

Degradation of Drag-Reducing Polymers*

DENNIS H. FISHER † and FERDINAND RODRIGUEZ,
*School of Chemical Engineering, Olin Hall, Cornell University,
Ithaca, New York 14850*

Synopsis

A simple, fixed-head flow device was used to characterize drag reduction by polymers in water. Using a parallel flow of water as a reference system, the Reynolds numbers ranged from 8600 to 12,000. The degradation of poly(ethylene oxide) and polyacrylamide during turbulent flow of dilute solutions (1 to 50 g/kl) was measured in terms of friction-reducing effectiveness. Poly(ethylene oxide) decreases in effectiveness more rapidly than polyacrylamide in a recycling test.

INTRODUCTION

Drag Reduction

Fabula¹ in 1963 reported a spectacular reduction in pressure drop for equal flow rates when a trace (a few parts per million) of poly(ethylene oxide) is added to water in turbulent flow. Although other workers had observed similar phenomena previously, Fabula's was the report which triggered a large number of investigations into drag reduction (also called friction reduction). A recent review² points out that a comprehensive understanding of the mechanism underlying the process has not yet been achieved.

Some drag-reducing agents appear to extend laminar flow to a higher critical Reynolds number, while others lower the pressure drop in what appears to be fully developed turbulent flow. Most investigators have dealt with aqueous systems, particularly with poly(ethylene oxide) and polyacrylamide as the polymeric additives. These two polymers, when molecular weight exceeds 10^6 , are particularly good examples of drag-reducing agents in turbulent flow. As low a concentration as 3.3 ppm was sufficient to cut in half the pressure drop for water in one of Fabula's experiments.

Polymer Degradation

A serious problem with drag-reducing agents is the breakdown in molecular weight during flow. The end result of this process is that many

* Presented at the 69th National Meeting of A.I.Ch.E., Cincinnati, Ohio, May 1971.

† Present address: U.S. Navy.

solutions after one or two passes through a pipe flow system revert to the behavior of unmodified solvent. Mechanical degradation under turbulent conditions was investigated for polyisobutylene in various organic solvents.³ Many of the generalizations made in that work, which centered on spinning discs at high speeds, can also be applied to other means of mechanical degradation such as ultrasonic irradiation of dilute solutions.⁴ According to the calculations and conclusions of Harrington,⁵ the hydrodynamic shear forces in fully developed turbulent flow should be insufficient to cause polymer scission by solvent-polymer interaction. Either an extensive laminar boundary layer or the occurrence of cavitation must be postulated. However, cavitation of the sort often seen in ultrasonic irradiation is not observed in the present experiments. Until more experimental evidence has been amassed, it would be risky to hypothesize a detailed mechanism for degradation in turbulent flow through pipes.

EXPERIMENTAL

Test System

In order to establish the pattern of shear degradation at the extremely low concentration effective in drag reduction, it is convenient to use drag-reducing efficiency itself as a criterion for molecular weight.⁶ What is needed is a means for recycling rather small quantities of solution without having pumps and mixing vessels in the system which might also degrade polymer.

A simple device is illustrated in Figure 1. The primary apparatus consists of two parallel systems each having the same dimensions. A 400-ml beaker is joined to a section of 0.8 cm I.D. glass tubing 116 cm in length. The next 31-cm section is made of rubber tubing of 0.85 cm I.D. The final portion of the system is 0.35 cm I.D. glass tubing 60.0 cm in length and is used as the flow-controlling conduit. The collection system consists of a pivoting catch board with four funnels, two bypass tubes, two burets, and two collection beakers arranged as shown in Figure 1. The flow is controlled by a spring-loaded clamp deforming the rubber tubing. In the apparatus, reservoirs I and II are filled with test solution and solvent, respectively, with the clamp closed. With the collecting assembly in position 2, the clamp is opened only long enough to permit each liquid to flow into burets I and II so that each can be adjusted to a reading of zero. Then, with the collecting assembly in position 1, the slide valve is opened. After a few seconds, the collecting assembly is shifted to position 2 for about 3 sec, then returned to position 1. The net result is that all the liquid in each reservoir is now in pans I and II or in the burets. The relative volumes collected in the burets, Q_I and Q_{II} , can be used as a direct measure of drag reduction ($Q_I > Q_{II}$), or they can be converted to a reduction in friction factor by appropriate trans-

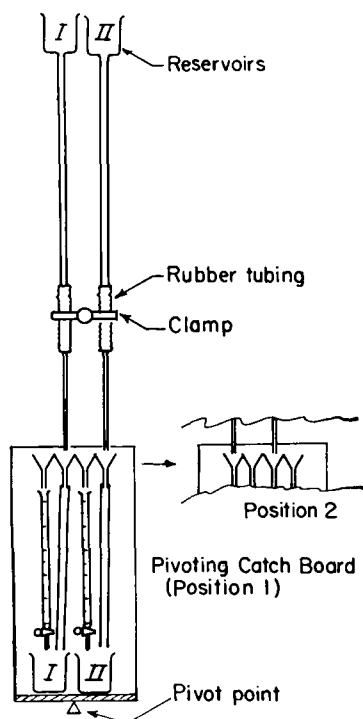


Fig. 1. Apparatus for measuring relative flow rates of solution and solvent.

formations. The time of collection is not important since the ratio Q_I/Q_{II} should be relatively independent of time.

