Electron Microscope Studies of Polymer Degradation

J. H. T. Wade* and P. Kumar†
McMaster University, Hamilton, Ontario, Canada

Degradation studies have been carried out on a dilute solution of a polyacrylamide, Polyhall 402, in distilled water with the aid of a simple rheometer, employing a capillary tube operating in the turbulent flow regime. The degraded samples, collected after each pass through the rheometer were analysed with the aid of an electron microscope. The analysis showed how the polymer molecules fracture under turbulent shear with the fragments in solution approaching asymptotically an average molecular weight of approximately 1.0×10^6 after a number of passes.

Introduction

Many interesting features regarding drag reduction in dilute solutions of high polymers have been investigated and during the past few years a number of publications have appeared on the subject.[1–4] Drag reduction is found to have a strong dependence upon the concentration of the polymer dissolved in the solvent. Experiments at the University of Southampton and elsewhere have indicated that the maximum drag reduction is obtained when the polymer concentration is between 20 wppm and 100 wppm depending upon the type of polymer used. Figure 1 shows some of the drag reduction data obtained using a capillary type rheometer for three different kinds of polyacrylamides at the University of Southampton.[5] In Fig. 1 the abscissa is the concentration in weight parts per million multiplied by the average molecular weight as obtained from the manufacturer. The ordinate $(T/T_o)^2$ is the ratio (squared) of the time-to-pass a specific amount of polymer solution, through the capillary test section, compared to the time taken for the same amount of distilled water. This ratio is in fact equivalent to the ratio of the drag coefficients if one neglects both the entrance losses to the capillary tube and the exit plane dynamic head. For low-flow rates the accumulative error is no more than 7% and the time-to-pass is a very convenient measurement to make.

Further experiments on these polymers have shown a decline in the drag reduction on repeated use of the polymer solution. This is thought to be due to the mechanical fracture of the long chain polymer molecules as a result of shear stresses. This process ultimately results in the decreased molecular weight of the polymer and is termed degradation. Figure 2 shows some of the degradation data obtained for various types of polymers at the University of Southampton.[5] The same ordinate has been used as in Fig. 1 while the abscissa defines the number of times the solution was passed through the capillary tube rheometer. These figures indicate that polyacrylamides are among the most useful polymers in the sense of drag reduction and furthermore, they exhibit the lowest rate of degradation when compared with polymers of different molecular structures. Thus, from an engineering point of view, a degradation study of a polyacrylamide in dilute solution is interesting in that it provides some evidence on the life-time of the dilute polymer solution exposed to shear.

Early experiments in polymer degradation include the work of Harrington and Zimm[6] who degraded polystyrene dissolved in reagent grade toluene, benzene, and methyl ethyl ketone over a range of concentrations from 400 wppm to 1000 wppm. The average molecular weights of polystyrene were reported to be 10.4×10^6 and 3.72×10^6 prior to degradation. The amount of degradation was found to be dependent upon the type of solvent used and estimated critical stresses were determined to be lower for the case of poor solvents. The molecular weight was observed to be reduced up to 50% of the original molecular weight depending upon the process of degradation employed. Capillary degradation of polystyrene with an initial average molecular weight of 10.4×10^6 resulted in an average molecular weight of 5.08×10^6 after 5 passes. The authors' results showed that under most conditions the reduction in molecular weight was a maximum during the first few passes after which the molecular weight tended to approach a constant value asymptotically. The minimum value of average molecular weight obtained for the high-molecular weight polystyrene (10.4×10^6) was 0.583×10^6 after 100 passes through a sintered glass disk of unspecified pore size.

Porter, Cantow and Johnson[7–10] degraded 9600 wppm and 9700 wppm solutions of polyisobutenes of molecular weight ranging from 2000 to 1×10^6 in hexadecane and trichlorobenzene, respectively, in homogeneous, laminar flow shear fields. The molecular weights which were obtained using both gradient elution and gel permeation fractionation techniques were shown to decrease continuously with the number of passes.

