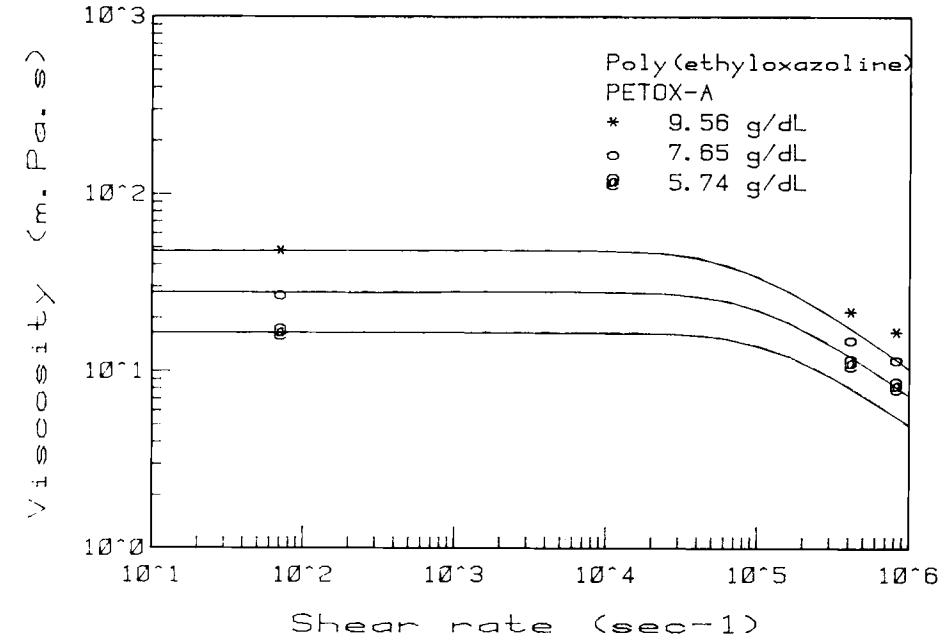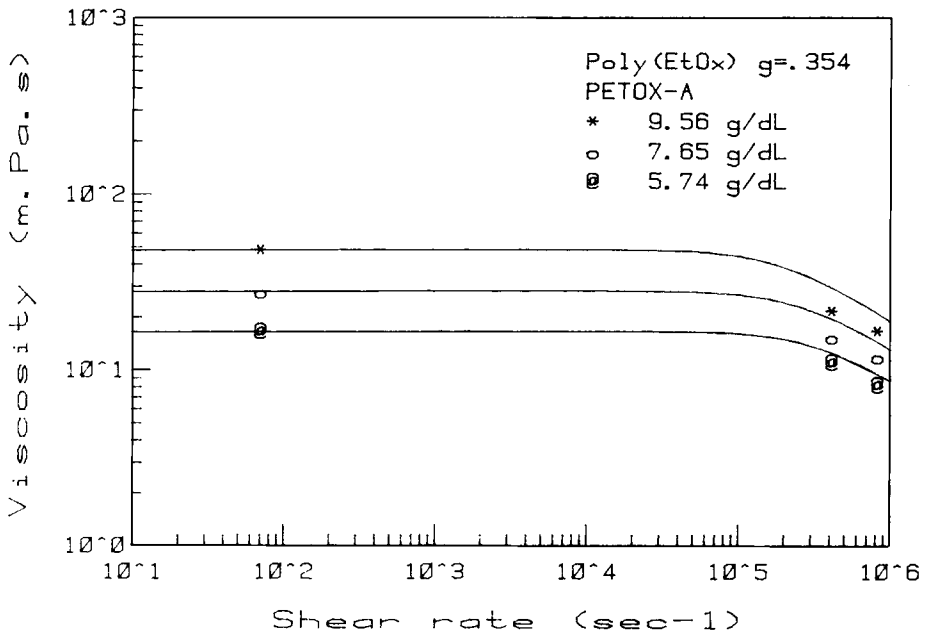
Fig. 8.   Rheological flow of poly(ethyloxazoline), sample PETOX-A, including data at three polymer concentrations