

## Characterization of Drag Reduction and Degradation Effects in the Turbulent Pipe Flow of Dilute Polymer Solutions

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### Synopsis

Turbulent drag reduction data were obtained at  $Re = 9000$  in a 0.62-cm-I.D. pipe for five Polyox compounds covering a wide range of molecular weights. The concentration dependence of drag reduction was shown to obey an improved form of Virk's drag reduction equation, which was previously applied only to flows in capillary tubes. The efficiency of the drag-reducing polymer additives on a unit concentration basis at infinite dilution was determined by using a characteristic parameter,  $DR_m/[c]$ , for each compound. A linear relationship was found to exist between this parameter and polymer molecular weight. The polymer degradation data were analyzed through use of a variable related to the dissipated energy in the wall region. The polymer molecular weight was found to decrease as a hyperbolic function of the dissipated energy function. By examining the change of molecular weight with respect to this function, a degradation index characteristic of the entire Polyox polymer family was established. This index may be of general application and provide a method by which the shear stability of various species of drag-reducing polymers may be meaningfully compared.

### INTRODUCTION

The ability of very high molecular weight polymeric additives to reduce frictional drag in the turbulent flow of Newtonian fluids has been known for more than two decades. For example, a 60% reduction in the friction of pure water in turbulent pipe flow can easily be achieved by the addition of as little as 5 parts per million by weight (ppm) of polymers such as poly(ethylene oxide). This phenomenon is of considerable engineering interest because of the great potential it offers in increasing the capacities of hydraulic pipelines and in the development of new marine systems capable of higher speeds and longer range. However, highly effective drag-reducing agents may have only limited technologic applications if they undergo very rapid breakdown in the flow field. Therefore, in designing a drag reduction system, the shear stability of a polymer solution is a factor of comparable importance to its drag-reducing effectiveness and should be carefully characterized in the laboratory.

Numerous investigators have observed a rapid decline of drag reduction effectiveness upon repeated use of a given polymer solution. Ellis<sup>1</sup> found

that a shear-treated 10 ppm Polyox [poly(ethylene oxide), Union Carbide Corporation] solution had lost a significant degree of drag reduction ability when compared with the 54% drag reduction obtained for the untreated solution. Paterson and Aberhathy<sup>2</sup> made molecular weight analyses together with drag reduction measurements using Polyox solutions and concluded that the degradation process ultimately results in a decrease in polymer molecular weight. A similar behavior for polyacrylamide was also reported by Ellis et al.,<sup>3</sup> Fisher and Rodriguez,<sup>4</sup> and Wade and Kumar.<sup>5</sup> While these studies contain an abundance of graphic information on the degradation behavior of aqueous polymer solutions, they merely compare the shear stability of different species in the specific flow apparatus used and do not introduce parameters that are useful for characterizing the polymer degradation phenomena.

It is generally accepted that the high shear field associated with the turbulence is responsible for polymer degradation. Since chemical and thermal degradations are negligibly small under ordinary conditions,<sup>2</sup> the turbulent shear stress presumably induces scission of molecular entanglements or of individual molecules associated with very high local shear rates. On the other hand, White<sup>6</sup> proposed that degradation is caused by a rapid chemical reaction initiated by turbulence. In this report, the dependence of drag reduction on concentration and molecular weight for five samples of the Polyox-WSR series is presented and discussed; a new method for the laboratory characterization of polymer degradation in turbulent pipe flow is also proposed. It is believed that application of this characterization technique to other drag-reducing polymer species will shed some light on those mechanisms responsible for the degradation process.

## EXPERIMENTAL

### Method

Consider a drag-reducing polymer solution flowing through a very long pipe. Downstream, the solution loses part of its drag-reducing ability because of the continuous exposure to the turbulent shear field. Laboratory simulation of such a case can be achieved by repeatedly running the same test sample in a once-through pipe system. By recording the change in drag reduction for every pass, the degradation history of the sample can be easily obtained. The only complication which might develop in this simulation would be from degradation effects which can conceivably take place when the liquid jet mixes with the stationary fluid at the exit of the pipe. However, it has been experimentally demonstrated<sup>7</sup> that the contribution of jet turbulence effects is extremely small and can be neglected. By studying drag reduction in pipes with entrances of different shapes, Fruman et al.<sup>8</sup> also demonstrated that the degradation effect at the entrance was negligible.

