

## Vortex Inhibition: A New Viscoelastic Effect With Importance in Drag Reduction and Polymer Characterization

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### Synopsis

We recently reported a new viscoelastic effect, wherein remarkably small quantities of certain high molecular weight polymers inhibit the tendency of water to form a vortex, as it drains from a large tank. This phenomenon is referred to as vortex inhibition (V.I.). Here, we examine the influence of molecular weight and molecular weight distribution on V.I. and the close relationship between those polymers which reduce drag and those which exhibit vortex inhibition. It has also been found that V.I. is a sensitive measure of polymer degradation, much more so than intrinsic viscosity. The significance of these findings in drag reduction, and for macromolecular characterization in general, is discussed.

### INTRODUCTION

It is well known that the resistance of certain solutions of long-chain polymers to *turbulent* flow is lower than that of the solvent alone. This effect, commonly referred to as "drag reduction (DR)," has been extensively studied, and much is now known about the dependence of DR on bulk flow conditions and molecular variables.<sup>1-3</sup>

An especially careful and penetrating study of DR was recently reported by Paterson and Abernathy.<sup>4</sup> These authors worked with five grades of Union Carbide's polyox [poly(ethylene oxide)] resins<sup>5</sup>: WSR 301, WSR 205, WSR 35, WSR N750, and WSR N80. These resins are known to have marked differences in molecular weight, molecular weight distribution, and drag-reducing ability. Paterson and Abernathy concluded that the WSR grades 301, 205, and 35 possess very broad molecular weight distributions, and that the high molecular weight "tails" of these distributions were primarily responsible for the drag-reduction effect. In addition, this high molecular weight tail was found to be preferentially degraded in a shear field, leading to large decreases in DR but only small decreases in intrinsic viscosity (which depends on the entire molecular weight distribution, not just the high molecular weight tail). Similar findings have been reported for polyisobutylene in organic solvents.<sup>6</sup>

For exactly the same reasons, the intrinsic viscosity, a measure of  $M_w$  for poly(ethylene oxide),<sup>7</sup> failed to correlate with the relative drag-reducing

effectiveness of the different polyox solutions. For example, a 75 wppm (weight parts per million) solution of WSR 35, with  $[\eta] = 2.51$  dl/g, was shown to exhibit far better drag reduction than a 75 wppm solution of WSR N750, with  $[\eta] = 3.46$ . Degradation of the WSR 35 solution by a turbulent shear field resulted in roughly a 60% increase in friction factor (drag), but only a 1% decrease in  $[\eta]$  (to 2.48). Numerous additional examples may be found in Paterson and Abernathy.<sup>4</sup>

It is clear, then, that there is a need for a rheological test (hopefully, of the same degree of simplicity as the measurement of  $[\eta]$ ) which uniquely correlates the drag-reducing ability of different macromolecular homologs and at the same time may be used as a sensitive measure of polymer degradation, especially degradation of the higher molecular weight components. In this paper, such a test is presented and discussed.

### VORTEX INHIBITION

As we recently reported in a brief note,<sup>8</sup> an interesting effect (referred to hereafter as vortex inhibition, V.I.) was observed during the course of some experiments on drag reduction. A square Plexiglas tank (Fig. 1.) was filled with tap water and stirred vigorously with a paddle. (The original experiments were performed with a cylindrical tank<sup>8</sup>; use of a square tank simplifies flow visualization studies.) The bottom plug was then removed, and after a few moments a vortex formed, extending from the surface of the liquid to the small drain hole at the bottom of the tank. The vortex was extremely stable, and once formed, it remained intact until the tank had drained. The same experiment was then repeated with a dilute polymer solution. This time, as long as the polymer concentration was above some minimum value (denoted by  $C_{VI}$ ), the vortex would not complete. Instead, it would begin to form, dip below the top surface of the liquid, start