and predictions according to Eq. (7). (a) Predictions assuming a linear random-coil polymer. (b) Predictions assuming a 3 armed star branched polymer.
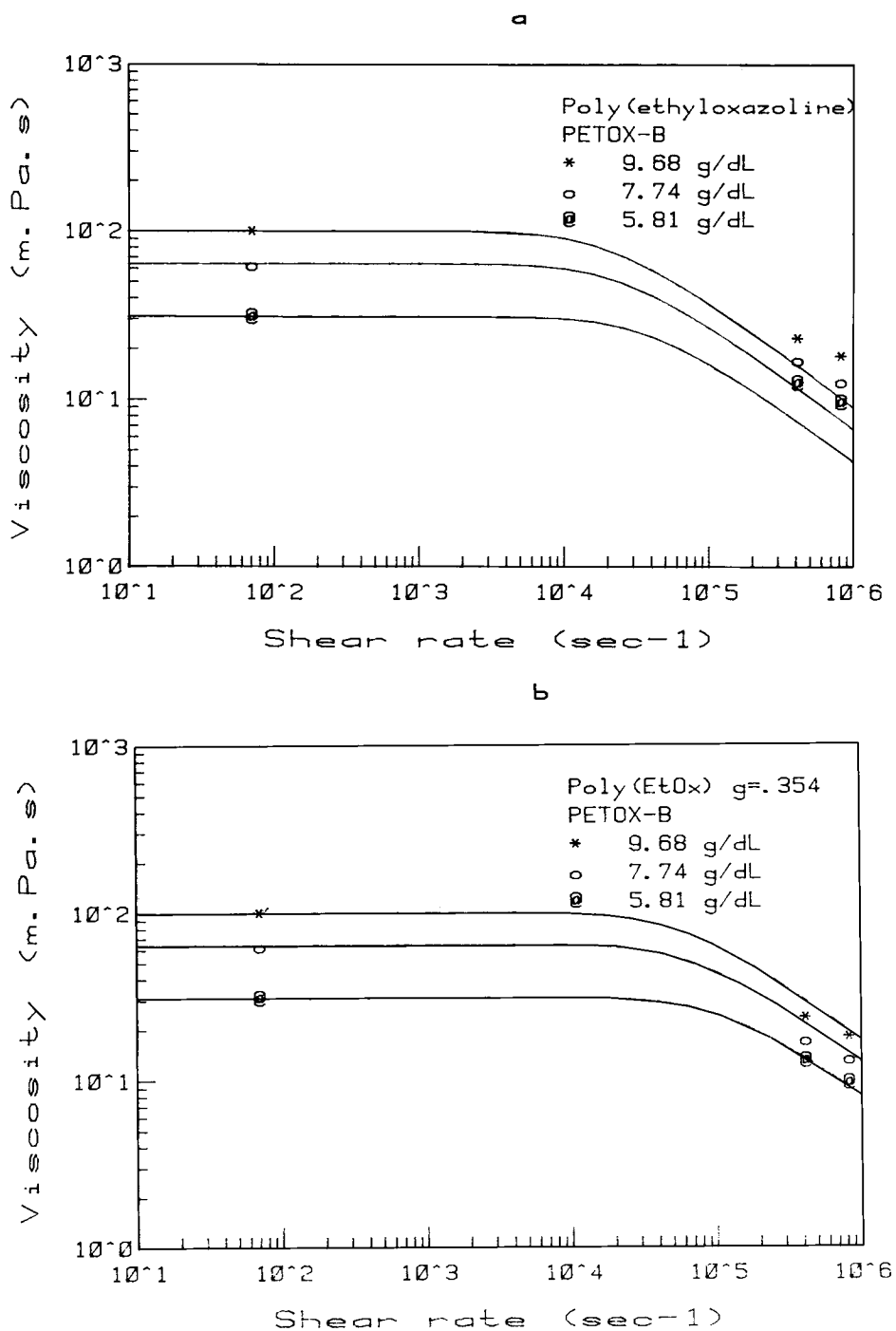
a

