Vena Contracta Suppression in Dilute Polymer Solutions

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Synopsis

Very small amounts of high molecular weight polymers were found to eliminate vena contracta formation in flow through a circular orifice. This effect was reflected in the decreased efflux time for drainage between two fixed levels in a tank, reductions up to 30% being obtained. Aqueous solutions of seven commercially available polymers were studied, consisting of a poly(acrylic acid), two polyacrylamides of different degrees of hydrolysis, and four poly(ethylene oxides) of widely differing molecular weights. The poly(acrylic acid) and two highest molecular weight poly(ethylene oxides) each caused a sudden drop in efflux time at a "critical concentration," which was 2, 50, and 90 wppm, respectively, for these three polymers. An explanation of this phenomenon in terms of the high Deborah number flow field existing near the orifice edge is advanced. In the case of the polyacrylamide solutions, a very gradual reduction in efflux time with increasing polymer concentration was observed, beginning at about 3 wppm. Coincident with this was the formation of a wine-glass stem or converging flow field upstream of the orifice. Such a flow field was not observed for the other solutions. It is suggested that vena contracta inhibition with polyacrylamide is simply a manifestation of solution die swell. The reason for the differing efflux time behavior between the various polymers is not known and represents a challenging problem for further study.

INTRODUCTION

During the past three decades, the striking differences in behavior between Newtonian and viscoelastic fluids have been well documented and extensively studied.[1,2] The majority of these studies have dealt with highly elastic fluids, such as concentrated polymer solutions and polymer melts, which exhibit pronounced normal stress effects, stress relaxation, and recoil. More recently, it has become evident that even very dilute polymer solutions, with polymer concentrations of the order of 1 to 50 wppm (parts per million by weight) may also show marked differences in flow behavior when compared to Newtonian solutions of approximately the same viscosity and density. Common examples include (i) turbulent drag reduction,[3] where the addition of minute quantities of linear long-chain polymers may reduce turbulent drag by 60–80%; and (ii) vortex inhibition,[4] in which a gross macroscopic property of Newtonian liquids, the tendency to form a vortex or "air core" during drainage from a tank, is totally suppressed with concentrations of certain polymers as low as 3 to 5 wppm. In this paper, we report on still another such viscoelastic effect operative at extremely low concentration levels, the elimination of vena contracta formation in flow through a circular orifice. (Vena contracta formation refers to the reduction

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in liquid jet diameter relative to orifice diameter which ordinarily occurs at high Reynolds numbers with Newtonian fluids.) As in the case of vortex inhibition,[4] the phenomenon seems to be a highly sensitive indicator of polymer conformational changes and degradation. Possible explanations of the vena contracta elimination are considered in terms of (i) fluid jet swell resulting from the extensional flow field upstream of the orifice, and (ii) the solid-like fluid response at the orifice edge resulting from the high Deborah number flow in this region. It appears that the actual mechanism involved varies from polymer to polymer, and these factors as well as others may play a role.

EXPERIMENTAL

The extent of vena contracta inhibition (VCI) was characterized by efflux time measurements made in a Plexiglas tank, 33 cm square and 38 cm deep, with provisions for interchangeable drain orifices (Fig. 1). (The more pronounced the VCI, the smaller the efflux time. This is corroborated by visual observations reported in a later section.) The orifice initially utilized consisted of a sharp-edged short piece of pipe (2.54 cm I.D., 2.29 cm in length), screwed in flush with the tank bottom. The tank was filled with 0.04 m^3 of the solution to be tested, and the liquid was allowed to stabilize for about 1 ks. This ensured that there was no residual fluid motion in the tank when the stopper was removed from the orifice. Such residual motion could lead to vortex formation during drainage. The time for the liquid level to drop from 32 to 4.6 cm relative to the tank bottom was arbitrarily designated as the efflux time t_E. (Repeated investigations have shown that the effects reported below are rather insensitive to the actual levels chosen.) All experiments were performed at room temperature, about 23°C.
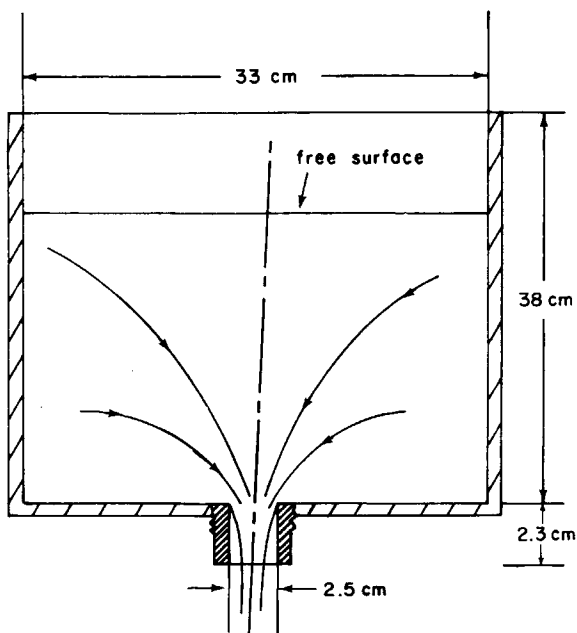

Fig. 1. Plexiglas tank used for efflux time measurements and flow visualization studies.

TABLE I
Summary of Polymer Data

Polymer	Manufacturer	Manufacturer designation	Designation in this paper	Relative drag-reducing ability in deionized water[a]	Molecular weight $\times 10^{-6}$	Vortex inhibition concentration[d], wppm	Pertinent remarks
Poly(ethylene oxide)	Union Carbide	Polyox FRA	P-FRA	1	5.7[b]	7.5	
Poly(ethylene oxide)	Union Carbide	Polyox WSR 301	P-301	2	3.3[b]	30	
Poly(ethylene oxide)	Union Carbide	Polyox WSR 205	P-205	3	0.62[b]	600	
Poly(ethylene oxide)	Union Carbide	Polyox WSR N-3000	P-3000	4		>1000	
Polyacrylamide	Dow	Separan AP 273	S-273	1	9[c]	3	approximately 30% hydrolyzed, highly ionic
Polyacrylamide	Dow	Separan MG 200	S-200	1	9[c]	5	small degree of hydrolysis, slight ionic character
Poly(acrylic acid)	Allied Colloids	Versicol S25	V-25	2	20[c]	3	highly ionized and extended in solution

a This is based on a scale of 1 to 5, with 1 = excellent drag reduction and 5 = no drag reduction. The actual drag-reducing ability depends on Reynolds number, tube size, temperature, etc., and hence these numbers may be used for approximate comparative purposes only.
b Estimated from intrinsic viscosity ($[\eta](dl/g) = 1.25 \times 10^{-4} M_w^{0.78}$).
c Manufacturer estimate.
d Gordon and Balakrishnan.[4]

