

## Diameter Dependence of the Cutoff Molecular Weights of Drag-Reducing Polymers

ROBERT Y. TING, *Naval Research Laboratory, Washington, D.C. 20375*

### Synopsis

Drag reduction data of poly(ethylene oxide) obtained in turbulent pipe flows were analyzed. A cutoff molecular weight for drag reduction was determined by correlating the drag reduction effectiveness with polymer molecular weight. Based on a time-correlation onset concept, this critical molecular weight was found to depend on the pipe diameter and Reynolds number. This effect is examined using available experimental data.

### INTRODUCTION

The drag-reducing property of certain high molecular weight polymers is now well known. When a few parts per million by weight of these polymers are dissolved in a good solvent, such as poly(ethylene oxide) in water, the turbulent frictional drag can be reduced by as much as 70% when compared with the case of solvent alone. The drag reduction effect normally will not take place until the polymer molecular weight exceeds a certain critical value, which may be termed the "cutoff molecular weight." Several investigators<sup>1,2,3</sup> have observed the existence of such a cutoff molecular weight, but found quite different values for it. In this report, the difference in these values is discussed in relation to the pipe diameters of the test apparatus used.

### EXPERIMENTAL

A series of poly(ethylene oxide) compounds (Polyox, Union Carbide) were used. Solutions were carefully prepared in freshly distilled water. Viscosity measurements were carried out using a multibulb viscometer to determine polymer molecular weights. The Mark-Houwink relation developed by Shin<sup>4</sup> was applied in this case at a shear rate of  $15 \text{ sec}^{-1}$ :

$$[\eta] = 1.03 \times 10^{-4} M_w^{0.78} \text{ (dl/g) in water at } 25^\circ\text{C} \quad (1)$$

Table I shows the physical properties of the samples.

The drag reduction property of the polymer solutions were obtained in a simple turbulent flow system described elsewhere.<sup>5</sup> Basically, it is a once-through pipe system at controlled flow rates with a pipe 0.62 cm in diameter. Pressure taps were mounted at approximately 135 and 175 diameters downstream from the entrance to measure the pressure difference. This pressure

drop was used to deduce the wall shear stresses  $\tau_w$ , from which the per cent drag reduction was computed:

$$\text{per cent drag reduction} = \left[ 1 - \frac{\tau_{w\text{-polymer}}}{\tau_{w\text{-water}}} \right] \times 100\% \quad (2)$$

### CUTOFF MOLECULAR WEIGHT

In turbulent pipe flows, the per cent drag reduction increases with polymer concentration at a fixed flow rate until a saturation drag reduction effect is produced. Then, the per cent drag reduction either remains constant or slowly decreases with further increase of concentration. On a unit concentration basis, drag reduction, therefore, becomes more efficient as polymer concentration decreases.<sup>6</sup> For the dilute solution range, Virk<sup>7</sup> found that the concentration dependence of drag reduction obeyed a drag reduction equation which, in the modified form suggested by Little,<sup>2</sup> appears as

$$\frac{DR}{DR_m} = \frac{c}{c + [c]} \quad (3)$$

where  $c$  is concentration,  $DR$  is per cent drag reduction,  $DR_m$  is the "maximum" drag reduction as  $c \rightarrow \infty$ , and  $[c]$  is the intrinsic concentration. The validity of this equation has been tested for many drag-reducing species<sup>8</sup> both in capillaries<sup>2</sup> and in laboratory-size pipes.<sup>3,7</sup>

By measuring the per cent drag reduction of a certain compound as a function of the solution concentration, one can easily determine the parameters in eq. (3), for it shows that a linear relationship exists between  $c/DR$  and  $c$ . The slope and the intercept of such a linear plot give values of  $DR_m$  and  $[c]$ , respectively. Drag reduction effectiveness of a polymer compound may be characterized by using the parameter  $DR_m/[c]$ , which denotes the "efficiency" of the polymer compound on a unit concentration basis at infinite dilution:

$$\lim_{c \rightarrow 0} \frac{DR}{c} = \frac{DR_m}{[c]} \quad (4)$$

This parameter is specially useful for it scales linearly with polymer molecular weight, as shown in Figure 1. A least-squares fit shows that the linear plot has an intercept of molecular weight  $3.3 \times 10^5$  at  $DR_m/[c] = 0$ . This may be taken as the cutoff molecular weight  $M_w^*$ , below which no drag reduction is observed under the flow condition of  $Re = 9000$  in the present pipe