In most polymer degradation studies reported to date a concentrated solution has been used in organic solvents. Also, from an engineering point of view, the polymers used have proven to be of little importance as far as drag reduction is concerned. Furthermore, most of the standard techniques available for the molecular weight analyses are of very little help in dealing with the higher molecular weights (of the order of 5×10^6–1×10^7) particularly for the lower concentrations (in the range of 20–100 wppm). The purpose of the present study was to develop a satisfactory technique of evaluating the molecular weight distribution of high-molecular weight polymers in dilute solutions and thus use this technique to evaluate the degradation characteristics of a polyacrylamide, exposed to repeated shear, in terms of molecular weight distributions.

Polymer Degradation System

The polymer chosen for the present study was polyacrylamide (Polyhall 402) due to its good drag reduction properties even after degradation as evidenced by Fig. 2. Since from the previous work[5] the drag reduction was observed to be optimum between concentrations of 20 wppm and 50 wppm, it was decided to use a 40 wppm solution in distilled water at room temperature (70°F) for the degradation study. The homogeneous solution was prepared by adding the required

---

Received May 10, 1971; revision received July 27, 1971.
Index category: Hydrodynamics.

* Professor, Department of Mechanical Engineering. Associate Fellow AIAA.

† Research Assistant, Department of Mechanical Engineering.

amount of polymer in distilled water while stirring slowly so as to minimize degradation of the polymer prior to the study. After the required amount of polymer had been added to the solvent, the solution was stirred continuously till the floating particles had completely disappeared.

The dilute polymer solution was immediately degraded by means of its passage through a simple Poiseuille flow rheometer similar in design to the Southampton instrument. The test section of the rheometer utilized a 15 in. length of 0.0628 in. inside diameter stainless steel capillary tube. A reservoir capable of being pressurized was installed at the upper end of the tube while the lower end of the tube was exposed to atmospheric pressure. A constant head pressure on the reservoir allowed a mass flow rate through the capillary to be established, as a function of the head, and enabled a Reynolds number based on the tube diameter, the average velocity of the fluid, and the properties of the solvent to be defined and measured. A further refinement would have been to calculate the Reynolds number using the solution viscosity which would have varied from pass to pass since $\mu = \mu(Mw)$. However using a solution of such low concentration (40 wppm) this type of refinement is considered unnecessary for the work at hand. Since the flow through the rheometer was turbulent on the basis of Reynolds number being greater than 2300, it was assumed that degradation was homogeneous throughout the solution. After each pass, a 10 cc sample of the solution was collected for the molecular weight study. The time to pass a 300 cc volume of solution through the capillary tube was obtained and compared to the time taken by an equal volume of distilled water to compute the drag reduction characteristics; later to be correlated to the number average molecular weight measured after each pass. The flow rate through the rheometer was variable but seldom exceeded 7 cc/sec.

Method of Distribution Analysis

The method used for the molecular weight distribution determination in this study was unique in the sense that it required only a small quantity of the dilute solution of polymer. A direct observation of 500–600 molecules under the electron microscope was evaluated in terms of molecular weights and thus a histogram was constructed on the basis of the percentage of the total number of molecules lying between a small range of molecular weights. The technique of obtaining single molecules of a polymer was first successfully developed by Richardson,[11] who obtained single molecules of polystyrene from a 0.5 wppm solution of the polymer in 68% benzene and 32% n-butanol system in which the benzene was used as a solvent and the n-butanol as a nonsolvent. The procedure was simple since the polymer was dissolved in the solvent and the nonsolvent was added to the well-stirred solution which was immediately sprayed at room temperature using a Vaponefrin nebuliser, onto a mica-backed film of evaporated carbon placed on a copper substrate. The substrate was shadowed at a sharp angle by means of metals which gave a good contrast when viewed under an electron beam. Richardson observed that the conditions for obtaining the single molecules were very critical in the sense that a better solvent resulted in a shapeless mass, while on the other hand a poorer solvent resulted in a conglomeration of molecules forming either large spheres or clusters of spheres. Using the procedure outlined earlier, he precipitated single molecules of chlorinated rubber from solution in a 85% chloroform and 15% ethanol system. On the other hand, single molecules of polyacrylamide could not be obtained even after the addition of large quantities of nonsolvent. However, the procedure was modified so that the solution was sprayed onto a heated substrate and single molecules were seen to collapse into a shapeless mass during the observation period under the electron microscope. Richardson attributed this phenomenon to some inherent weakness of the polymer structure when exposed to electron irradiation.