Seven commercially available water-soluble polymers were investigated, consisting of four "grades" of poly(ethylene oxide) (each grade corresponding to a different molecular weight and molecular weight distribution), one highly ionic and one slightly ionic polyacrylamide, and one poly(acrylic acid). The relative drag-reducing ability of the polymers, the vortex inhibition concentrations, the approximate molecular weights, manufacturer, and other pertinent information are listed in Table I. All solutions were made up in deionized water in concentrated master batches of 1000 wppm and diluted with additional deionized water to the required concentration. Care was taken to minimize degradation during the preparation process. Solution pH was varied by NaOH and HCl addition, and the counterion concentration was increased with NaCl. Solution viscosities of the different polymers were measured in a Wells-Brookfield cone-and-plate viscometer (Brookfield Engineering, Stoughton, Mass.). The shear rate used was 115 sec^{-1}, and the temperature was 25°C.

RESULTS

The efflux time-versus-concentration curves for the seven polymers in deionized water are presented in Figure 2. These curves were obtained by measuring the efflux times at a given initial concentration of 300–500 wppm, and then diluting the solutions to successively lower concentrations. For V-25, P-FRA, and P-301 (for polymer designations, see Table I), the efflux times are identical to that of water below some minimum concentration C_{VC}. However, at the concentration C_{VC} the efflux times suddenly drop by ~30% and then increase very slowly with further increases in concentration. The two polyacrylamides S-273 and S-200 also show a decrease in efflux time above some minimum concentration, but this is of a much more gradual nature, and the maximum reduction attained is smaller. Neither of the two lowest molecular weight samples of poly(ethylene oxide), P-205 and P-3000, showed any significant
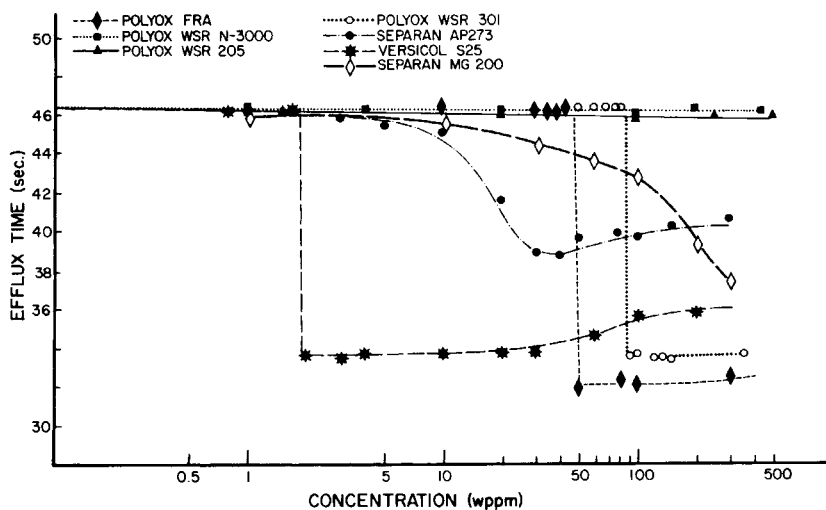

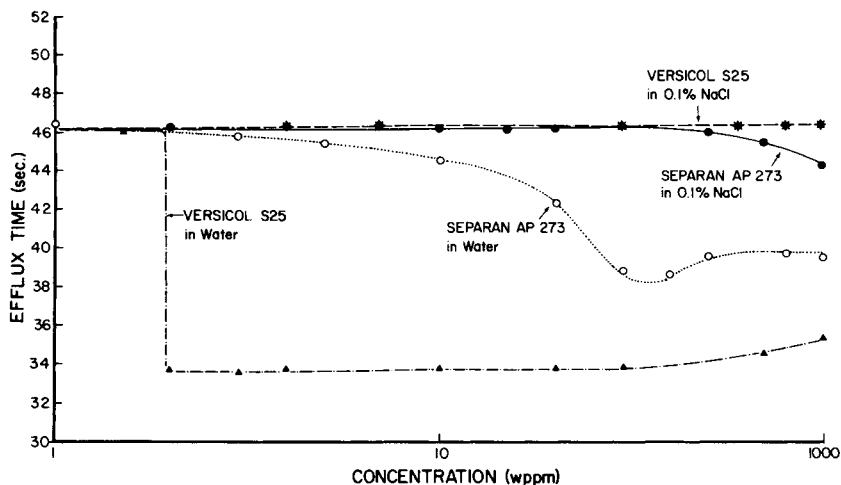Fig. 2. Efflux time vs. concentration behavior for seven polymer samples in deionized water.

Fig. 3. Influence of electrolyte addition on efflux time behavior, 0.1% NaCl.

change in t_E up to the highest concentration level tested, which was 1000 wppm for these polymers.

Conformation Changes

Polyelectrolytes exhibit marked changes in shape and flexibility as solution pH or the counterion concentration is varied. The influence of these changes on the efflux time phenomenon was studied for V-25 and S-273. Figure 3 illustrates the effects of salt addition for both polymers. At a salt level of 0.1%, the efflux time reduction (and any change in vena contracta) was completely eliminated. Figure 4 indicates that a minimum salt concentration of 0.0025% (25 wppm) is sufficient to nullify the efflux time reduction in a 3 wppm po-
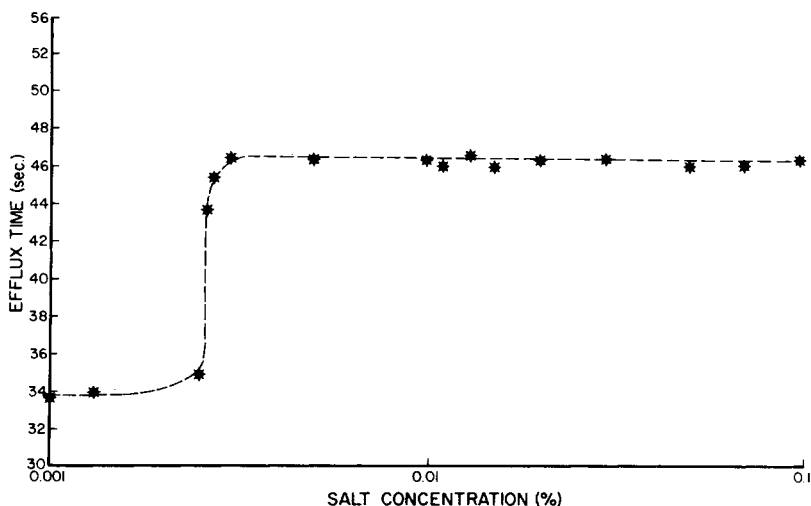

