Influence of molecular weight upon drag reduction by polymers

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With 5 figures and 3 tables

Introduction

While there have been many publications concerned with the reduction of turbulent friction brought about by small concentrations of high molecular weight polymer in water, comparatively little has been published on the influence of polymer molecular weight. Hoyt and Fabula (1) recognised the dependence of the concentration, c, required to produce a given drag reduction upon the molecular weight, $M$, expressing their results relating to the reduction of the torque on a rotating disc in the form $c \propto M^{-a}$, using the manufacturer's values for $M$, $a$ being near 0.5 for polyethyleneoxides (Union Carbide Polyoxes) with $M$ in the range $2 \times 10^5 - 6 \times 10^5$. Later Merrill et al. (2) published results, obtained at a lower shear stress in a Couette apparatus, on a greater range of Polyoxes which had been characterized by light scattering measurements and viscometry. These, with one exception, fit a similar power relationship well but the value of $a$ is very different, approximately 2.6. The anomalous behaviour of one sample accompanied by inconsistencies between light scattering and viscosity results drew attention to the significance of the molecular weight distribution. Recently Paterson and Abernathy (3) reached a similar conclusion, pointing out that the drag reduction depends strongly upon the concentration of the constituent of highest molecular weight.

The main part of this paper describes work carried out at two shear stress values on polymer samples with a relatively narrow molecular weight distribution obtained by fractionation of commercial polymers.

Factors influencing relationships between drag reduction and molecular weight

The relative concentrations of polymers producing the same drag reduction are generally very similar in value at all levels of drag reduction (4). This becomes obvious when drag reduction effects are plotted against log (concentration), the curves for different polymers running closely parallel (2). We have therefore derived as far as possible average values of the relative concentrations over an appreciable portion of these curves, aiming for greater accuracy and generality. Because on the one hand the shape of the curve may show a dependence upon molecular weight in the region of maximum drag reduction, notably when the wall shear stress ($\tau_w$) is low, and on the other hand the early part of the curve is less accurately determined, the region from about 40% to 80% of maximum drag reduction has been preferred. The results are reported here as relative efficacies, denoted by $E$, and defined as the reciprocal of the average relative concentration with reference to a standard (Polyox WSR-301, sample A) giving the same drag reduction. $E$ increases with molecular weight, the results referred to in the introduction now being described by relationships of the form $E \propto M^a$.

$E$ values depend upon $\tau_w$. This follows necessarily from the fact that for any particular polymer there is a characteristic $\tau_w$ value, related to its molecular weight, below which drag reduction does not occur (5, 4). $E$ values must therefore change as $\tau_w$ drops towards these characteristic inception values. Table 1 shows this effect for two Polyox samples of lower molecular weight than the reference standard, the data presented being obtained from experiments in a number of tubes varying widely in diameter and considerably in length.

The $E$ values for the lower molecular weight WSR-205 sample drop more rapidly with diminishing $\tau_w$ as a consequence of its higher characteristic inception $\tau_w$. The effect is pronounced when $\tau_w$ is below $10^2$ dyn/cm$^2$.

The consistent results for 25 mm diameter tubes and 1 mm diameter tubes indicate that $E$ values of general applicability can be obtained using a small bore tube. With such apparatus it is possible to investigate, as described in the main part of the paper, the efficacies of very small samples of polymers, in particular of those prepared by fractionation of commercial samples and characterized by a relatively narrow molecular weight distribution.

As is well-known polymers are subject to degradation in turbulent flow, the extent increasing with molecular weight (4). Hence
one effect of degradation is to reduce the value found for the index $a$ in relationships of the form $E \propto M^a$ describing molecular weight dependences. As described later an estimate was made of the extent to which our results on molecular weight dependences were affected by degradation.

**Experimental details**

The majority of results were obtained with fractions from commercial polyethyleneoxides (two Polyox WSR-301 samples and a Polyox WSR-205 sample) and a commercial nonionic polyacrylamide (Superfloc 972). Unfractionated polymers were also investigated, including the above, two additional nonionic polyacrylamides (Superfloc 905 and Cyanamid P-250) and some ionic polyacrylamides (Superfloc 835, Cyanamid E-264 and Separan AP-273, NP-10, NP-20 and MGL).

Solutions were made in distilled water employing dispersing agents (about three times the polymer weight of ethylene glycol for polyethyleneoxide and of polypropylene glycol for polyacrylamide) to reduce the formation of lumps of gel. Bactericide, either 1% of formalin or 0.02% of sodium azide, was also added to the solutions.

Fractionation was carried out by gel permeation chromatography employing Sepharose-2B (a 2% agarose gel from Pharmacia Ltd.), with about 1400 ml of gel in a 2 inch diameter column. 50 ml of solution was applied to the column and similar volume fractions were collected on eluting with water containing the bactericide. It was found that solutions containing up to 0.1% of the highest or 1% of the lowest molecular weight polymers could be fractionated satisfactorily i.e. 50 mg to 500 mg polymer per run.