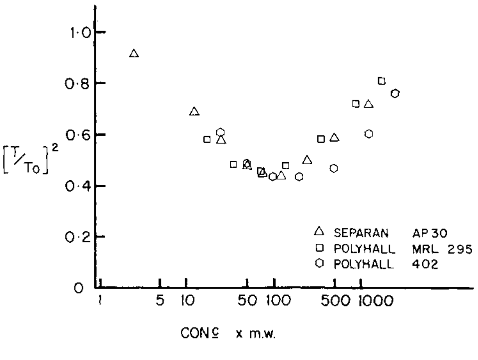

Fig. 1 Drag reduction curves for representative polyacrylamides.

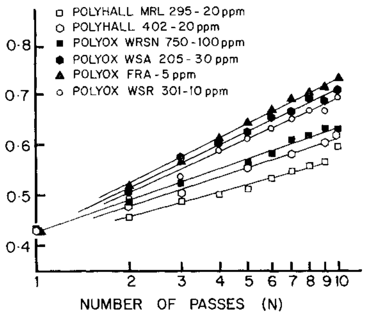

Fig. 2 Degradation results obtained for a number of polymers using a Poiseuille flow rheometer.

Quayle[12] developed the technique of obtaining and observing single molecules of polyacrylamide also using the electron microscope. The method consisted of spraying a very dilute solution of polyacrylamide in water and n-propanol system at room temperature onto an evaporated carbon film backed with freshly cleaved mica, and then shadowed with a 50% platinum mixture, floated off onto distilled water and picked up on a copper microscope grid. The critical value for obtaining single molecules was determined to be a 20% water and 80% n-propanol system. For a solvent containing a higher percentage of water, the polymer formed a filamentous structure which collapsed as the critical conditions were approached. The finest filaments were thought to be single molecular chains although this fact could not be clearly established. The procedure used for obtaining single molecules was rather long and involved, especially if it were to be applied to the present degradation study where only dilute solutions were available and a large number of specimens were required. A 10,000 wppm solution of the polymer was made in water and 10% of it by weight was precipitated by adding methanol. A 1 wppm solution of the precipitate was prepared in 20% water and 80% n-propanol system; the alcohol being added while stirring vigorously. The substrates were prepared in the manner described previously, which when viewed at a magnification of 20,000 resulted in well-formed single molecules of polyacrylamide. Quayle's procedure had to be modified for the present work because the solutions available were dilute, and a 10% precipitate from the solution was not considered to contain a proper statistical sample. For example, preliminary results showed in all cases the existence of two molecular weight peaks (one high and one low) and it was considered entirely possible that a 10% precipitate might contain the wrong percentages of high and low molecular weight fractions.

Specimen Preparation and Electron Micrographs

A 40 wppm undegraded solution of Polyhall 402 in distilled water was sampled at room temperature and n-propanol was

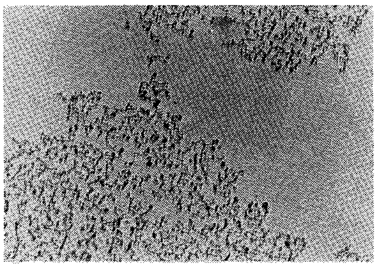

Fig. 3 Polymer structure obtained using a 50% water and 50% *n*-propanol system.