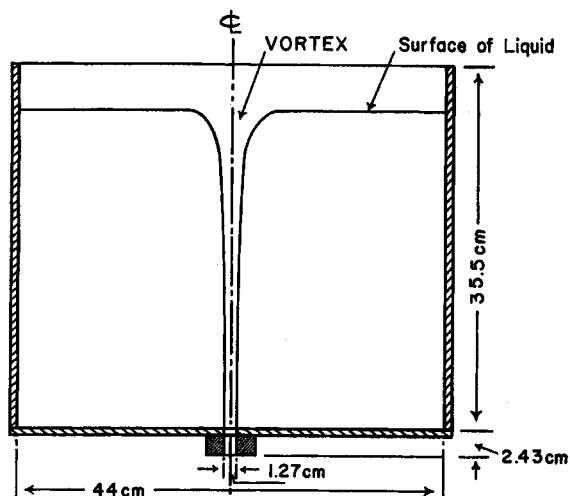


Fig. 1. Vortex inhibition tank. Illustration of vortex formation in water.

TABLE I  
Summary of Data

Polymer designation	Polymer type	Manufacturer	$C_{vi}$ , wppm	$C_{Dn}$ , wppm	$[\eta]$ , dl/g
Polyox FRA	poly(ethylene oxide)	Union Carbide	7.5	9	23.5
Polyox WSR 301	poly(ethylene oxide)	Union Carbide	30	20	15.1
Polyox WSR 205	poly(ethylene oxide)	Union Carbide	600	150	4.1
Polyox WSR N750	poly(ethylene oxide)	Union Carbide	3000	550	3.3
Separan AP 273	polyacrylamide	Dow	3	5	50 <sup>a</sup>
Separan AP 30	polyacrylamide	Dow	40	35	31 <sup>a</sup>
Polyhall 295	polyacrylamide	Stein Hall	10	9	25 <sup>a</sup>
Cellulose gum 7H	carboxymethylcellulose	Hercules	400	600	25 <sup>a</sup>

<sup>a</sup> These values are for  $\eta_{sp}/c$  at 20 wppm. The  $\eta_{sp}/c$ -vs.- $c$  curves turned up sharply at lower concentrations, and precise extrapolation to  $c = 0$  was not possible. All data are for tap water.

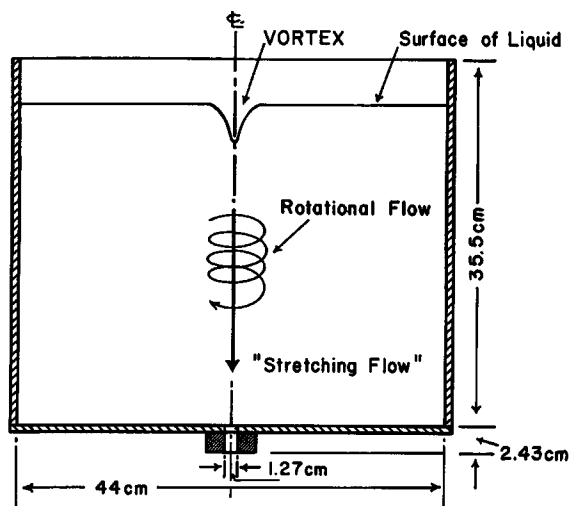


Fig. 2. Vortex inhibition tank. Illustration of vortex inhibition with polymer solution and proposed flow field.

to oscillate rather rapidly, but never reach the bottom drain hole. As the concentration of polymer was reduced below  $C_{VI}$ , the vortex began completing more and more frequently (i.e., it would complete, break, and then complete again), until finally at sufficiently low concentrations the vortex became stable (identical to water). On the other hand, as the polymer concentration was continually increased above  $C_{VI}$ , the vortex became increasingly stunted (Fig. 2), and the rapid oscillations—which are most pronounced at concentrations near  $C_{VI}$ —disappeared completely.

The most striking aspect of this effect is the extremely low concentrations required (Table I). For Polyox FRA and AP 273, some vortex inhibition could be observed at concentrations as low as 1 to 2 wppm. As the following results illustrate, V.I. correlates extremely well with the drag-reducing ability of various polymers, especially for the better drag reducers. It is also exceptionally sensitive to polymer degradation, much more so than intrinsic viscosity. These findings strongly suggest that V.I. is a property associated with the very largest molecules in a given polymer sample. Thus, the phenomenon may prove useful, in conjunction with other standard techniques, as a simple method for characterizing molecular weight distribution.