Table I  
Polyox Physical Properties

Sample	$[\eta]$ , dl/g	$M_w \times 10^{-6}$
FRA	24.3	7.73
WSR-301	18.0	5.26
Coagulant	12.5	3.30
WSR-1105	4.3	0.84
WSR-205	3.9	0.74

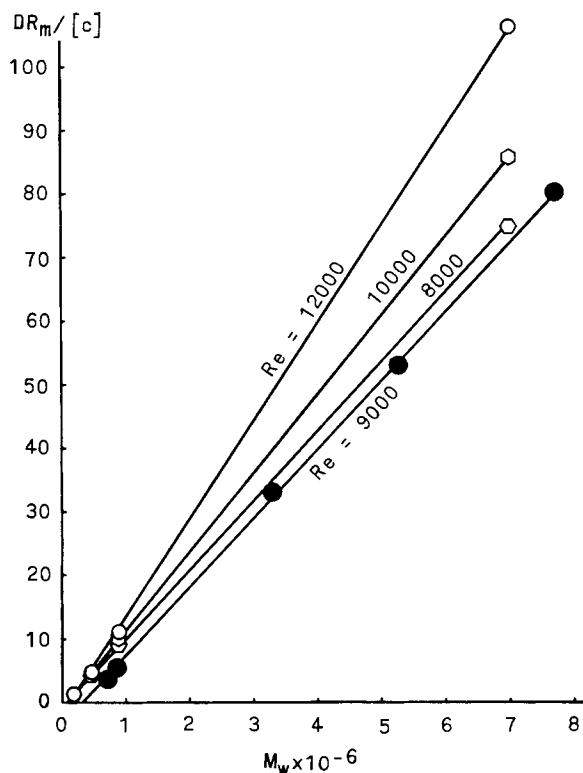


Fig. 1. Drag reduction efficiency as a function of polymer molecular weight. The open data points are results from Little.<sup>2</sup> The closed data points are of the present study.

system.  $Re$  is the Reynolds number defined as  $Re = uD/\nu$ , where  $u$  is the flow velocity,  $D$  is the pipe diameter, and  $\nu$  is the kinematic viscosity.

Polyox drag reduction data reported by Little<sup>2</sup> and Virk<sup>7</sup> were also analyzed using the same procedure to evaluate the effectiveness parameter  $DR_m/[c]$ . Linear scaling effects were also observed, as shown in Figures 1 and 2. These data show that the slope of the plot has a strong dependence on the Reynolds number. Increased slope with increasing Reynolds number indicates that a greater drag reduction effect is obtained at higher Reynolds numbers (provided that mechanical degradation does not occur<sup>6</sup>). Within experimental error, the cutoff molecular weight  $M_w^*$ , on the other hand, remains reasonably constant for each flow system. For three sets of experimental results,  $M_w^*$  ranges from  $1.4 \times 10^5$  to  $3.3 \times 10^5$ . This difference will now be discussed.

### DIAMETER EFFECT

Under a given flow condition, i.e., a given pipe diameter and a specified flow rate, one may carry out pressure drop measurements using a series of polymer samples with increasing molecular weight. When the molecular weight gradually increases and exceeds the cutoff value  $M_w^*$ , drag reduction effect will take place. Therefore, the cutoff molecular weight may be viewed as an analogy to the onset of the drag reduction effect. Numerous investiga-

tors have examined the onset phenomenon based on a correlation of polymer relaxation time with the flow time.<sup>9-11</sup> Lumley<sup>12</sup> recently considered the dynamics of an isolated polymer molecule in flow and showed that the onset criterion is for

$$\frac{u_*^2 \lambda}{\nu} > \frac{3}{2} \quad (5)$$

where  $u_*$  is the shear velocity and  $\lambda$  is the terminal relaxation time. The ratio  $\nu/u_*^2$  is the smallest time scale characterizing the flow. Since the shear velocity is defined by