added to this sample while stirring continuously by means of a magnetic stirrer, to obtain solutions of the polymer in 50% water and *n*-propanol, 40% water and *n*-propanol, 30% water and *n*-propanol and 20% water and *n*-propanol systems. These solutions were sprayed onto evaporated carbon films, floated off onto distilled water and picked up on copper substrates. Micrographs were obtained at a magnification of 20,000 on a Phillips EM 40 electron microscope. Figure 3 shows some of the very fine structure obtained from a solution of the polymer in a 50% water and 50% *n*-propanol system. The structure appears to show a single polymer molecular chain. However, when the 20% water *n*-propanol solution was sprayed and shadowed, the single molecules were seen to collapse to lumps of about 1500 μ in diameter with no shadows, while the latex spheres of 2640 Å in diameter, used for calibration, had perfectly well-formed shadows. Moreover, the carbon film was found to break at a number of places. This was analysed to be due to the heavy shadowing and weak backing of the carbon film. The technique was repeated with the solution being sprayed onto evaporated carbon films backed by a thin film of Formvar on copper substrates and shadowed lightly. This modification resulted in well-formed molecules, but with poor contrast. This was compensated for by using a low aperture on the microscope at the cost of illumination. The same procedure was repeated for the sample solution taken after each of the seven passes. Figure 4 shows typical micrographs obtained for pass zero to pass six as indicated. The molecular diameters were determined by measuring the shadow lengths and diameters under a travelling microscope. All the molecules on a micrograph were first numbered and then the sizes were measured; between five hundred and six hundred molecules were analysed for each pass.

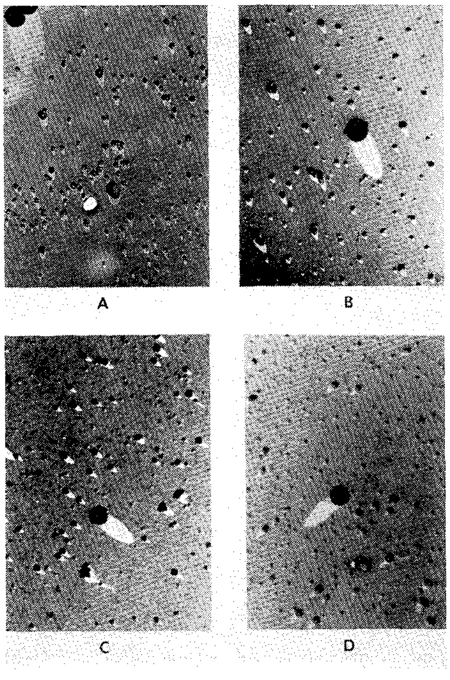

Fig. 4 Typical micrographs obtained at a magnification of 20,000 showing the molecular structure after: a) zero pass; b) second pass; c) third pass; d) sixth pass, through the rheometer.

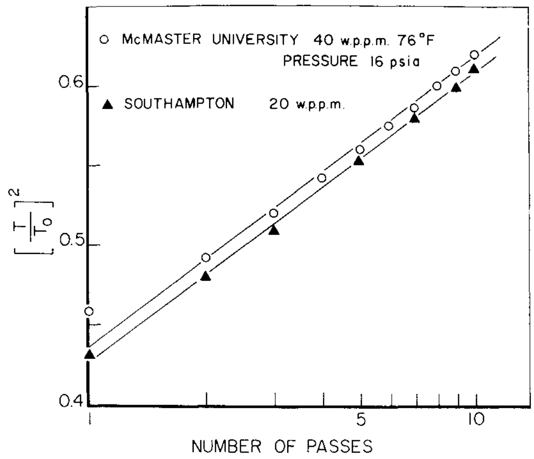

Fig. 5 Drag reduction as a function of the number of passes through the rheometer for Polyhall 402.

If one assumed that no astigmatism was present in the micrograph the shadow angle of the calibration sphere could be determined with an accuracy of ±2%. Three separate measurements were made of each polymer molecule including two diameters and a shadow length. The diameters were averaged to provide an apparent center point for the molecule from which the shadow length could be measured. The accuracy of these measurements which were made to provide an average molecular diameter was approximately ±7%. Relative to the calibrated sphere the measurement accuracy was therefore close to ±10%.

Experimental Results and Discussion

Figure 5 shows the drag reduction characteristics of the 40 wppm solution of Polyhall 402 in distilled water, with degradation by its passage through the rheometer. The trend is as observed in Fig. 2 for the same polymer. Figure 6 shows a typical histogram for the undegraded polymer. The number average molecular weight of the undegraded polymer is esti-