## EXPERIMENTAL

The vortex inhibition tests were carried out in the square Plexiglas tank illustrated in Figure 1.  $C_{VI}$  was defined as the lowest concentration at which the vortex would not complete. Completion was, of course, easily observed visually and was accompanied by a "slurping" sound as air was drawn out of the exit hole. The following dilution sequence was used in

measuring  $C_{VI}$  (in wppm): 3000, 2000, 1500, 1000, 800, 600, 400, 300, 200, 150, 100, 75, 50, 40, 30, 20, 15, 10, 7.5, 5, 4, 3, 2, 1. For most polymers, the sequence was started well below 500 wppm.

For each concentration, the tank was filled to 65 liters, stirred vigorously, and allowed to drain. If the vortex completed while the liquid level was between 58 and 53 liters,  $C_{VI}$  was taken as the next highest concentration.\* Thus, if completion occurs at 20 wppm,  $C_{VI} = 30$  wppm. Perhaps surprisingly, the results of this somewhat arbitrary procedure were remarkably reproducible.

Drag-reduction measurements were carried out with a cylindrical Plexiglas tank, 64.5 cm tall and 44 cm in diameter, to which was attached a stainless steel tube of 0.45 cm diameter and 185 cm length. The times for the liquid level in the tank to drop from 92 to 87 liters and 91 to 86 liters were measured and averaged for water and for the various polymer solutions. These averaged times are denoted by  $t_w$  and  $t_p$ , respectively. Per cent drag reduction was then calculated as follows:

$$\% \text{ DR} \equiv 100(t_w - t_p)/t_w.$$

## RESULTS

### Drag Reduction and Vortex Inhibition

The polymers used in our study are listed in Table I, along with corresponding values of  $C_{VI}$ ,  $[\eta]$ , and  $C_{DR}$ .  $C_{DR}$  is the lowest concentration at which each polymer showed maximum drag reduction. The per cent drag reduction versus concentration curves are given in Figure 3. All reported experimental results are for tap water, at approximately 70°F. A few experiments were performed with distilled water. These resulted in rather slight variations in  $C_{VI}$  and  $C_{DR}$ , but  $[\eta]$ —for the polyelectrolyte solutions (Separan, Polyhall, and Cellulose gum 7H)—increased by roughly a factor of 10.

Inspection of Table I and Figure 3 reveals that  $C_{VI}$  is an excellent ordering parameter for the drag-reducing effectiveness of the different polymers. In particular the most effective drag reducers, with maximums in their DR-versus-concentration curves in the range 5–40 wppm, also exhibit vortex inhibition in approximately the same concentration range. On the other hand, the less effective polymers, such as WSR 205, WSR N750, and CMC 7H (Cellulose gum 7H), have values of  $C_{VI}$  and  $C_{DR}$  about one to two orders of magnitude higher. It is also evident that intrinsic viscosity by itself is not as useful in predicting relative drag-reducing effectiveness, except in the case of homologous series of macromolecules (of similarly "shaped" molecular weight distributions<sup>4</sup>).

\* The drop from 65 to 58 liters was a "stabilization period," arbitrarily chosen, to eliminate effects associated with the initial stirring. If completion occurred above 58 liters, it usually also occurred between 58 and 53 liters.