$$\tau_w = \frac{1}{2} \rho u_*^2 = \frac{f}{8} \rho u^2 \quad (6)$$

and the frictional factor is related to the Reynolds number

$$f = 0.3164/\text{Re}^{0.25} \quad (7)$$

at the onset,<sup>13</sup> one may have the following expression for the flow time:

$$\frac{\nu}{u_*^2} = \frac{12.64D^2}{\nu \text{Re}^{1.75}} \quad (8)$$

The terminal relaxation time is given in the molecular theories such as that of Zimm:<sup>14</sup>

$$\lambda = \frac{6\eta_s[\eta]_0 M_w}{\pi^2 R T} \quad (9)$$

where  $\eta_s$  is the solvent viscosity,  $[\eta]_0$  the intrinsic viscosity at zero shear rate,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. Generally,  $[\eta]_0$  is related to the molecular weight by the Mark-Houwink relation:<sup>15</sup>

$$[\eta]_0 = K M_w^a \quad (10)$$

Therefore, one may write the onset condition of eq. (5) as

$$0.048 \frac{\eta_s K M_w^{*1+a}}{R T} \cdot \frac{\nu \text{Re}^{1.75}}{D^2} \sim \frac{3}{2} \quad (11)$$

For a given polymer-solvent combination at, say, room temperature, eq. (11) reduces to

$$M_w^{*1+a} \sim (\text{constant}) \frac{D^2}{\text{Re}^{1.75}} \quad (12)$$

Similarly, if the Kolmogorov time scale<sup>16</sup> is used as the basis of the interaction between polymer molecules and the dissipative range of turbulent flows, then the flow time is taken to be

$$\tau = \left(\frac{\nu}{\epsilon}\right)^{1/2} \sim \left(\frac{\nu D}{u' 3}\right)^{1/2}$$

where  $\epsilon$  is turbulent dissipation and  $u'$  is the root-mean-square turbulent fluctuation. Experimental measurements indicated that  $u'/u_*$  is nearly independent of the Reynolds number in both the Newtonian<sup>17</sup> and drag-reducing fluids.<sup>18</sup> From eqs. (6) and (7), it can be shown that  $u'/u$  is a weak function of the Reynolds number. At onset, it therefore requires

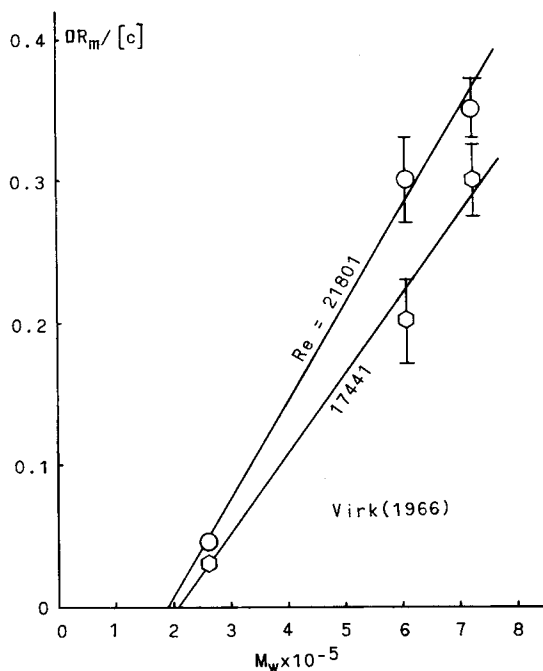


Fig. 2. Drag reduction efficiency as a function of polymer molecular weight. Results are from Virk.<sup>7</sup>