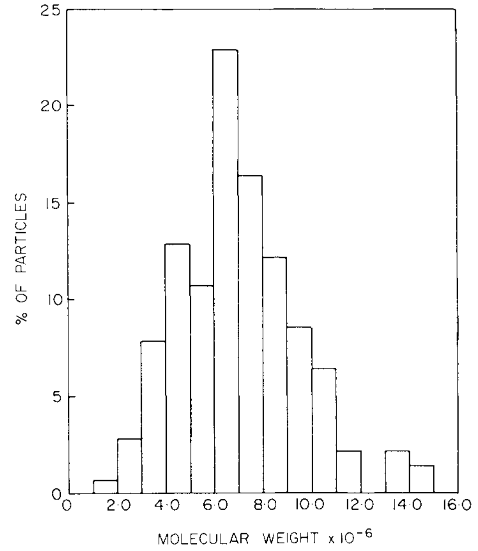

Fig. 6 Histogram for molecular weight distribution of undegraded Polyhall 402.

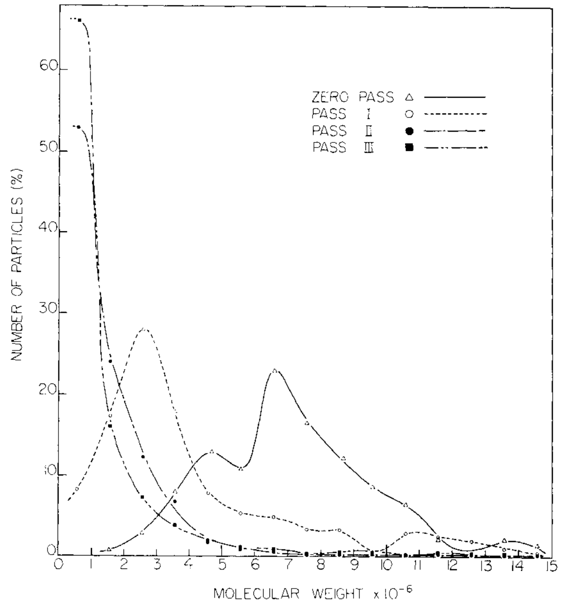

Fig. 7 Molecular weight distribution of Polyhall 402 after the first, second and third pass compared to the undegraded polymer.

mated to be 7.04 × 10^6 from this figure, which is within the range specified by the manufacturer.

Results of changes in molecular weight distribution with turbulent shear degradation are shown in Figs. 7–9 which were obtained in the same manner as Fig. 6 with the abscissa and ordinate representing the discrete molecular weight intervals and percentage of the total number of molecules, respectively. Figure 7 shows the distribution curves for the undegraded as well as the degraded polymer after the first, second and third passes with the molecular weight scale at discrete intervals of 1 × 10^6. This figure indicates that the molecular weight of the polymer reduces very quickly to smaller values; for example, the peak value shifts from 6.5 × 10^6 to 2.5 × 10^6 during the first pass and then to 1.5 × 10^6 during the second pass with only the peak height increasing at the third pass. Since the molecular weight of most of the molecules is below 3 × 10^6, Figs. 8 and 9 show the results for the seven passes in this range at a smaller discrete interval of molecular weight (0.2 × 10^6). The peak value is found to decrease from 2.1 × 10^6 to 0.3 × 10^6 during the second pass after which the value remains constant with only the peak height increasing during the third, fourth, and fifth passes. However, in Fig. 9 the peak height is found to decrease for the sixth pass and then increase for the seventh pass. This is quite in agreement with the trend observed for other molecular weight fractions, where the percentage keeps on increasing and decreasing with the number of passes.

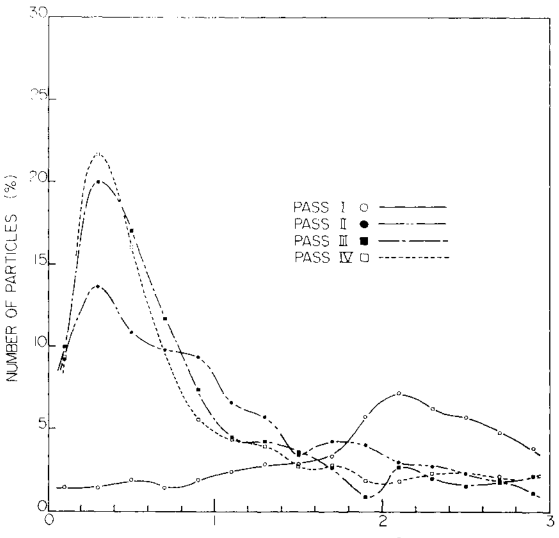

Fig. 8 Molecular weight distributions up to 3 × 10^6 for passes one to four inclusive.