### Equipment

A once-through turbulent pipe flow system, similar to the type previously described by Hoyt,<sup>9</sup> was used in measuring the drag reduction of the polymer solutions. The device was basically a metal syringe, driven by a linear actuator, which directly pushed the test liquid through a 0.62-cm-I.D. pipe. The actuator was driven by a 1/4-hp electric motor the delivery rate of which was determined by a motor speed controller. The travel limits of the actuator were set by microswitches within the actuator gear box. A precision electric timer recorded the exact time for each stroke of the plunger. The flow rate was monitored by a small d.c. generator coupled to the motor drive. At the pipe entrance, a 0.47-cm-I.D. orifice was placed to ensure fully developed turbulent flow in the test section. Two pressure taps were placed at approximately 135 and 175 diameters from the upstream end of the flow. The pressure difference between taps was measured by a differential pressure transducer. The outputs from the d.c. generator and the transducer were recorded continuously on a dual-channel recorder. The flow rate and the pressure drop due to the resulting turbulent flow in the pipe were then calculated using the calibrated constants of the apparatus. The per cent drag reduction ( $DR\%$ ) was computed by the following relationship:

$$DR\% = \left[ 1 - \frac{f_{\text{polymer}}}{f_{\text{water}}} \right] \times 100\% \quad (1)$$

where  $f_{(\ )}$  is the fractional factor,  $8\tau_w/\rho u^2$ ;  $\tau_w$  is the wall shear stress;  $\rho$  is the liquid density; and  $u$  is the mean velocity in the pipe. The viscosity and density of water at the test temperature were used for calculation purposes. The total experimental error in evaluating the per cent drag reduction was estimated to be less than  $\pm 2\%$ .

### Materials

Polyox samples were obtained from the Union Carbide Corporation and were used as received. The viscosity-average molecular weights were determined by the following relation<sup>10</sup>:

$$[\eta] = 1.25 \times 10^{-4} M_w^{0.78} \quad \text{at } 30^\circ\text{C}. \quad (2)$$

Physical properties of these Polyox samples are included in Table I. Freshly distilled water was used exclusively in preparing all solutions. Since irreproducible mixing techniques can cause large variations in solution properties, all solutions were prepared carefully by the following procedures. The additives in powder form were sprinkled uniformly over a large surface of distilled water to avoid clumping of particles. Solution was allowed to take place through diffusion at 5°C for a period of several days. Occasional gentle stirring with a glass rod ensured adequate dispersion of solute. Visual inspection of the fluid after that period showed no inhomogeneities which could be detected through local refractive index

TABLE I  
Properties of Polyox Polymers

Polymer	$[\eta]$ , dl/g	$M_w \times 10^{-6}$	$[c]$ , ppm	$DR_m$ , %
WSR-205	4.00	0.60	9.09	58.0
WSR-1105	6.02	1.00	6.25	67.0
Coagulant	11.05	2.20	2.10	76.3
WSR-301	15.30	3.33	1.41	79.0
FRA	19.60	4.58	1.01	80.5

differences. When these procedures were instituted, reproducible results were obtained if solutions were used within one week of preparation.

## RESULTS AND DISCUSSION

### Concentration Dependence of Drag Reduction

Little<sup>11</sup> has recently introduced a simplified form of Virk's universal drag reduction relation<sup>12</sup> to account for the concentration dependence of drag reduction in capillary tubes. The equation takes the form