Fig. 4. Influence of electrolyte addition on efflux time behavior for 3 wppm poly(acrylic acid) solution.
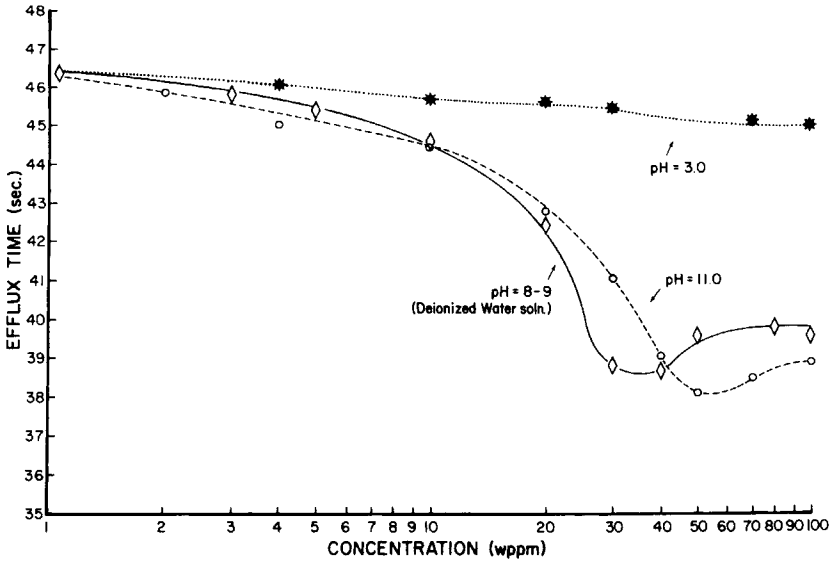
Fig. 5. Change in efflux time behavior with variation in solution pH for polyacrylamide (S-273).

ly(acrylic acid) solution. The influence of solution pH is illustrated in Figures 5 and 6. Both S-273 and V-25 show maximum effectiveness in deionized water, with a corresponding pH level of approximately 8–9. Elevating solution pH causes a modest shift in the t_E curves toward higher concentrations, while at low pH levels the efflux time behavior is identical to that of water.

Degradation

The influence of polymer degradation on efflux time behavior was studied for P-FRA and V-25. These polymers exhibit large differences in their resistance to shear degradation, with P-FRA being much less resistant.[8] Degradation was
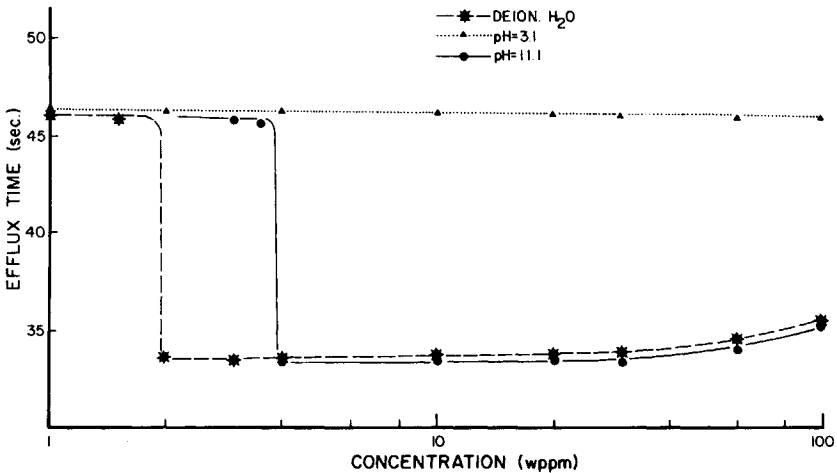

Fig. 6. Change in efflux time behavior with variation in solution pH for poly(acrylic acid) (V-25).
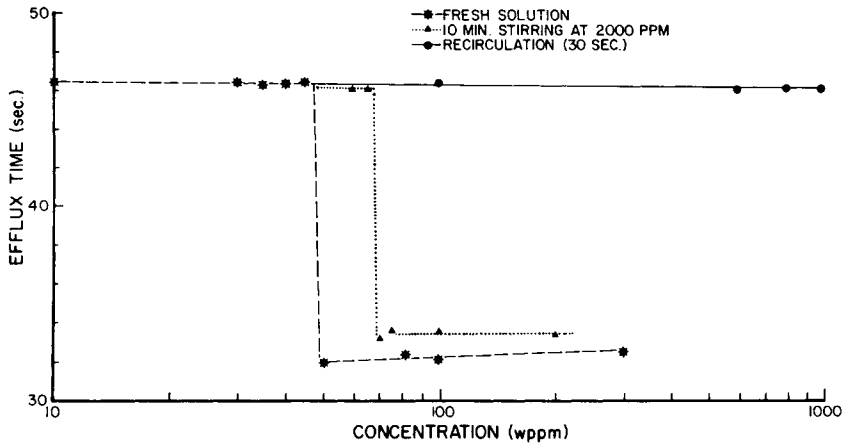
Fig. 7. Influence of degradation on efflux time behavior for poly(ethylene oxide) (P-FRA).

accomplished by either (i) stirring a 2000 wppm solution of the polymer in a large beaker with a high-speed mixer, or (ii) recirculating the polymer solution in a closed flow loop by means of a small centrifugal pump. In technique (ii), the concentrations used were 1000 wppm for P-FRA and 100 wppm for V-25 (this gave approximately equal solution viscosities). Our experience has been that technique (ii), because of the presence of the centrifugal pump, leads to much more severe degradation. This is evident in the case of P-FRA in Figure 7, where 30 sec or recirculation completely eliminates the efflux time reduction, while 10 min of high speed stirring causes only a modest change in behavior. Figure 8 illustrates the variation in efflux time–concentration behavior for V-25 for various levels of degradation. The much greater resistance of this polymer to degradation is evident.