Each fraction was characterized by a determination of the limiting viscosity number, $N$, defined by

$$[\eta] = \eta_s / \eta_0 = \eta_0 / \eta_s$$

where $[\eta]$ is the solute viscosity, $\eta_s$ the solvent viscosity and $c$ the polymer concentration, in g/ml. The polymer concentration was determined turbidimetrically, using Reinecke's salt, ammonium tetrathiocyanatodiamino-chromate, for polyethylene-oxide (6) and tungstophosphoric acid for polyacrylamide (7). Viscosity measurements were made at 30°C on very dilute solutions using a BS suspended level viscometer at a $\tau_w$ value of 9 dynes/cm². Any necessary extrapolation to lower concentration was made by employing the Huettig equation, $(\eta/\eta_0) - 1 = (\eta_0) + k(N)^x$, having previously established the appropriate value of $k$.

Drag reduction measurements were made in 1 mm bore tubes, the essential details of which are given in table 1, at two $\tau_w$ values, $10^5$ dyn/cm² and $4 \times 10^6$ dyn/cm² (respective Reynolds numbers $5 \times 10^5 - 7 \times 10^5$ and $1.1 \times 10^4 - 1.4 \times 10^4$). The time for a specified volume to flow through was measured by means of photoelectric sensors at two levels in the reservoir which operated an electronic timer whenever the meniscus passed. Timings were generally reproducible to better than 0.05 see i.e. usually within 1%. The value of $E$ (compared with the polymer standard, WSR-301 sample A, with very accurately determined drag-reducing characteristics) was based as far as possible upon measurements at two or three concentrations. These were usually consistent to $\pm 5\%$ or better.

The stock solutions of unfractionated polymers (with a concentration of 0.1% w/v or more) proved to be very stable, the drag reduction characteristics generally showing no sign of change over periods of months. With one exception $N$ values were similarly reproducible. The exception related to the solution of the highest molecular weight Polyox WSR-301 sample (A), the $N$ value of which dropped from 1770 ml/g to 1360 ml/g without detectable change in drag-reducing properties. The latter is regarded as the true value as passing the solution through the gel column had the same effect as ageing. The high value was therefore attributed to persistent molecular entanglements which were only broken down on ageing or by passage through the gel.

**Results and discussion**

The results for polyethyleneoxide are presented in fig. 1 from which two conclusions may be drawn. Firstly $E$ is more steeply dependent upon $N$ (i.e. molecular weight) at the lower $\tau_w$ value. This is a necessary consequence of the divergence of the log $E$ vs. $\tau_w$ curves as $\tau_w$ is reduced, as indicated by the results in table 1. Secondly the curves change shape, apparently beginning to level off, when $N$ rises above 1200. For values of $N$ between 200 and 1200 corresponding to molecular weights between about 2 · $10^6$ and 2 · $10^6$ (8) the results are described satisfactorily by a power relationship, $E \propto N^x$, with $x \simeq 2.3$ and 3.5 at the higher and the lower $\tau_w$ values respectively. Earlier results at a much lower $\tau_w$ of 180 dyn/cm² in a 4.2 mm bore tube had indicated a still

<table>
<thead>
<tr>
<th>Tube dia. mm</th>
<th>Tube entry length, no. of dias.</th>
<th>Measurement length of tube, no. of dias.</th>
<th>$\tau_w$ dyn/cm²</th>
<th>Relative efficacy, $E$, for WSR-301 sample B</th>
<th>WSR-205 sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60</td>
<td>100</td>
<td>$4.5 \times 10^2$</td>
<td>0.76</td>
<td>0.10</td>
</tr>
<tr>
<td>1</td>
<td>17</td>
<td>100</td>
<td>$4.0 \times 10^3$</td>
<td>0.73</td>
<td>0.11</td>
</tr>
<tr>
<td>25</td>
<td>No. of pressure tappings</td>
<td>Up to 140</td>
<td>$3.2 \times 10^8$</td>
<td>0.63</td>
<td>0.11</td>
</tr>
<tr>
<td>25</td>
<td>No. of pressure tappings</td>
<td>Up to 140</td>
<td>$2.5 \times 10^8$</td>
<td>0.63</td>
<td>0.09</td>
</tr>
<tr>
<td>1</td>
<td>17</td>
<td>100 or 220</td>
<td>$1.0 \times 10^3$</td>
<td>0.57</td>
<td>0.09</td>
</tr>
<tr>
<td>1.5</td>
<td>60</td>
<td>200</td>
<td>$3.6 \times 10^3$</td>
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<td>0.08</td>
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<tr>
<td>4.6</td>
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<td></td>
<td>$1.0 \times 10^9$</td>
<td>0.21</td>
<td>0.09</td>
</tr>
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</table>

Drag reduction results for polyox samples in various tubes.