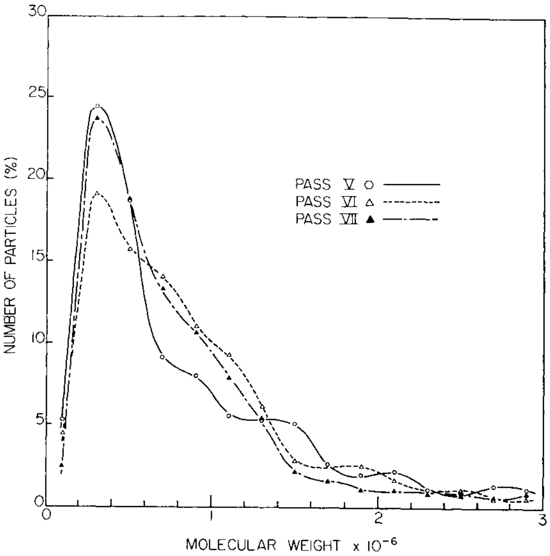

Fig. 9 Molecular weight distributions up to 3 × 10^6 for passes five to seven inclusive.

The fluctuations are better visualized with the aid of Fig. 10 where the percentage of total number of molecules is plotted against the number of passes for discrete values of molecular weight in steps of 1 × 10^6. For every molecular weight fraction, at least two maxima or minima are observed; indicating that during the process of degradation, all the molecules are not sheared simultaneously to smaller molecules of various sizes. The molecules are rather sheared in a particular fashion and only in steps. This is quite in agreement with Bueche's[13] discussion on the location of the fracture of long chain molecules. Bueche's theoretical model consists of a chain-like molecule immersed in a viscous matrix which in turn is subjected to a shearing action. It is assumed in the

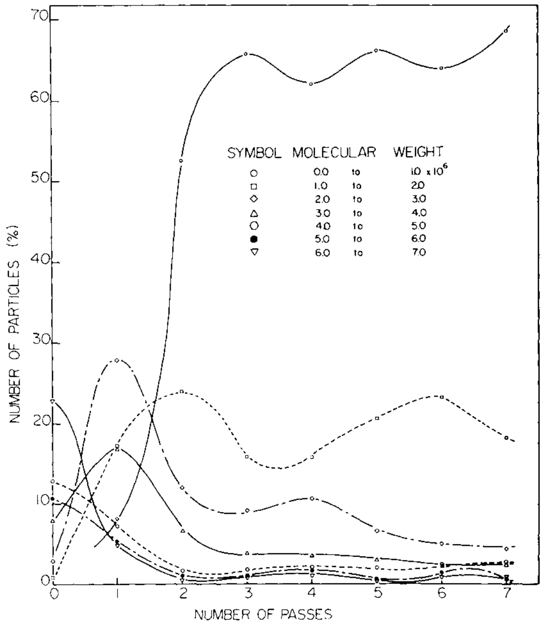

Fig. 10 Percentage of the total number of particles as a function of the number of passes through the rheometer.

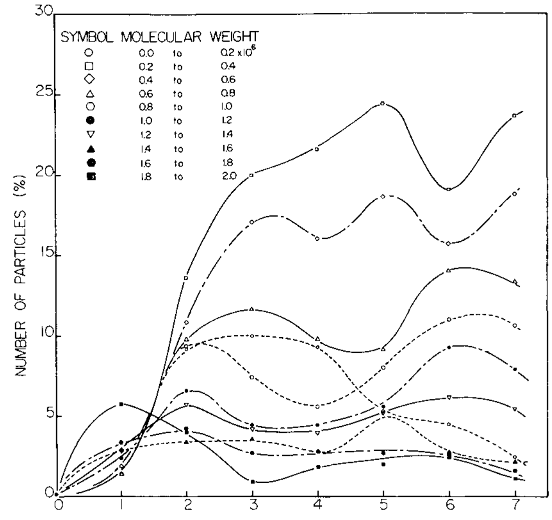

Fig. 11 Percentage of the total number of particles as a function of the number of passes for discrete steps of 0.2 × 10^6 in molecular weight.