Visual Studies

It was observed that for polymer concentrations below C_{VC}, the emerging liquid jet formed a pronounced vena contracta, indistinguishable from that for
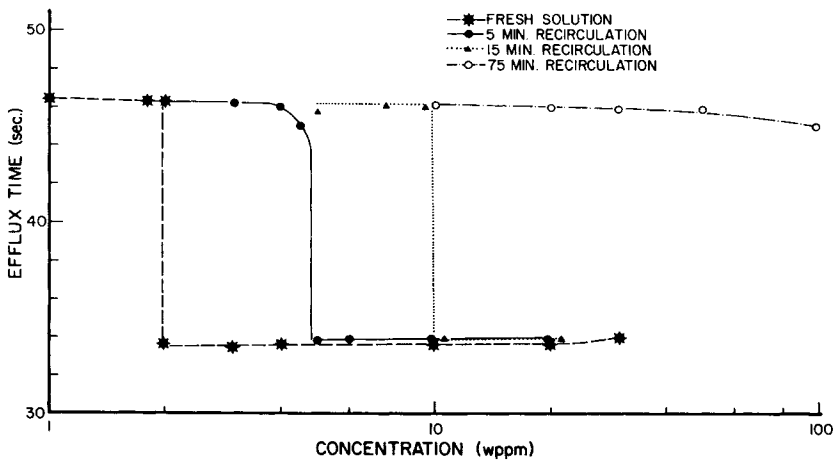

Fig. 8. Influence of degradation on efflux time behavior for poly(acrylic acid) (V-25).
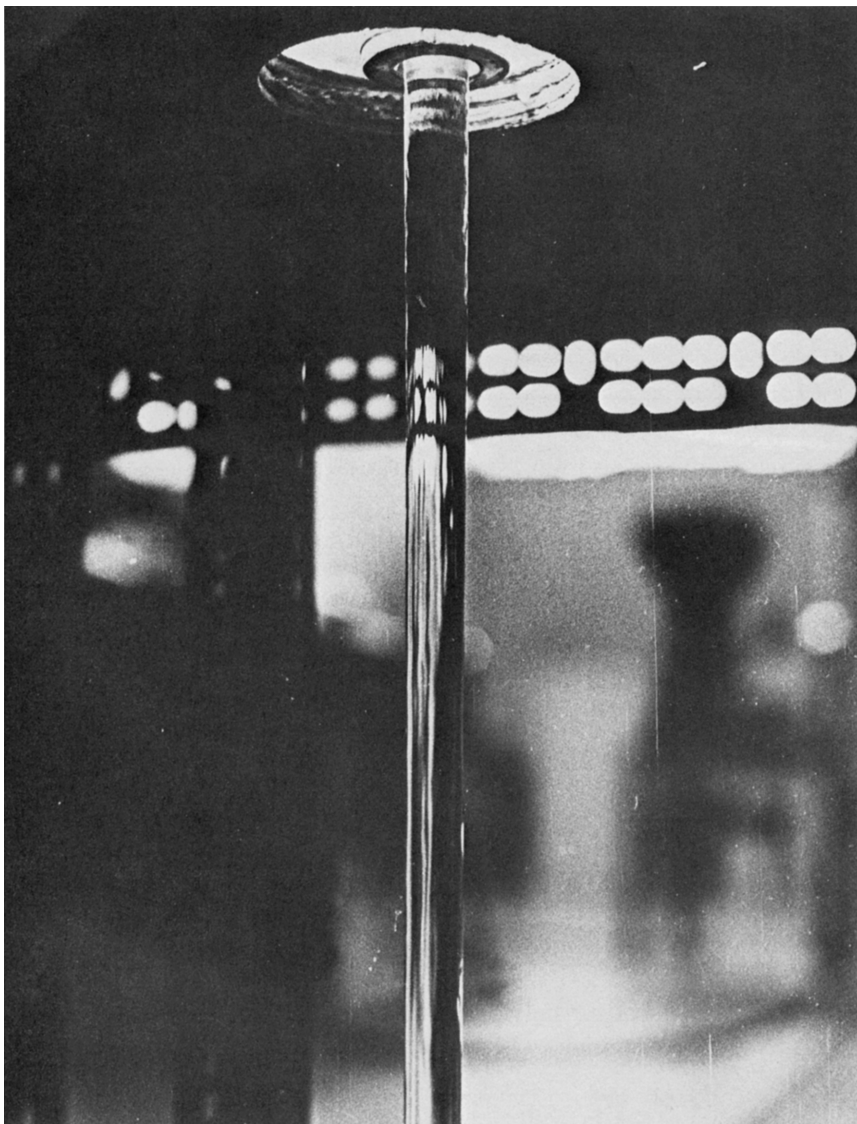
Fig. 9. Vena contracta formation with water.

pure water. The appearance of the water jet is illustrated in Figure 9. On the other hand, above C_{VC}, there was a striking change in the jet appearance, with elimination of the vena contracta. Typical jet appearance for V-25 and P-FRA for concentrations above C_{VC} is illustrated in Figures 10 and 11. A critical concentration for S-273 or S-200 is difficult to define precisely, owing to the very gradual reduction in t_E. However, we did observe a concomitant gradual elimination of the vena contracta. Typical jet appearance for S-273 at 40 wppm is illustrated in Figure 12.