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

at a fixed Reynolds number, where  $c$  = concentration,  $DR$  = per cent drag reduction,  $DR_m$  = the "maximum" drag reduction as  $c \rightarrow \infty$ , and  $[c]$  = intrinsic concentration. Rearrangement of eq. (3) leads to

$$\frac{c}{DR} = \frac{[c]}{DR_m} + \frac{c}{DR_m} \quad (4)$$

Equation (4) indicates that a linear relationship exists between  $c/DR$  and  $c$  when the concentration dependence of drag reduction obeys eq. (3). This was tested by applying eq. (3) to the results obtained in the present system, and it was found that this relation holds very well for all the Polyox samples over a wide range of per cent drag reduction values. As a typical example, Figure 1 presents the results of Polyox Coagulant at Reynolds number 9000. While the per cent drag reduction increases up to 66% when the polymer concentration increases from 0 to 15 ppm, a plot of  $c/DR$  versus  $c$  is linear and shows the validity of eq. (3). The intercept value at  $c/DR = 0$  yields the intrinsic concentration,  $[c]$ , and this quantity divided by the intercept at  $c = 0$  permits evaluation of  $DR_m$ . The values of  $[c]$  and  $DR_m$  for all the Polyox polymers tested are tabulated in Table I.

It is significant that the present results extend the validity of this drag reduction equation from flows in capillary tubes to those in larger pipes, at least to the 0.62-cm pipe used here. The parameters  $[c]$  and  $DR_m$ , being constants characteristic of a given polymer compound, may serve as a measure of the drag reduction effectiveness and thus are handy tools for laboratory characterization of drag-reducing polymers. The physical

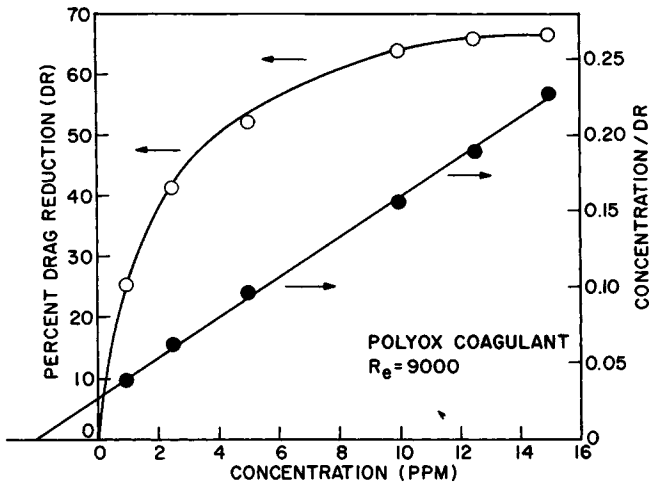


Fig. 1. Concentration dependence of drag reduction for Polyox Coagulant.

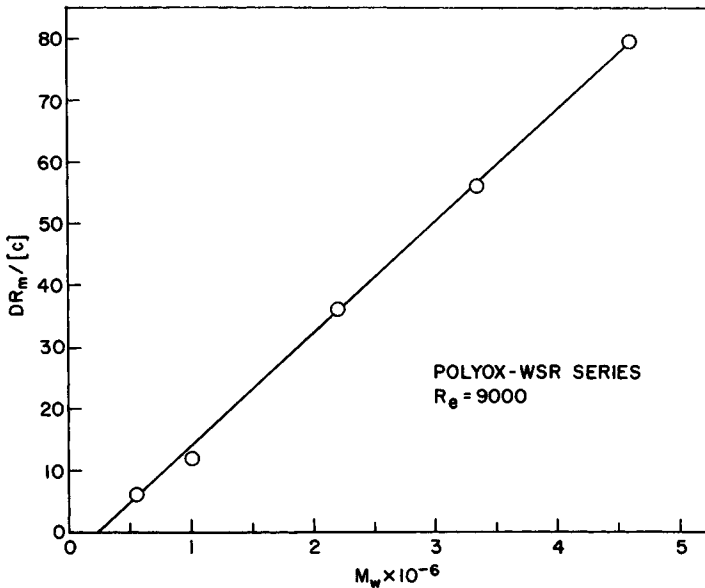


Fig. 2. Plot of  $DR_m/[c]$  vs. molecular weight for Polyox polymers.

significance of these parameters becomes very clear if the limit of eq. (3) at zero concentration is examined:

$$\lim_{c \rightarrow 0} \frac{DR}{c} = \lim_{c \rightarrow 0} \frac{DR_m}{c + [c]} = \frac{DR_m}{[c]} \quad (5)$$