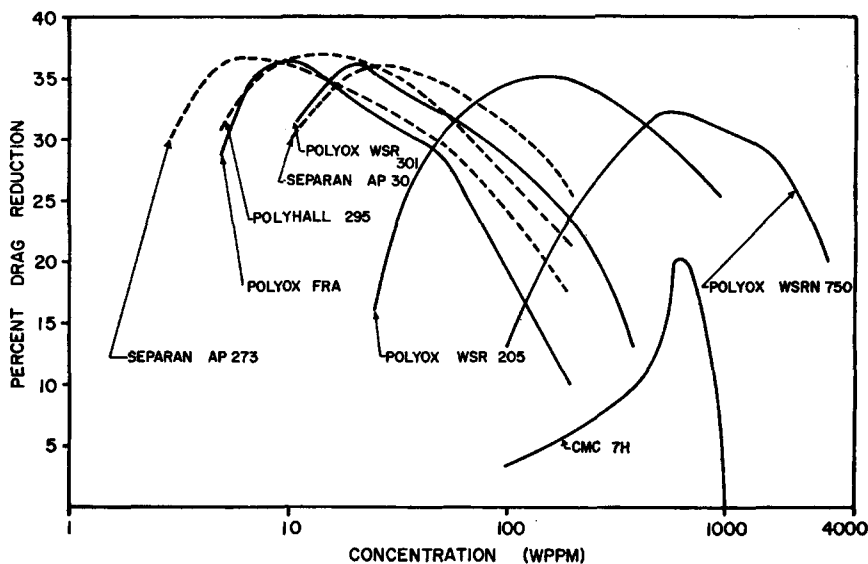


Fig. 3. Summary of drag-reduction data.

These results strongly suggest that vortex inhibition may be used to predict a priori whether or not a given macromolecule will be an effective drag reducer. By "effective" we mean exhibiting pronounced DR at concentrations below, say, 50 wppm. To our knowledge, no other rheological test presently available is capable of characterizing drag-reducing ability in such dilute solutions. It has been suggested that pitiuity,<sup>4,5</sup> i.e., the ability of a polymer solution to pull out in long threadlike structures, might also be used in such a manner, but this turns out not to be true in practice. Pitiuity is barely exhibited at the low concentrations of interest, except for Polyox FRA and WSR 301. The polyacrylamides, which are of the same degree of drag-reducing ability as the Polyoxes, show significantly less pitiuity at all concentrations. There is also the as yet unresolved question of how to "measure" pitiuity.

### Polymer Degradation

As noted previously, we believe V.I. is dependent on only the highest molecular weight components in a given molecular weight distribution. This would explain why  $C_{VI}$  for FRA is three orders of magnitude smaller than  $C_{VI}$  for WSR N750, which possesses a much smaller "tail." Since sharply fractionated samples of polymer were not at our disposal, other ways were sought to test this assumed dependence on the high molecular weight components.

One obvious test is polymer degradation. Theory and experiment both suggest that in dilute solutions, the higher molecular weight components are preferentially degraded by a shear field.<sup>4,6,9</sup> Thus, we subjected

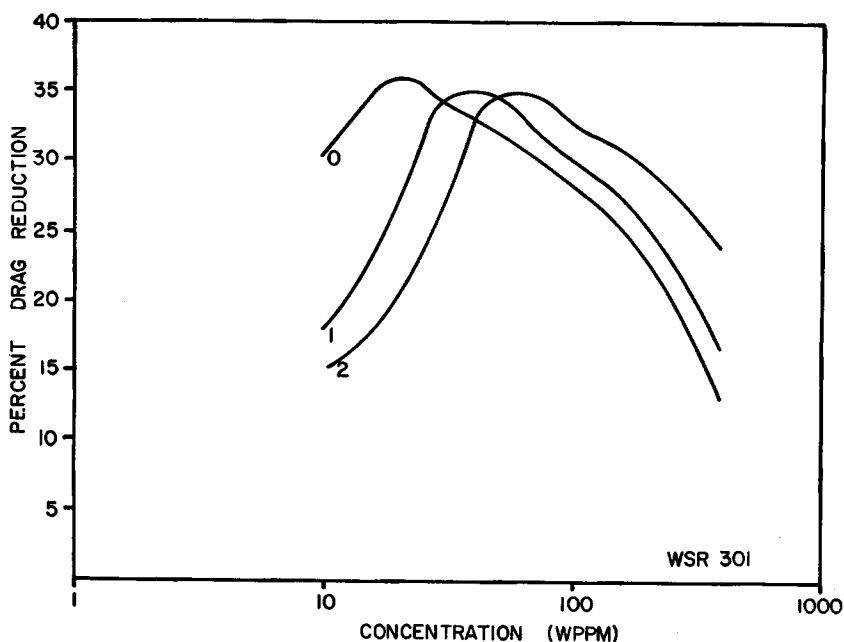


Fig. 4. Drag reduction vs. concentration for various amounts of degradation in WSR 301 solutions.