b

Fig. 9. Rheological flow of poly(ethyloxazoline), sample PETOX-B, including data at three polymer concentrations and predictions according to Eq. (7). (a) Predictions assuming a linear random-coil polymer. (b) Predictions assuming a 3-armed star branched polymer.
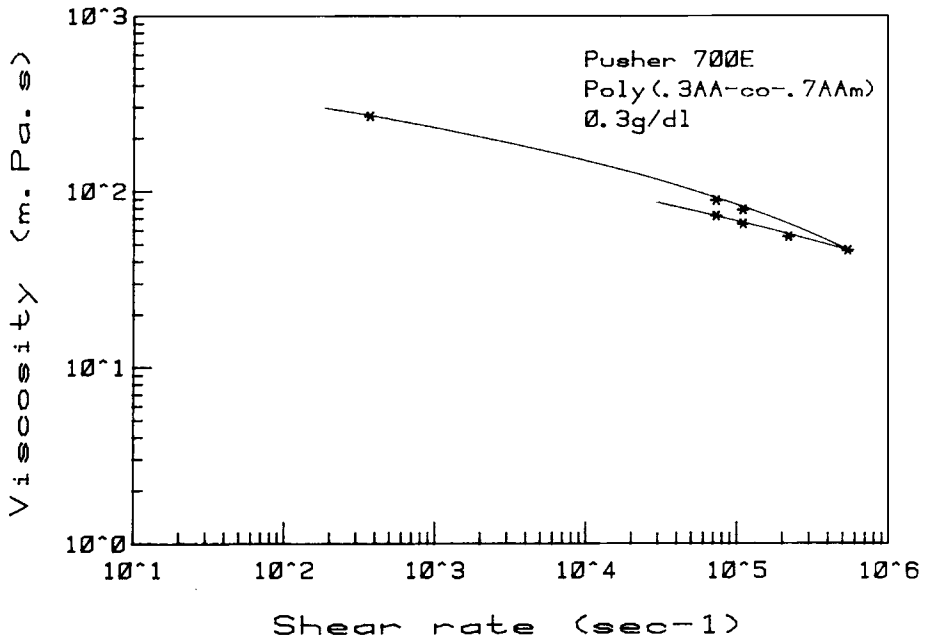
Fig. 10. Rheological flow of poly(.3 sodium acrylate-co-.7 acrylamide), sample PUSHER 700E (Trademark of The Dow Chemical Company). The data points are connected with a smooth curve not according to Eq. (7) and show the viscosity upon first increasing the shear rate and then decreasing the shear rate.
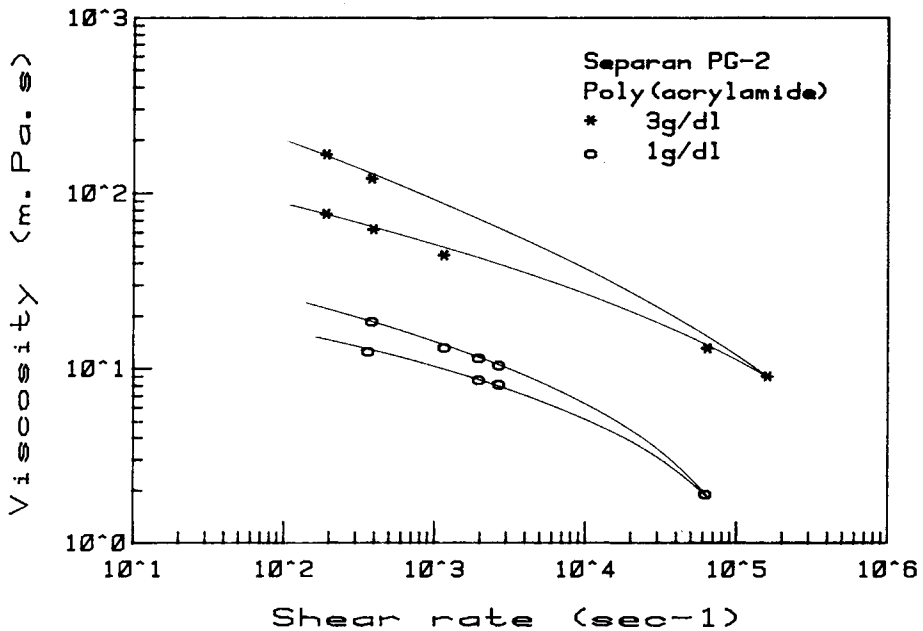

Fig. 11. Rheological flow of poly(acrylamide), sample SEPARAN (Trademark of The Dow Chemical Company) PG-2, at two polymer concentrations. The curves connecting the data points are not according to Eq. (7) and show the viscosity upon first increasing the shear rate and then decreasing the shear rate.

solution [Figs. 8(a), 9(a)]. Litt[7] has suggested that poly(ethyloxazoline) is branched. If we therefore modify the relaxation time of the polymer by a factor $g = 0.354$, which is the factor for a three-armed star polymer,[9] and include this change in Eq. (7), curves are produced which fit the data much better [Figs. 8(b), 9(b)]. The curves drawn in Figures 10 and 11 are not due to Eq. (7). Predictions on these were not attempted because of the significant drops in viscosity which suggested degradation.