This parameter,  $DR_m/[c]$ , becomes a measure of the "efficiency" of the polymer additives on a unit concentration basis at infinite dilution. Figure 2 shows a correlation between this drag reduction "index" and the polymer

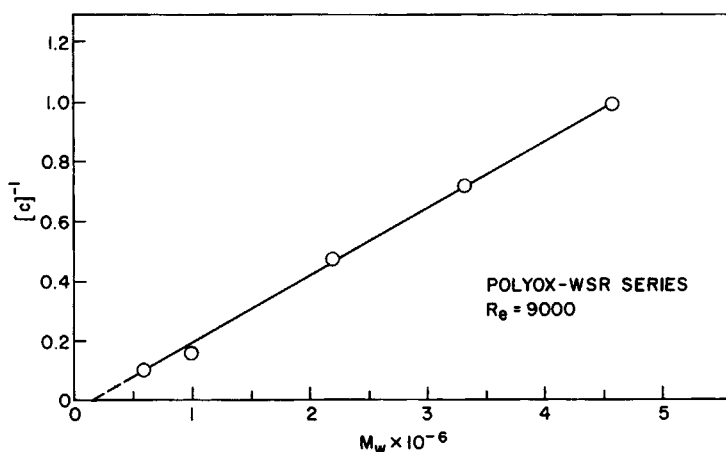


Fig. 3. Plot of  $1/[c]$  vs. molecular weight for Polyox polymers.

molecular weight. The plot is surprisingly linear over a wide range of molecular weights. A least-squares fit of the data yields a slope of  $18.35 \times 10^{-6}$  and an intercept value of  $M_w = 2.46 \times 10^5$ , suggesting a cutoff point in molecular weight below which no drag reduction takes place at this Reynolds number (9000).

Little<sup>11</sup> has successfully normalized the drag reduction data of three Polyox compounds by using  $[c]$ . He also found, while considering  $DR_m$  as approximately a constant, that the reciprocal of intrinsic concentration is a linear function of the molecular weight of these compounds. Such a linear relationship is also established for the present results as shown in Figure 3, represented by

$$M_w \times 10^{-6} = \frac{4.57}{[c]} + 0.23. \quad (6)$$

A cutoff molecular weight of approximately  $2.3 \times 10^5$  was observed in this case, higher than the values reported by Little<sup>11</sup> and Hoyt and Soli.<sup>13</sup> The difference in the values of cutoff molecular weight is believed to be related to the difference in tube diameters and will be discussed in a separate article.  $DR_m$  has also been correlated with the molecular weight as shown in Figure 4 and a good approximation is

$$DR_m = \frac{85.84 M_w}{M_w + (2.8 \times 10^5)} \quad (7)$$

as evidenced by the linear plot of  $M_w/DR_m$  versus  $M_w$ . It is clear that  $DR_m$  has a much weaker dependence on  $M_w$  than  $[c]$ . It should be added at this point that although  $DR_m$  is the "maximum" drag reduction to be obtained at higher concentrations, it is not really a value attainable in the experiment. As in the case of any empirical correlation, the validity of the equation depends on proper application. Equation (3) successfully describes the drag

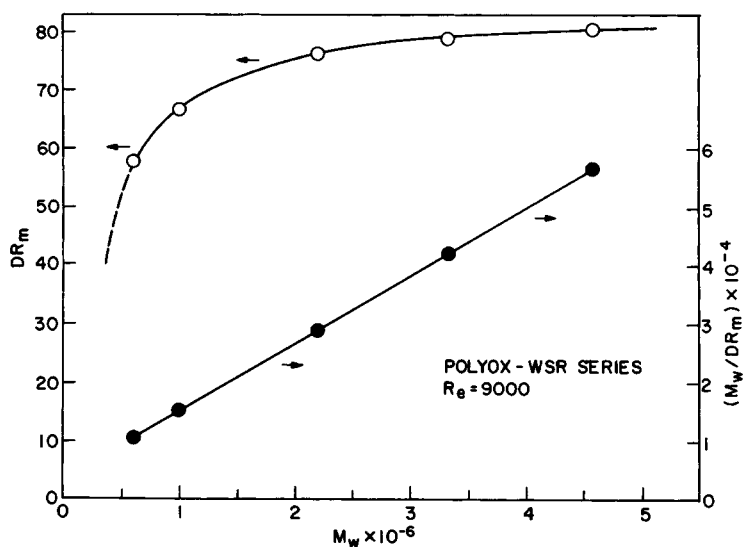


Fig. 4. Plot of  $DR_m$  vs. molecular weight for Polyox polymers.