In addition to these studies, we also investigated the velocity field upstream of the orifice using dye injection for flow visualization. Except for S-273 and S-200, the streaklines in the polymer solutions were indistinguishable from those
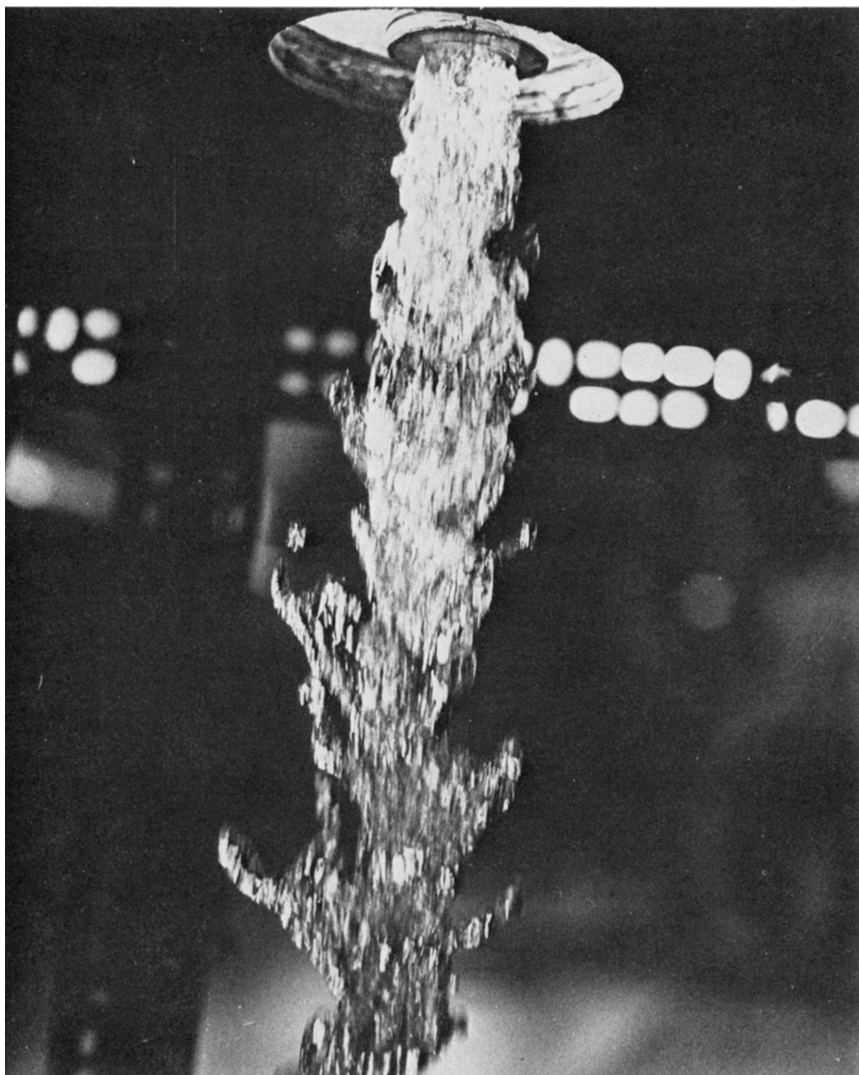
Fig. 10. Appearance of poly(acrylic acid) (V-25) jet for concentration of C_{VC} or larger ($C_{VC} = 2$ wppm).

for pure water, the fluid entering the orifice from a full 180° angle. For both Separan polymers, however, we observed the well-known "wine glass stem" flow field,[5,6] which became pronounced at the concentration level corresponding to the minimum in the t_E–concentration curve.

Influence of Orifice Inlet

The previous results clearly associate the efflux time reduction with elimination of the vena contracta. This may also be demonstrated by utilizing an orifice with the same nominal dimensions as that illustrated in Figure 1, but with a gradually tapered entrance. In this case, there is no vena contracta formation with water. The efflux time results in Figure 13 show no reduction with polymer
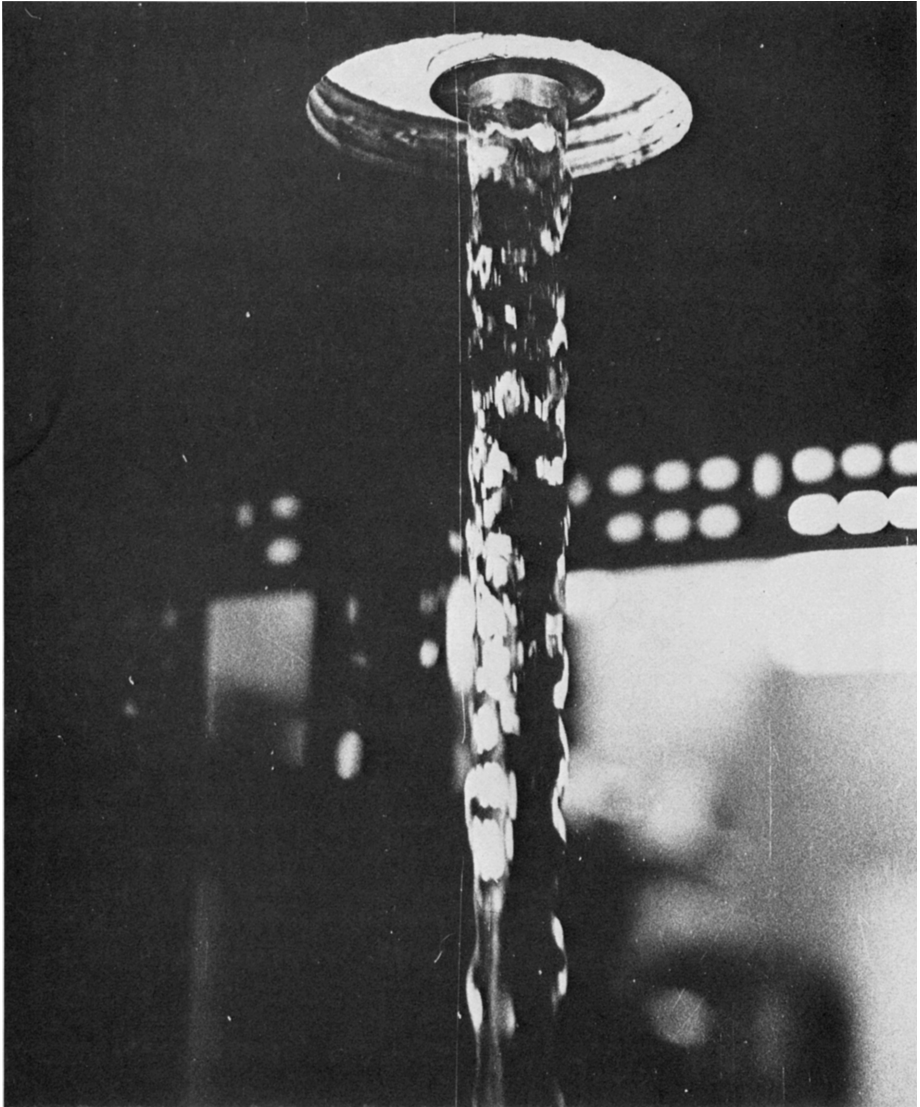
Fig. 11. Appearance of poly(ethylene oxide) (P-FRA) jet for concentration of C_{VC} or larger (C_{VC} = 50 wppm).

addition, and, in fact, a large increase in t_E takes place for S-273 with increasing polymer concentration.