solutions of FRA, WSR 301, and AP 273 (200, 400, and 200 wppm, respectively) to increasing amounts of degradation as follows: (0) fresh solution; (1) fresh solution pumped through 24 ft of 0.5-in. i.d. Tygon tubing at 7 gallons/min by a Randolph positive displacement pump (known to impart a rather gentle shearing action); (2) fresh solution pumped through 24 ft of 0.5-in. i.d. Tygon tubing at 5-7\* gallons/min by a centrifugal pump (known to produce an intense shearing action); (3) 180 liters of fresh solution recirculated for 9 min in a closed-loop system using a centrifugal pump and then subjected to procedure (2) (roughly equivalent to two passes through pump); (4) same as (3) but 18 min of circulation (roughly equivalent to three passes through pump); (5) same as (3) but 36 min of circulation.

The results of this study are given in Figures 4-7 and Table II. In Figure 7, we have plotted  $\eta_R/\eta_{R0}$  ( $\eta_{R0}$  = relative viscosity of fresh solution;  $\eta_R$  was measured at 200, 400 and 100 wppm for FRA, WSR 301, and AP 273, respectively) versus degree of degradation, rather than following the time-honored procedure of characterizing polymer degradation through intrinsic viscosity. The present method was preferred, since calculation of changes in  $[\eta]$ , from measured values of  $\eta_R$ , leads to a mathematical, but not actual, enhancement of the sensitivity of viscosity measurements to degradation. For example, if  $\eta_{R0} = 1.3$  and  $\eta_R$  (after degradation) = 1.2,

\* Depending on fluid pumped. Output was greatest for polymer solutions.

TABLE II  
Results of Degradation Study

Polymer		Degree of degradation					
		0	1	2	3	4	5
Polyox FRA	$\eta_R$ @ 200 wppm	1.57	1.46	1.29	1.26		
	$C_{VI}$	15	40	175	>200		
Polyox WSR 301	$\eta_R$ @ 400 wppm	1.75	1.68	1.57			
	$C_{VI}$	40 <sup>a</sup>	75	>400			
Separan AP 273	$\eta_R$ @ 100 wppm	1.61	1.61	1.56		1.53	1.49
	$C_{VI}$	3	3	7.5		40	75

<sup>a</sup>  $C_{VI}$  varied from 30 to 40 for this polymer.

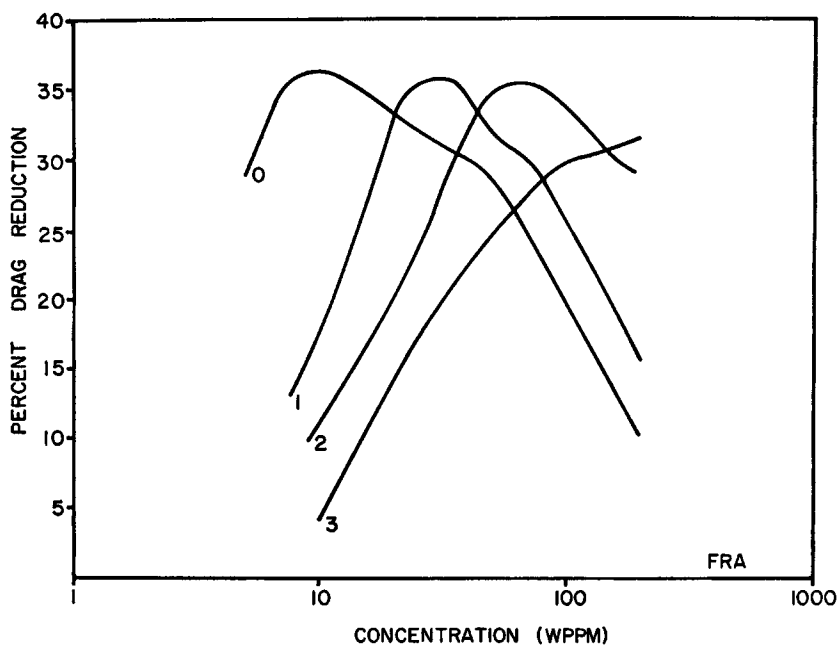


Fig. 5. Drag reduction vs. concentration for various amounts of degradation in FRA solutions.

both for 200 wppm, then  $\eta_R/\eta_{R0} = 0.92$  corresponding to an 8% decrease in viscosity. However,

$$[\eta]/[\eta]_0 = \frac{(\eta_R - 1)/c}{(\eta_{R0} - 1)/c} = \frac{0.2}{0.3} = 0.67,$$

neglecting the Huggins correction to  $[\eta]$ , or we calculate approximately a 33% drop in intrinsic viscosity.