$$M_w^* 1+a \sim (\text{constant}) \frac{D^2}{\text{Re}^{1.3125}} \quad (13)$$

It is known<sup>12</sup> that drag reduction not only depends on the Reynolds number, but also scales with the pipe size to show a diameter effect. Therefore, in discussing the drag reduction phenomenon, both  $D$  and  $\text{Re}$  are to be treated as independent variables. Both eqs. (12) and (13) suggest that the cutoff molecular weight varies with the pipe diameter  $D$  and the flow rate through  $\text{Re}$ . The prediction of the Reynolds number dependence is slightly different; the accuracy of available drag reduction data is not sufficient to distinguish this difference and it requires more experimental data to resolve in the future. Specially, the presently available data of Little<sup>2</sup> and Virk,<sup>7</sup> as shown in Figures 1 and 2, seem to indicate that the cutoff molecular weight is rather insensitive to the variation of Reynolds number over a wide range. In this case, eq. (12) may be approximated by

$$M_w^* \sim (\text{constant}) \frac{2}{D^{1+a}}$$

which gives the diameter dependence of the cutoff molecular weight in drag reduction.

The values of  $M_w^*$  deduced from the results for three different flow systems were plotted in Figure 3 as a function of the pipe diameter. It shows that as the diameter increases, the onset of drag reduction does not take place until a higher molecular weight polymer species becomes available. This is probably because the size of dissipative turbulent eddies increases with the physical dimension of the flow system. Bigger molecules of higher molecular

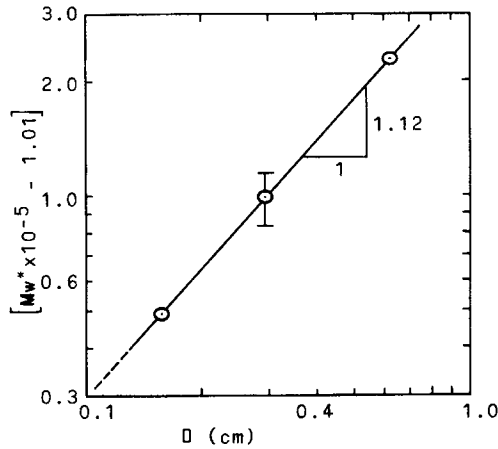


Fig. 3. The cutoff molecular weight as a function of the pipe diameter.

weight are required in order to effectively interact with such eddies so to reduce viscous dissipation and thus frictional drag. These data were obtained for poly(ethylene oxide) compounds, which have  $\alpha = 0.78$  from eq. (1). Therefore,

$$M_w^* \sim (\text{constant})D^{1.12} \quad (14)$$

The experimental data clearly indicate that the correlation between  $M_w^*$  and  $D$  does not pass through the origin. The solid curve in Figure 3 is the representation of

$$M_w^* \times 10^{-5} = 3.93 D^{1.12} + 1.01 \quad (15)$$

with the pipe diameter  $D$  in centimeters. The second term on the right-hand side of eq. (15), as it is different from eq. (14), represents a shift of the axis. This may be attributed to the polydispersity of the Polyox material used in these experiments. While Lumley's onset criterion was developed for monodispersed polymers, Polyox compounds are known to be highly polydispersed, i.e., characterized by a very broad molecular weight distribution. Recent efforts<sup>19,20</sup> have attempted to examine the effect of polydispersity on drag reduction, but progress so far has been limited.

It should be noted that Virk used Polyox-WSRN series in his work.<sup>7</sup> These compounds were different from the Polyox-WSR series used by Little<sup>2</sup> as well as in this study. As part of the manufacturing process, the WSRN series polymers were treated with high-energy neutron bombardment so that the high molecular weight tail of the distribution has suffered extensive breakdown. Consequently, the average molecular weight shifts to much lower values and the molecular weight distribution becomes comparatively narrower. The molecular weights of the compounds used by Virk were less than one million, as can be seen in Figure 2. On the other hand, the WSR series Polyox compounds had retained the high molecular weight tail, and the average molecular weights were as high as several millions. Therefore, the data presented here are from polymers with very different but broad molecular weight distributions. But, in experimentally characterizing the drag-re-

ducing property of these highly polydispersed materials, the present results seem to suggest that the viscosity-averaged molecular weight is extremely useful. By examining the linear scaling law of the drag reduction efficiency with this molecular weight for different polymer species at various Reynolds number ranges, additional light may be shed on a more basic understanding of the interaction between polymer molecules and turbulence.

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