Influence of Orifice Size

A preliminary investigation of the influence of orifice dimensions on VCI was undertaken. Using a solution of 10 wppm of V-25, we examined a number of different orifice diameters and lengths (Table II). It was found that pronounced reduction in efflux time only occurs over a relatively narrow range of the D/L ratio. For low values of D/L, there is no VC formation, even with water; for large values of this ratio, the polymer is apparently incapable of suppressing VC for-
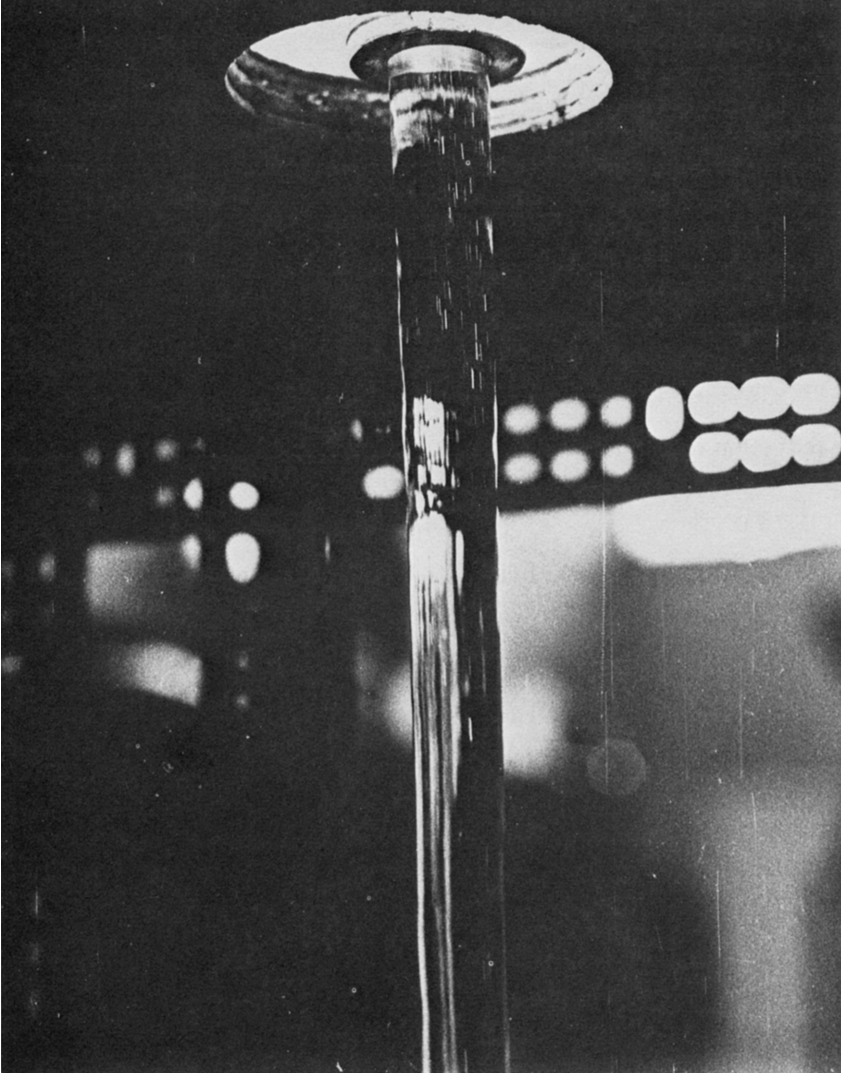
Fig. 12. Appearance of polyacrylamide jet (S-273) for concentration of 40 wppm or larger.

mation. Our studies indicate that VCI occurred only within the approximate limits

$$1.1 \leq D/L \leq 1.3$$

DISCUSSION

The experimental findings presented above demonstrate that the efflux time reduction phenomenon is a sensitive indicator of both polymer conformational changes and degradation. One of the most striking aspects of this effect is the extremely low concentrations of polymer involved: a 30% reduction in t_E occurs with the addition of 2 wppm of Versicol S-25! Figures 9–13 show that the efflux

Fig. 13. Efflux time–concentration behavior with 2.5 cm I.D. tapered entrance tube.

time reduction results from elimination of the vena contracta at the exit orifice. If the volumetric flow rate leaving the orifice is expressed in the form

$$q = CA_0\sqrt{2gh}$$
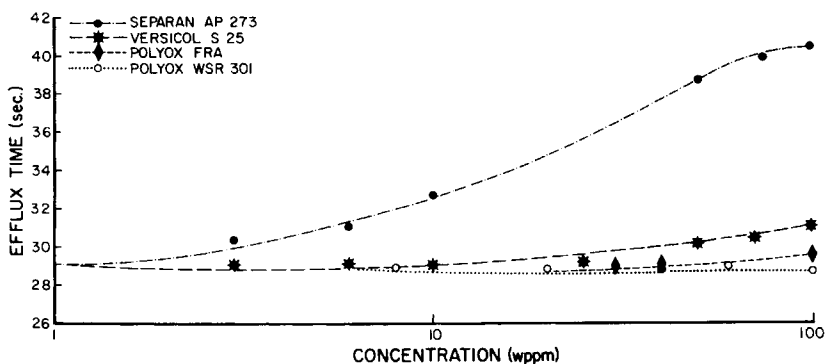
where C is the discharge coefficient, then for water we find $C_W = 0.69$, a reasonable value. On the other hand, for V-25, or P-FRA above C_{VC}, $C_P \approx 0.93$, implying a 35% increase in cross-sectional area.