reduction results up to concentrations below that needed to produce a saturation drag reduction effect. In other words, it only accounts for dilute solution behavior. Further increases in concentration cause substantial increases in solution viscosity and, therefore, decreases in drag reduction ability; hence the equation will fail.

#### Analysis of Polymer Degradation

Repeated passes of the same sample solution through the pipe system produced continuing decreases in the observed drag reduction. The degradation of the Polyox (Coagulant) solutions is shown in Figure 5 at several different concentrations where the per cent drag reduction is plotted against the number of passes through the pipe. Such plots are useful only in a qualitative sense and contribute little to the characterization of degradation effects. In an attempt to analyze the degradation data, a new function,  $E$ , will be introduced as the time integral

$$E = \int_0^t \tau_w \dot{\gamma} dt \quad (8)$$

Here  $\dot{\gamma}$ , taken to be  $u/r$ , may be considered as a mean shear rate in the flow if  $r$  is the pipe radius;  $\tau_w$  is the turbulent wall shear stress experienced by the polymer sample in the pipe. Based on the data as shown in Figure 5,  $\tau_w$  can be calculated as a function of the number of passes by using eq. (1), in which the frictional factor for the Newtonian fluid is known through the Blasius relation<sup>14</sup>:

$$f_{\text{water}} = \frac{0.3164}{\text{Re}^{0.25}} \quad (9)$$

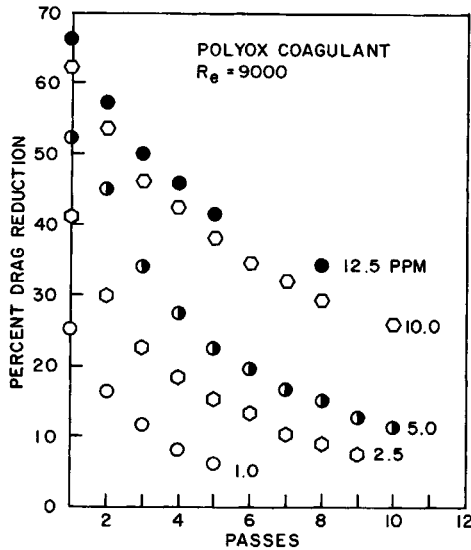


Fig. 5. Degradation history of Polyox Coagulant at different concentrations.

Since the degradation history obtained by the present procedures is considered to be a laboratory simulation of flows through a very long pipe, the variation in  $\tau_w$  can then be viewed as a continuous function of time,  $t$ , by knowing the flow time of each pass. Consequently by performing the time integral in eq. (8), the new variable  $E$  becomes a measure of the dissipation energy near the pipe wall, which is involved in the degradation of the polymer solutions, since degradation mainly occurs in the viscous sublayer adjacent to the wall.<sup>7</sup> The function  $E$  could thus relate the degradation behavior of the polymer solutions more directly and closely to its basic mechanisms.

For a given concentration, the variations of  $[c]$  and  $DR_m$  as the number of passes increases can be obtained in a similar way by using eq. (3). Since the polymer degradation process produces a decrease in molecular weight, it was necessary to find methods to characterize these molecular weight changes. This was accomplished by following the simple procedures illustrated in Table II, where the relationships of eqs. (6) and (7) have been applied. When the calculation was performed on a CDC-3600 computer, the iterative process involved in deriving  $DR_m$  converged in no more than three iterations. The molecular weights derived were correlated with the dissipated energy function  $E$ . Figure 6 shows how the degradation data for Polyox Coagulant solutions at selected concentrations are reduced to a single curve when this function  $E$  is applied. Hence, this result suggests that the energy dissipation function is the relevant variable to be considered in characterizing the degradation effects of Polyox family.