Figure 7 illustrates that  $C_{VI}$  is an extremely sensitive measure of polymer degradation. One pass of a 400 wppm solution of WSR 301 through the centrifugal pump increased  $C_{VI}$  from 40 to well over 400 wppm (at this concentration, there was hardly any evidence of inhibition in the degraded



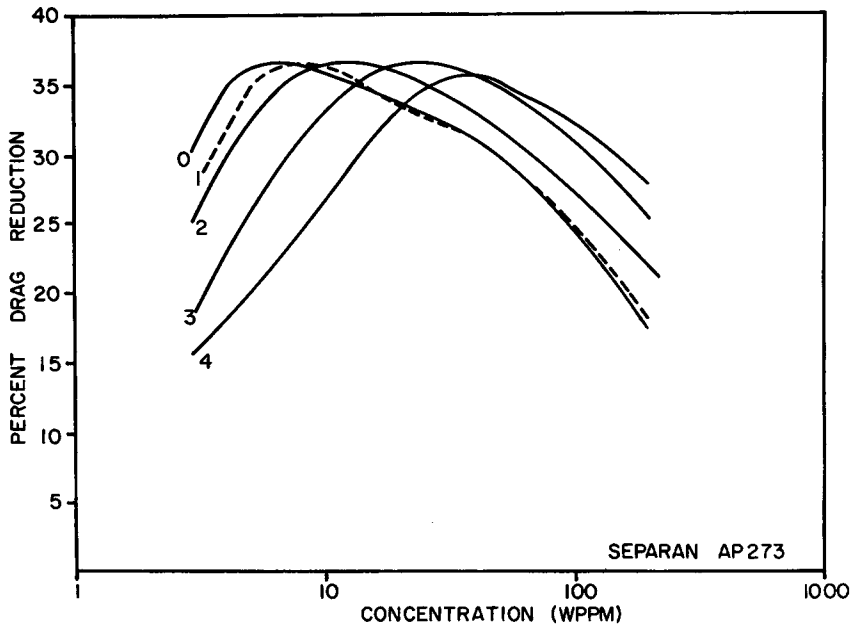


Fig. 6. Drag reduction vs. concentration for various amounts of degradation in AP 273 solutions.