Correlation with Drag Reduction and Vortex Inhibition

One rather surprising finding of the present study is that there does not appear to be a close correspondence between drag-reduction effectiveness and effectiveness with regard to vena contracta inhibition. This is evident in the case of V-25 [poly(acrylic acid)], with a C_{VC} of only 2 wppm. This value is a factor of 16 lower than C_{VC} for P-FRA, a superior drag reducer. Even more surprising is a comparison of the V-25 and S-273 results. S-273 is significantly more effective in drag reduction than V-25 and has an identical vortex inhibition concentration, but is far less effective in reducing vena contracta formation. Also of interest is the fact that both Separan polymers show only a gradual reduction in t_E, rather than a sharp discontinuity. S-273 is chemically quite similar to V-25, having undergone approximately 25–30% hydrolysis of the acrylamide units to sodium acrylate. It should be emphasized that there was no vortex formation or surface "dimple" formation during any of these experiments. This was achieved by the long stabilization period prior to testing.

Influence of Conformation

Figures 3–6 illustrate the effects of changes in polymer conformation on vena contracta inhibition. Salt addition to either S-273 or V-25 causes a marked reduction in coil expansion owing to the increased shielding of ionized carboxyl groups from one another. This is reflected by the large drop in solution viscosity (Table III). The efflux time reduction is no longer observed.

Coil expansion may also be diminished by variations in solution pH. Raising the pH to 11 causes a modest drop in viscosity and a small decrease in VC inhibition ability for both V-25 and S-273. HCl addition to a pH of 3 causes a large

TABLE II
Influence of Orifice Size on Efflux Time Reduction[a]

Orifice diameter, cm	2.54	1.91	1.55	0.83	0.75	0.67	1.55	0.75
Orifice length, cm	0.64	0.64	0.64	0.64	0.64	0.64	1.28	0.32
D/L	4.0	3.0	2.4	1.31	1.18	1.05	1.22	2.38
Efflux time, water, sec	23.0	40.0	58.5	208	275	267	62.8	266
Efflux time, polymer, sec	23.0	40.0	57.4	204	224	268	48.3	253
C_W	0.65	0.66	0.68	0.66	0.62	0.78	0.64	0.63
C_P	0.65	0.66	0.70	0.68	0.75	0.78	0.82	0.67
C_W/C_P	1.0	1.0	1.03	1.02	1.22	1.00	1.28	1.07

[a] Efflux time taken as time for level to drop from 27.5 to 13.8 cm. Polymer solution used in all cases was V-25 at 10 wppm.

TABLE III
Summary of Viscosity Data

Polymer	Solution	Concentration (wppm)	Viscosity[a] (Ns/m^2)
	At 200 wppm[b]		
S-273	deionized water (pH ≈ 8.6)		0.0086
S-273	high pH (≈11.5)		0.0058
S-273	low pH (≈3.5)		0.0025
S-273	0.1M NaCl		0.0020
V-25	deionized water (pH ≈ 8.1)		0.011
V-25	high pH (≈11.5)		0.0070
V-25	low pH (≈3.5)		0.0013
V-25	0.1M NaCl		0.0025
	At Concentration Corresponding to Onset of Vena Contracta Inhibition		
S-273	deionized water	3	0.0012[c]
S-200	deionized water	4	0.0012
V-25	deionized water	2	0.0013
P-FRA	deionized water	50	0.0012
P-301	deionized water	90	0.0011

[a] All measurements were made in a cone-and-plate viscometer at a shear rate of 115 sec^{-1} and a temperature of 25°C. Attempts to measure viscosity in a laboratory capillary viscometer for the polyelectrolytes were frustrated by the continual presence of undissolved gel-type particles, which caused plugging and erratic behavior.

[b] At this concentration, the effects of variation in solution environment are much more readily apparent.

[c] Reproducibility for viscosities below about 0.002 Ns/m^2 was quite poor (±30%).

decrease in viscosity and concomitant elimination of the efflux time reduction.

In a recent study, we have shown that both the poly(acrylic acid) and polyacrylamide molecules appear to assume much "stiffer" structures in low pH solution than in salt solution, at approximately the same degree of extension.[7] In either case, the efflux time reduction is no longer observed, suggesting that the stiffness of the coil does not play an important role. On the other hand, molecular extension in space, as reflected by the solution viscosity, appears to be a significant factor.

Degradation

Figures 7 and 8 indicate that the present phenomenon is a sensitive indicator of polymer degradation. It is clear from these results that V-25 offers much more resistance to shear degradation than P-FRA, in agreement with earlier findings, both by Ting and Little[8] and also our group.[9] Since degradation is known to preferentially attack the highest molecular weight species in a given sample, it appears that VC inhibition is most dependent on these highest molecular weight molecules.

THEORETICAL EXPLANATION OF VENA CONTRACTA SUPPRESSION

There appear to be at least two possible qualitative explanations of vena contracta inhibition. The first of these is in terms of solution die swell, which

would be expected to assume increasing importance at higher polymer concentrations. The second explanation takes account of the high Deborah number flow field existing near the orifice. Such a flow could induce an effective solid-like response in the solution, ultimately resulting in an "effective rounding" or tapering of the orifice edge. Let us now examine these two possible explanations in more detail.

Die Swell

Polymer solutions are known to expand upon exiting from a tube, the expansion increasing with increasing flow rate and decreasing tube length. This die swell, or extrudate expansion, will also in general increase with increasing polymer concentration. Theoretically, one may relate the amount of swelling to the fluid tensile stress T_E acting in the flow direction just upstream of the tube exit, as follows:[10]

$$\left(\frac{d_e}{d}\right)^2 = \frac{1}{\dfrac{8}{(\bar{v}d)^2} \displaystyle\int_0^{d/2} r\left(v^2 - \frac{T_E}{\rho}\right) dr}$$

here, d_e is the diameter of the emerging jet, d is the tube diameter, $\bar{v}$ is the average velocity, and v is the local velocity. In the present experiment, T_E is determined by the flow field upstream of the orifice, which in the case of S-273 and S-200 assumes the well-known wine-glass stem pattern in the concentration range coincident with t_E reduction. As Metzner has noted, such a flow can lead to extremely large values of T_E.[6,11] (We have recently reported polymer "recoil" with S-273 at 20 wppm, another manifestation of the large T_E.[12]) Thus, the results for both polyacrylamides are consistent with a die swell type of mechanism—a gradual decrease in t_E with increasing concentration and a pronounced converging flow into the orifice. On the other hand, P-FRA, P-301, and V-25 show an abrupt transition in t_E and do not exhibit a wine-glass stem flow field in the concentration range of interest. It would appear that these latter three polymers cause VC inhibition by a qualitatively different mechanism.