present study that the polymer molecule because of its small size sees the solute as a viscous matrix and consequently the fracture mechanism as proposed by Bueche can be applied qualitatively to the present experimental results. According to Bueche, the force along a molecular chain during hydrodynamic shearing reaches a maximum at the center. Thus, the most probable place for the chain to break is at its center. He estimates that one break occurs at $\frac{1}{3}$ of the way out from the center for every 10 breaks occurring near the center. Furthermore, the amount of degradation and thus the final molecular weight is found to have a strong dependence upon the shear rate. For this reason, it is found that the molecular weight decreases very fast during the first few passes and then tends to approach a constant value asymptotically. This is because the shear rate is approaching a critical value which is not large enough to break molecules within the final molecular weight range. Figure 11 shows the same effect as Fig. 10 in a smaller range of molecular weights (0.0–2.0 × 10^6) for discrete steps of 0.2 × 10^6. However, if instead of the percentage of the total number of molecules, the percentage mass of molecular weight is plotted as in Fig. 12, two clear peaks are observed for each pass with no significant fluctuations. One of these peaks is at the lower end of the molecular weight scale and the other at the higher end of the scale. The latter peak exists at the original molecular weight of the undegraded polymer. This is in accordance with the observation made by other research workers on various polymers.

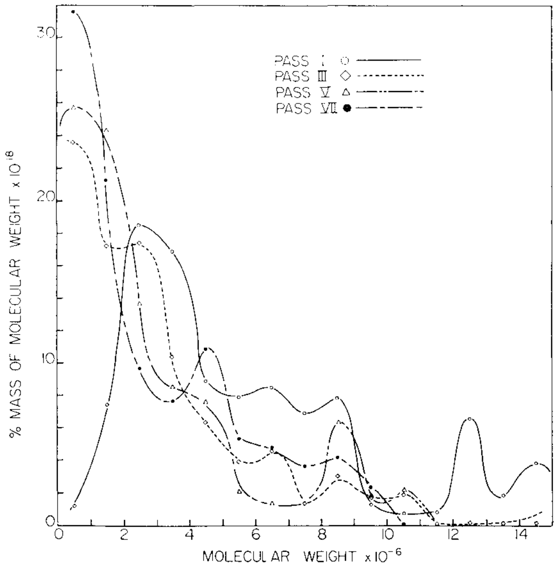

Fig. 12 Percentage mass as a function of molecular weight for Polyhall 402 for passes 1, 3, 5 and 7.

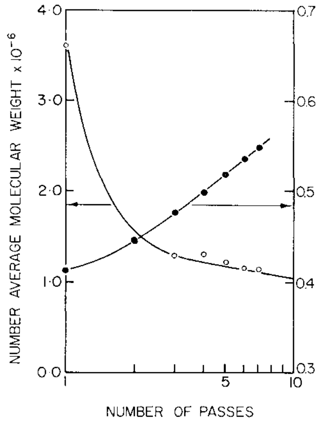

Fig. 13 Graphs showing the number average molecular weight and skin friction ratio as a function of the number of passes through the rheometer.

Figure 13 illustrates how the number average molecular weight varies with the number of passes through the rheometer. On a separate scale is shown the drag coefficient measured at each pass as a ratio of the drag coefficient for distilled water. This ratio is equivalent (as mentioned in the Introduction) to the time-to-pass ratio $(T/T_o)^2$ shown in Fig. 5 if the bulk mean velocity in the capillary tube is low enough to neglect the outlet velocity head (and inlet loss) which comes about by the application of Bernoulli's equation across the system.

The experimental results shown in Fig. 13 can be fitted with an exponential curve and shows that the number average molecular weight approaches a value of approximately 1 × 10^6 after repeated exposure to turbulent shear. A larger percentage of the particles in solution however have a lower molecular weight, in the range 0.3–0.4 × 10^6, as shown in Fig. 9.