As shown in Figure 6, the initial change in polymer molecular weight is very rapid. This rate of molecular weight decrease becomes less with in-



TABLE II  
Degradation Data Reduction Procedures

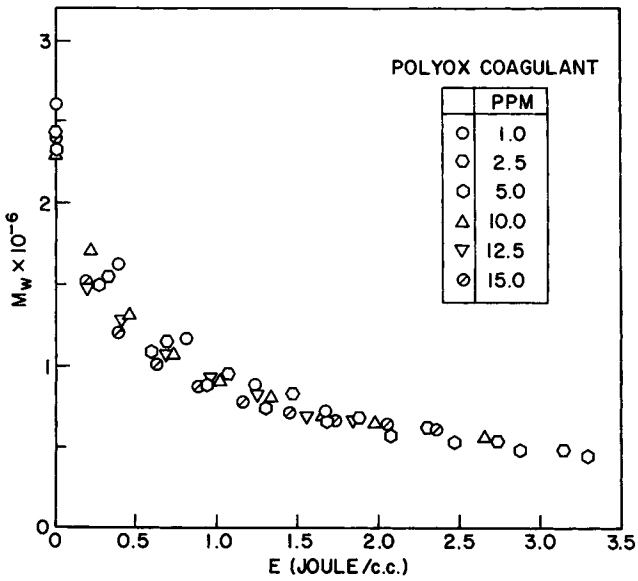
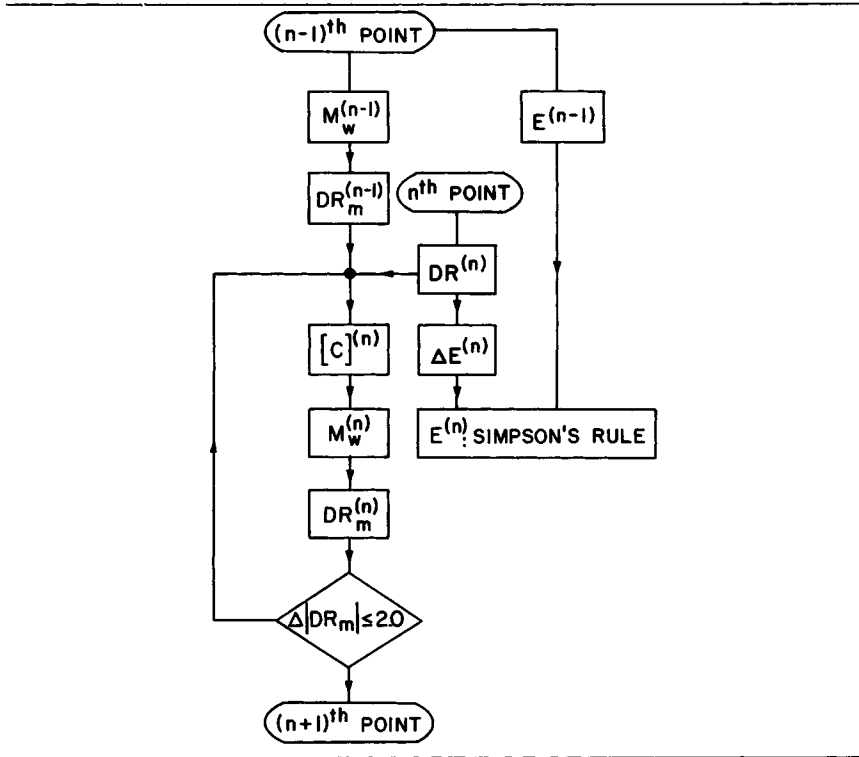


Fig. 6. Plot of molecular weight vs. dissipated energy function for Polyox Coagulant.

creasing  $E$  as the result of further viscous dissipation. This effect is consistent with the expected change in the drag-reducing ability of polymer solutions. Initially, the high molecular weight molecules, being of large molecular dimensions, are able to interact with the turbulent eddies very effectively as indicated by the high drag reduction values. However, they are at the same time more vulnerable to chain scission resulting from this intense interaction with the turbulent field. As the molecular weight decreases, polymer-turbulence interactions also decrease and the observed drag reduction falls to lower values.