Deborah Number Considerations

Metzner and co-workers[13-15] have noted that when the ratio of polymer solution relaxation time to characteristic flow time approaches unity, the fluid may exhibit "solid-like" behavior. This dimensionless ratio is referred to as the *Deborah number*, N_{De}, and is defined quantitatively by[13]

$$N_{\text{De}} = \theta\sqrt{\frac{D\Gamma}{Dt}} \tag{1}$$

where θ is the solution relaxation time, D/Dt is the material derivative, and Γ is the square root of the second invariant of the rate of strain tensor. This concept has successfully explained a variety of viscoelastic phenomena including the insensitivity of heat transfer probes to velocity[14] and the abnormally high pressure drops in flow through porous media.[15]

Consider the region of flow near the section of tank wall adjacent to the perimeter of the orifice. It is in this region that the solution experiences the largest

rate of change in deformation levels. If these are sufficiently high, such that N_{DE} → 1, we would expect the fluid to behave like a solid "blob,"[14] resulting in a pronounced reduction in the velocity contribution normal to the orifice center line. Since it is this normal velocity which gives rise to the vena contracta,[16] the extent of vena contracta formation should be significantly suppressed.

To test this hypothesis, a numerical estimate of N_{De} is required. An analytical solution to the flow through a related geometry, a two-dimensional orifice, has been obtained for the case of an inviscid fluid, with a calculated contraction coefficient[17] of 0.61.

This is in excellent agreement with the high Reynolds number result for flow through a circular orifice, and we assume that this solution may be used to obtain reasonable estimates of $D\Gamma/Dt$, at the same mean velocities as in the three-dimensional orifice.

The actual calculation of $D\Gamma/Dt$ presents some difficulty, because of the fact that the velocity field is not given explicitly. One starts with the following implicit equations for u and v, the x and y components of the velocity vector, obtained from potential flow theory:[17]

$$\frac{2.575}{d}(x + iy - id) = i(\lambda - 1) - (1 - \lambda^2)^{1/2} + \tanh^{-1}(1 - \lambda^2)^{1/2} \quad (2)$$

$$\lambda = i\sinh\left(\ln\frac{u_0}{q} + i\theta\right) \quad (3)$$

here q is the speed $(\sqrt{u^2 + v^2})$, $\theta = \tan^{-1}(-v/u)$, λ is a dummy variable, d is the orifice diameter, u_0 is the free-stream velocity, and x and y are measured from the center of the orifice (with x in the flow direction).

From eqs. (2)–(4), one may obtain the velocity field within the region of interest. Following this, straightforward numerical techniques are used to estimate

$$d_{ij} = \begin{bmatrix} \dfrac{\partial u}{\partial x} & \dfrac{1}{2}\left[\dfrac{\partial u}{\partial y} + \dfrac{\partial v}{\partial x}\right] & 0 \\[2ex] \dfrac{1}{2}\left[\dfrac{\partial u}{\partial y} + \dfrac{\partial v}{\partial x}\right] & \dfrac{\partial v}{\partial y} & 0 \\[2ex] 0 & 0 & 0 \end{bmatrix}$$

$$\Gamma = \sqrt{\frac{1}{2}d_{ij}d_{ji}}$$

and

$$\frac{D\Gamma}{Dt} = u\frac{\partial\Gamma}{\partial x} + v\frac{\partial\Gamma}{\partial y}$$

at each point in the flow field. The results of thic calculation indicate that fairly large values of $\sqrt{D\Gamma/Dt}$ may occur, particularly in the vicinity of the orifice edge. At a free stream velocity of 200 cm/sec (a typical value), calculated values of $\sqrt{D\Gamma/Dt}$ vary from 5 to well over 200 sec^{-1}. As a very conservative estimate, we shall choose 10 sec^{-1} as a characteristic flow time. It follows that solid-like response should occur when the polymer solution relaxation time is of the order of

$$\theta \approx \frac{1}{10\text{ sec}^{-1}} = 0.1\text{ sec}$$

TABLE IV
Relaxation Time Calculations

Polymer	Concentration	Relaxation time[a] $\theta = \dfrac{0.42\,(\eta - \eta_s)M}{cRT}$, sec
P-FRA	50	0.006
P-301	90	0.0009
V-25	2	0.7
S-273	3	0.1
S-200	4	0.1

[a] Uncertainties in $(\eta - \eta_s)$ and M can lead to large errors in the calculated values of θ. These values should be considered rough order-of-magnitude estimates only.

Calculated values of θ at the onset of vena contracta inhibition are listed in Table IV. (For S-273 and S-200, this onset was chosen at the concentration at which the efflux time reduction first begins.) These were obtained from the Zimm Theory,[18] using the expression

$$\theta = \frac{0.42\,(\eta - \eta_s)M}{cRT} \tag{4}$$

where η is the solution viscosity and η_s is the solvent viscosity. In principle, eq. (4) is valid only for a monodisperse solution in a theta solvent, but it is expected to also give a reasonable estimate for polydisperse solutions in good solvents. In this case, M must be some suitable molecular weight average. Considering the uncertainty in estimating θ, the values in Table III must be considered no more than order of magnitude approximations. Nevertheless, we see that for the three polyelectrolytes S-273, S-200, and V-25, θ is of the right magnitude, while for P-FRA or P-301 it appears to be too small for a Deborah number type of explanation to be valid. Complicating this finding is, of course, the fact that the polyacrylamide and poly(acrylic acid) polymers behave so dramatically different in the present experiment.

CONCLUSIONS

The above experimental results establish vena contracta inhibition as a potentially useful viscoelastic phenomenon, operative at extremely low concentrations. The explanation of this phenomenon is still somewhat obscure. The presence of an extensional (wine-glass stem) flow along with a gradual reduction in t_E for both polyacrylamides suggests a die swell effect occurring here, while the large value of N_{De} for poly(acrylic acid) implies a "solid-like" response, with consequent reduction of radially directed fluid into the emerging jet. One still wonders, though, why the polyacrylamides behave so differently from the other polymers and why the estimated values of θ for poly(ethylene oxide) are so low. Qualitatively, polyacrylamide appears to more readily form three-dimensional network structures, perhaps as a result of strong hydrogen bonding ability, and this may have some bearing on the flow field. The low values of θ for poly(ethylene oxide) are based on an average molecular weight and solution viscosity. For a sufficiently broad distribution, much larger relaxation times may occur.

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