Conclusions

The electron microscope is a unique tool for examining the molecular weight distribution of high polymers in a range which is difficult to handle, using for example, the gel permeation chromatograph. The measurements are obviously statistical in nature and rely heavily on the ability of the researcher to obtain a proper sample of the polymer in solution, to fix the polymer molecules on a very small substrate for use with the electron microscope, and to analyse the size of the particles with the aid of a calibration sphere. It appears that the lower end of the molecular weight spectrum can be measured using the smallest calibration spheres available (about 600 Å) while there is no apparent limit to measurements at the upper end of the molecular weight range.

After repeated passes through a turbulent flow rheometer the number average molecular weight of polyacrylamide, Polyhall 402, falls from an average value of 7.04 × 10^6 to about 1.0 × 10^6 in an asymptotic fashion. The distribution shows, however, that the majority of the particles have molecular weights lying in the range of 0.3–0.4 × 10^6.

The general conclusions reached by Bueche on the mode of fracture of long chain molecules under shear appears to be substantiated by the present study. The results also show that the drag reduction for a polyacrylamide is a strong function of molecular weight and concentration. As long as there is some higher molecular weight fractions available in the solution the drag reduction continues to decrease with the exposure to turbulent shear until the critical value of molecular weight is obtained. At this stage, the drag reduction curve will level off to a constant value corresponding to that molecular weight and solution concentration.

References

[1] Pruit, G. T. and Crawford, H. R., "Effect of Molecular Weight and Segmented Construction on the Drag Reduction of Water Soluble Polymers," Rept. DTMB-1, April 1965, The Western Co., Dallas, Texas.

[2] Sherman, B. A., "Effect of Concentration and Molecular Structure on the Drag Reduction of Dilute Polymer Solutions," TN 246/67, July 1967, Admiralty Underwater Weapons Establishment (N), Portland, U.K.

[3] Middleton, J. A., "An Experimental Study of the Boundary Layer Formed on a Flat Plate in a Dilute Homogeneous Polymer Solution," M.Eng. thesis, June 1969, Dept. of Mechanical Engineering, McMaster University, Hamilton, Ontario, Canada.

[4] Verma, S. K., "Turbulent Drag Reduction in Tubes with Polymer Solutions," M.Eng. thesis, April 1970, Dept. of Mechanical Engineering, McMaster University, Hamilton, Ontario, Canada.

[5] Millward, A., Private communication, Feb. 1970, Dept. of Aeronautics and Astronautics, The University of Southampton, Southampton, U.K.

[6] Harrington, R. E. and Zimm, B. H., "Degradation of Polymers by Controlled Hydrodynamic Shear," *Journal of Physical Chemistry,* Vol. 69, No. 1, Jan. 1965, pp. 161–175.

[7] Porter, R. S., Cantow, M. J. R., and Johnson, J. F., "Polymer Degradation VI—Distribution Changes on Polyisobutene Degradation in Laminar Flow," *Polymer,* Vol. 8, London, 1967, pp. 87–96.

[8] Porter, R. S., Cantow, M. J. R., and Johnson, J. F., "Polyisobutene Degradation in Laminar Flow: The Effect on Molecular Weight Distribution," *Journal of Polymer Science,* Pt. C, No. 16, 1967, pp. 1–12.

[9] Cantow, M. J. R., Porter, R. S., and Johnson, J. F., "A Comparison of Molecular Weight Distributions for Polyisobutenes as Determined from Gel Permeation and Gradient Elution Chromatographic Fractionation," *Journal of Polymer Science,* Pt. C, No. 16, 1967, pp. 13–21.

[10] Porter, R. S. and Johnson, J. F., "Polyisobutene Degradation in Laminar Flow; Composition and Shear Variables," *Journal of Applied Physics,* Vol. 35, No. 11, Nov. 1964, pp. 3149–3151.

[11] Richardson, M. J., "The Direct Observation of Polymer Molecules and Determination of their Molecular Weights," *Proceedings of the Royal Society,* Ser. A, Vol. 279, 1964, pp. 50–61.

[12] Quayle, D. V., "An Electron Microscopical Study of Polyacrylamide," *Polymer,* Vol. 8, London, 1967, pp. 217–224.

[13] Bueche, F., "Mechanical Degradation of High Polymers," *Journal of Applied Polymer Science,* Vol. IV, No. 10, 1960, pp. 101–106.