The degradation data for all the Polyox samples studied are presented in Figure 7, where a normalized molecular weight  $M_R$  is plotted against the energy function  $E$ .  $M_R$  is obtained by dividing the observed molecular weight by the initial molecular weight of each compound,  $M_w^0$ , determined before the degradation treatment:

$$M_R = \frac{M_w}{M_w^0} \quad (10)$$

It can be seen that for each compound, the degradation data are now represented by a single curve. The initial rate of decrease strongly depends on the initial molecular weight of the compound. For example, high molecular weight samples suffer more rapid decreases than samples of lower molecular weight. Least-squares plots of the Polyox degradation data indicate that the decrease in molecular weight with increasing energy is best described by a hyperbolic curve of the form

$$M_R = \frac{1}{1 + K_1 E} \quad (11)$$

where  $K_1$  determines the rate of decay and is expected to be related to the initial molecular size; that is to say, upon application of a given shear field, the force tending to rupture polymer coils will be higher for larger molecules than smaller ones. Analysis of the variation of  $K_1$  with the initial molecular weight leads to the result

$$M_R = \frac{1}{1 + K_d [\eta] E} \quad (12)$$

where  $[\eta]$  is the initial intrinsic viscosity of the Polyox polymer. If  $[\eta]$  is in units of dl/g, the parameter  $K_d$  has a constant value of 0.13 in the present studies and will be termed the "degradation index" of the Polyox family.

Although eq. (12) generally fits the data very well as seen in Figure 7, a few remarks are fitting in regard to its general application. It is well known that a certain critical wall shear stress is to be exceeded before the drag reduction effect occurs. It is believed that there also exists a critical shear stress below which no degradation takes place. Virk et al.<sup>12</sup> found that degradation became severe once the wall shear stress exceeded the onset wall shear stress for drag reduction. However, because of the complica-

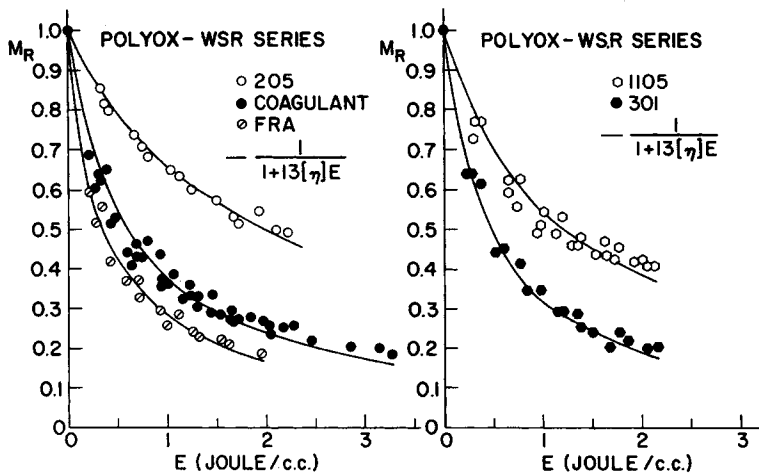


Fig. 7. Plot of normalized molecular weight vs. dissipated energy function for Polyox family.

tions accompanied with the turbulent flow in which the present degradation effect was observed, it is difficult to quantitatively determine the critical shear stress for degradation. This critical shear stress, as suggested by Patterson and Abernathy,<sup>2</sup> may also depend on the pipe diameter and the Reynolds number of the flow. It should be pointed out that the application of eq. (12) implicitly assumes the flow to be in the range where the wall shear stress is above the critical value for degradation.