The predictive power of Eq. (7) is therefore quite good over the range of concentration and molecular weight investigated here. All the samples investigated showed some shear thinning at shear rates approaching 1 million reciprocal seconds, even the lowest molecular weight poly(vinylalcohol). Even lower molecular weights will be necessary if Newtonian rheology at these very high rates remains a requirement for an aqueous hydraulic fluid. As a necessary consequence of lower molecular weight, a higher polymer concentration (> 10 g/dL) will be required to achieve the viscosity goal of 40 m $\cdot$ Pa $\cdot$ s $\cdot$.
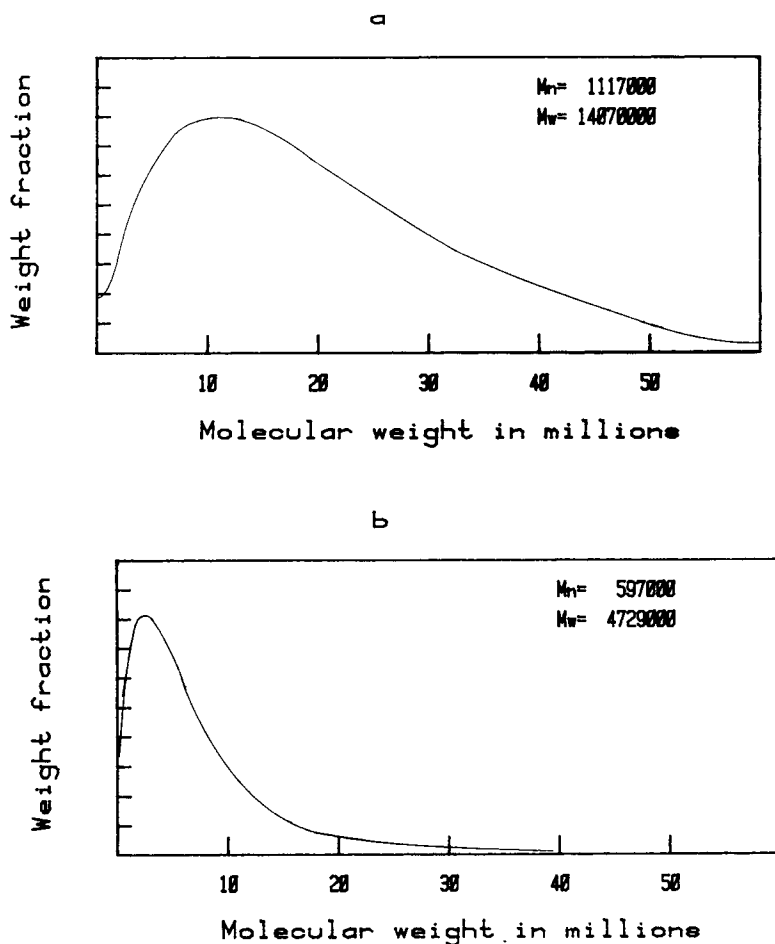