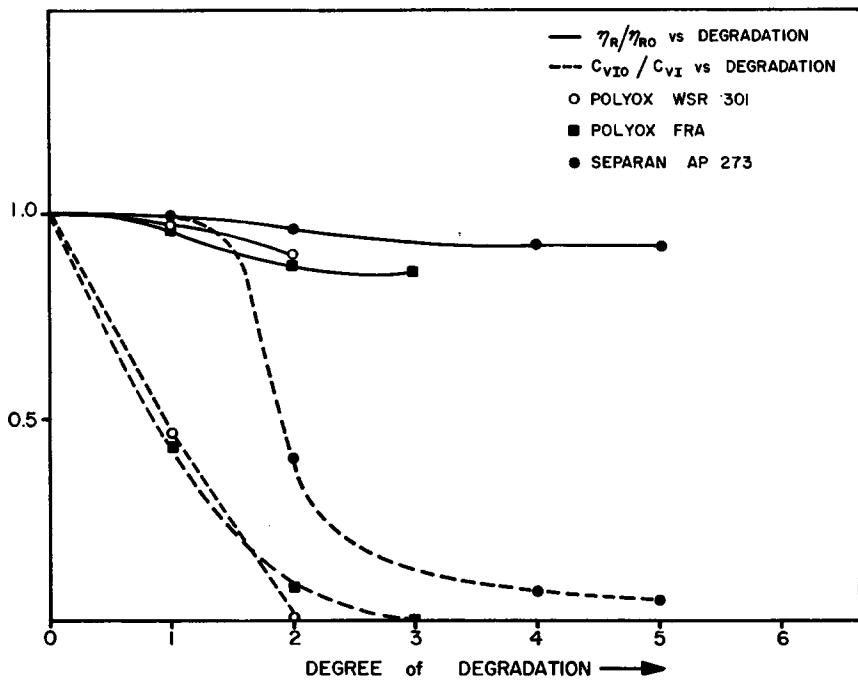


Fig. 7. Graphic summary of degradation results.

TABLE III  
Vortex Inhibition of Polyox Mixtures\*

Mixture, parts of weight		$C_{VI}(\text{add})$	$C_{VI}(\text{tail})$	$C_{VI}(\text{exptl})$
FRA	WSR 205			
1	1	300	15	15
1	2	400	22.5	22.5
1	3	450	30	30
1	4	480	37.5	37.5

\* FRA ( $C_{VI} = 7.5$ ) and WSR 205 ( $C_{VI} = 600$ ).

solution). This should be contrasted with a negligible change in  $\eta_R$ , and a slight shift to the right for the drag-reduction curve (Fig. 4). Similar results were obtained for FRA and AP 273. (Note that AP 273 is much more resistant to shear degradation than FRA or WSR 301.) These findings suggest that  $C_{VI}$  is primarily dependent on the highest molecular weight species in a given solution, even more so than drag reduction (at least for the low Reynolds numbers, 8500–13,500, in this experiment). Thus, we envision a small "select" group of macromolecules, lying at the extreme right end of the distribution curve, which determine  $C_{VI}$  and are preferentially degraded in a shear field.

Further indirect proof of our hypothesis may be inferred from the results of studies with mixtures of FRA and WSR 205. If  $C_{VI}$  does indeed depend solely on the largest macromolecules, then  $C_{VI}$  for mixtures should be equal to that value calculated on the basis of the fraction containing the high molecular weight component. Thus,  $C_{VI}$  for a 1:1 mixture of FRA and WSR 205 should be approximately  $C_{VI}(\text{tail}) = 2 \times C_{VI}$  for FRA alone, the WSR 205 contributing an essentially negligible number of very high molecular weight molecules. On the other hand, if  $C_{VI}$  depends on the entire distribution, then  $C_{VI}$  for a 1:1 mixture should be about  $C_{VI}(\text{add}) = [C_{VI}(\text{FRA}) + C_{VI}(\text{WSR 205})]/2.0$ . In Table III, values of  $C_{VI}(\text{tail})$ ,  $C_{VI}(\text{add})$ , and  $C_{VI}(\text{exptl})$  are given for various FRA–205 mixtures. (A slightly different dilution sequence than that given previously was used in this study.) As expected, the  $C_{VI}(\text{tail})$  values agree with the experimental findings, again indirectly suggesting the almost exclusive dependence of V.I. on the highest molecular weight molecules.

### IMPORTANCE OF STRETCHING MOTIONS

Probably the single most commonly accepted explanation of DR is that it is a result of the unusually high resistance of dilute polymer solutions to stretching motions.<sup>4,10–12</sup> Recent theoretical calculations indicate that this resistance increases dramatically with increasing molecular weight,<sup>13</sup> consistent with the dependence of DR on the higher molecular weight fractions.

Visual observations of the flow in our V.I. experiments revealed the presence of long filamentary structures continuously being pulled out

from the tip of the vortex. The flow in this region appeared to consist of a stretching or pure extentional motion, superimposed on which is a rotational flow (Fig. 2). This picture is, of course, strictly qualitative and requires much more thorough study. Such a stretching motion would, however, in light of our previous remarks, explain why vortex inhibition occurs.

### CONCLUSIONS

The primary result of this study is the demonstration that the phenomenon of vortex inhibition is a sensitive measure of drag-reducing ability and macromolecular degradation. Indirect evidence suggests that V.I. depends on only the highest molecular weight components in a given distribution. Thus, the effect may also be of use in molecular weight distribution studies.

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