Furthermore, eq. (12) indicates that as  $E \rightarrow \infty$ , the molecular weight approaches zero. This result is in contrast to the generally known fact that a limiting final molecular weight exists<sup>15</sup> and suggests that eq. (12) should more correctly bear the form

$$\frac{M_R - M_R^L}{1 - M_R^L} = \frac{1}{1 + K_d[\eta]E} \quad (13)$$

where  $M_R^L = M_w^L/M_w^0$  is the normalized limiting molecular weight. Since the present characterization uses the per cent drag reduction as a probe to determine the degree of degradation, the technique fails below the cut-off molecular weight for drag reduction; hence, it is difficult to determine the limiting molecular weight precisely. It does not suffice to approximate  $M_w^L$  by the cut-off molecular weight for drag reduction because the degradation process is likely to continue even below this molecular weight, especially when the wall shear stress is very high. Harrington and Zimm<sup>15</sup> have observed a limiting molecular weight as low as 40,000, depending on the intensity of the shear field. The present study is concerned with turbulent drag reduction and degradation effects in the initial molecular weight range of 1,000,000 and above. Consequently, for such cases the quantity  $M_R^L$  which appears in eq. (13) will be only several per cent of the lowest  $M_R$  value observed and can be effectively neglected; eq. (12) thus serves as a

very satisfactory approximation. However, when the molecular weight is less than 350,000 or so, the  $M_E^L$  correction term becomes important and the deviation of eq. (12) from eq. (13) is noticeable. This can be seen from Figure 7 for the cases of low molecular weight compounds such as Polyox-WSR 205. As  $E$  increases, the experimental data tend to level off and deviate from the prediction of eq. (12) shown by the solid curve. Nevertheless, for degradation of very high molecular weight polymers taking place in flows of very high Reynolds number where turbulent drag reduction is observed, eq. (12) is very useful for the characterization of degradation effects because the shear stress will be high and the limiting molecular weight which results will be small.

It should be noted that the inverse of  $K_d$  has the dimension of energy per unit weight of polymer, suggesting that this is a measure of the energy involved in degrading a unit weight of the polymeric additive in the flow. If, as suspected,  $K_d$  is characteristic of a given polymer species, values of  $K_d$  may be profitably used to compare the shear stability of various families of drag-reducing polymers. The relation of  $K_d$  to other parameters such as the bond energy or an activation energy for certain turbulence-initiated chemical reactions is unknown at the present time. At any rate, the analysis presented here should represent a substantial improvement over the graphic methods presently used to characterize polymer degradation. Studies in determining  $K_d$  for other drag-reducing polymers may also lead to the resolution of the mechanisms responsible for polymer degradation in turbulent pipe flows.

### References

1. H. D. Ellis, *Nature*, **226**, 352 (1970).
2. R. W. Paterson and F. H. Abernathy, *J. Fluid Mech.*, **43**, 689 (1970).
3. A. T. Ellis, R. Y. Ting, and R. H. Nadolink, *J. Hydraulics*, **6**, 66 (1972).
4. D. H. Fisher and F. Rodriguez, *J. Appl. Polym. Sci.*, **15**, 2975 (1971).
5. J. H. T. Wade and P. Kumar, *J. Hydraulics*, **6**, 40 (1972).
6. D. A. White, *Chem. Eng. Sci.*, **25**, 1255 (1970).
7. B. J. S. Barnard and R. H. J. Sellin, *Nature, Phys. Sci.*, **236**, 13 (1972).
8. D. Fruman, G. Loiseau, G. Norgeot, and J. M. Piau, paper presented at 1970 International Symposium of Heat and Mass Transfer in Rheologically Complex Fluids, Herceg Novi, Yugoslavia, Sept. 1970.
9. J. W. Hoyt, in *Symp. Rheol.*, A. W. Morris and J. T. S. Wang, Eds., ASME, New York, 1965, p. 71.
10. F. E. Bailey, J. L. Kucera, and L. G. Imhof, *J. Polym. Sci.*, **32**, 517 (1958).
11. R. C. Little, *J. Colloid Interfac. Sci.*, **37**, 811 (1971).
12. P. S. Virk, E. W. Merrill, H. S. Mickley, K. A. Smith, and E. L. Mollo-Christensen, *J. Fluid Mech.*, **30**, 305 (1967).
13. J. W. Hoyt and G. Soli, *Science*, **149**, 1509 (1965).
14. H. Schlichting, *Boundary Layer Theory*, 2nd ed., McGraw-Hill, New York, 1960.
15. R. E. Harrington and B. H. Zimm, *J. Phys. Chem.*, **69**, 161 (1965).

Received March 9, 1973

Revised April 16, 1973