Fig. 12.   Molecular weight distributions for polymer sample PUSHER (Trademark of The Dow Chemical Company) 700E, (a) before shearing in the Savant Viscometer and (b) after shearing in the Savant Viscometer.
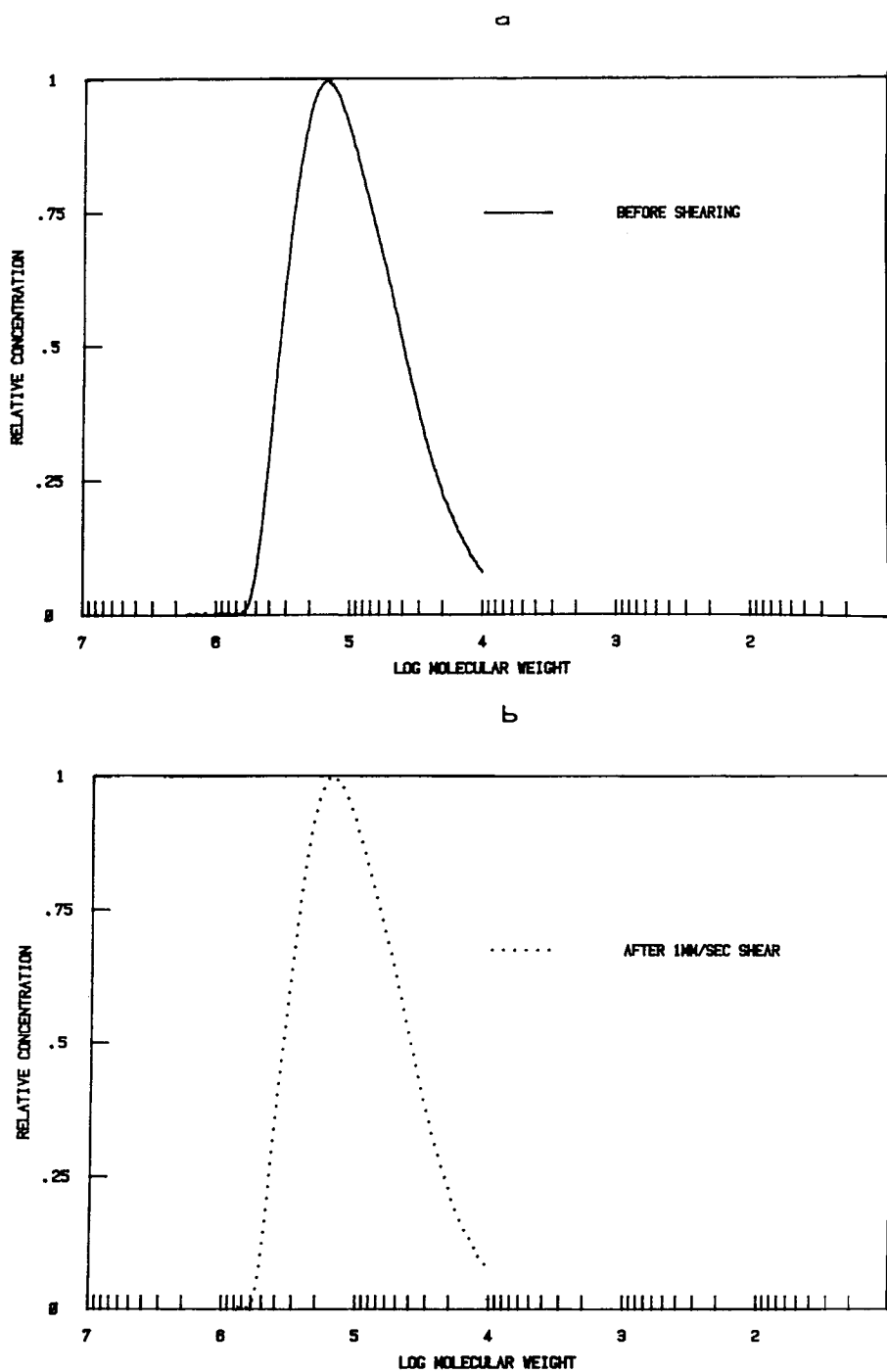
a

b

Fig. 13. Molecular weight distributions for polymer sample R641-41, (a) before shearing in the Savant Viscometer and (b) after shearing in the Savant Viscometer.

Shear Stability

The stability of a polymer molecule to mechanical stress such as shearing depends on both the molecular weight and on the applied shear stress.[8] In this study, we measured the molecular weight distributions of two of the polymer samples both before and after exposure to the high shear stress of the TBS Viscometer. Figure 10 shows the viscosity behavior for the very high molecular weight PUSHER* polymer as the shear rate is first increased and then decreased, and Figure 12 gives the respective molecular weight distributions. Both viscosity and molecular weight distribution are severely affected in this case.

Figures 3 and 13 show the viscosity and molecular weight distributions for the moderate molecular weight R641-41 polymer sample, before and after shearing at high rate. No significant change in the properties of this sample is observed. These examples clearly show that shear stable polymers can be obtained even though they exhibit non-Newtonian (shear thinning) rheology.

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