In the system shown, about 200 ml of solution is required. The entrance and exit effects account for less than one fifth of the total pressure drop during flow under these conditions. The Reynolds number is 8500 for water under these circumstances. Since we are dealing only with very dilute solutions with $Q_I > Q_{II}$, the Reynolds number for solutions should always exceed that for water. Degradation is measured in terms of the change in Q_I/Q_{II} as a function of the number of passes through the apparatus.

Conversion of Raw Data to Friction Factor Ratios

The raw data obtained are in the form of Q_I/Q_{II} , which is the same as u_s/u_w , the ratio of solution velocity (average) to solvent velocity at the same overall head h_t . In comparing flow data at various concentrations, the ratio u_s/u_w may be a sufficient measure of drag reduction. However, we can convert it to a ratio of friction factors by taking into account the end effects and calculating the friction factor for water from the Blasius equation.

Because we know how the friction factor for water changes with velocity, it is convenient to estimate the friction factor for the solution f_s at

u_s from the experimental data, and to calculate the friction factor for water f_w from the Blasius equation⁷:

$$f_w = 0.079N_{re}^{-1/4} \quad (1)$$

The Reynolds number N_{re} is given by $Du_s\rho/\eta$, where D is the pipe diameter in dm, u_s is the solution velocity in cm/sec, and η/ρ is the kinematic viscosity of water (0.0091 cm²/sec) at 24.5°C, the testing temperature. The friction factor for the solution is calculated from the measured velocity u_s and the total head h_t :

$$f_s = (h_t - h_e)Dg_c/(2Lu_s^2), \quad (2)$$

where g_c is 981 cm/sec², L is the pipe length, and h_e is the loss in head due to effects outside the pipe (primarily entrance and exit losses). In the present apparatus it was established that

$$h_e = 1.3 \times 10^{-3}u_s^2. \quad (3)$$

The h_e was not affected measurably by drag-reducing agents. Therefore, the ratio of friction factors at u_s can be calculated by combining eqs. (1) through (3) together with the calibration data (Table I) to give

$$\frac{f_s}{f_w} = \frac{(h_t - 1.3 \times 10^{-3}u_s^2)Dg_c}{2Lu_s^2 \cdot 0.079} \left(\frac{Du_s\rho}{\eta} \right)^{1/4} \quad (4)$$

$$u_s = 225Q_I/Q_{II}$$

It must be admitted that data at constant velocity would be easier to correlate, but that advantage is worth giving up in exchange for a single but sensitive system such as the one used here.

Drag Reduction: Concentration Dependence

Three samples of poly(ethylene oxide) were examined (Table II). The main feature of the friction reduction-concentration diagram is an optimum concentration which increased with decreasing molecular weight (Fig. 2). A consequence of the measuring technique used here is that the average velocity changes with f_s/f_w . However, the range of average velocity is not large ($225 < u_s < 320$ cm/sec). Paterson,⁸ who used various velocities in a 0.63-cm-diam. pipe, found only a small change in efficiency with velocity in this range. It is hard to compare the results of any two workers with poly(ethylene oxide) because the polymer is notoriously sensitive to handling. It degrades somewhat on standing and more rapidly on stirring or shaking. However, two of Paterson's samples show the same qualitative decrease in friction with increasing concentration (Fig. 2). The reduction in friction factor is not as great as found by Fabula.¹ Fabula's values of f_s/f_w went down as far as 0.2. However, his velocities were in the range of 500 to 2000 cm/sec in a 1-cm-diam. pipe.

A high molecular weight sample of polyacrylamide was prepared by photopolymerization and subsequently degraded ultrasonically to give

TABLE I
Apparatus Constants and Calibration Data

Tube length L	60.0 cm
Tube diameter D	0.346 cm
Total head h_t	214 cm
Average velocity for water	225 cm/sec
Reynolds number for water	8630
Viscosity of water at 24.5°C	0.0091 stokes

TABLE II
Polymers Studied^a

Sample	Mfr's name (Union Carbide)	Intrinsic viscosity [η] ₁ dl/g	Mol. wt $\times 10^{-6}$	Optimum concn. c_0 , ppm
Poly(ethylene Oxide)				
PEO-A	Polyox FRA	19.5	4.6	2.5
PEO-B	Polyox W301	13.0	2.8	20
PEO-C	Polyox Coagulant	9.8	1.8	75
Polyacrylamide				
PAM-A		11.7	3.8	17.5
PAM-B		9.3	2.9	24
PAM-C		7.3	2.1	38

^a Intrinsic viscosity not corrected for non-Newtonian flow. Molecular weights calculated from eqs. (5) and (6).

a total of three samples seen in Figure 3 and Table II. Once again, the optimum concentration increases with decreasing molecular weight. There seem to be few data on polyacrylamide solutions in the literature. Most workers have used partially hydrolyzed polyacrylamides such as Polyhall 295 (Stein, Hall and Company, Inc., New York) or Dow Et 597 (Dow Chemical Company, Midland, Michigan).⁹ In the present apparatus, a sample of Polyhall 295 acts about like Polymer PAM-B (Fig. 3), even though its dilute solution viscosity is several times larger than that of PAM-B. It is typical of polyelectrolytes like partially hydrolyzed polyacrylamide to give increasing values of reduced viscosity on dilution.^{10,11} The polyacrylamides used here show normal polymer behavior with a Huggins constant¹² of about 0.4 in distilled water.

RESULTS AND DISCUSSION

Flow-Induced Degradation

The lowering of molecular weight by free-radical attack during storage and by mechanical stresses in flow has been a complicating factor in characterizing drag-reducing solutions. This is especially true of poly-(ethylene oxide) solutions. One way to look at the changes in molecular weight is to compare the drag-reducing effect as a function of the number

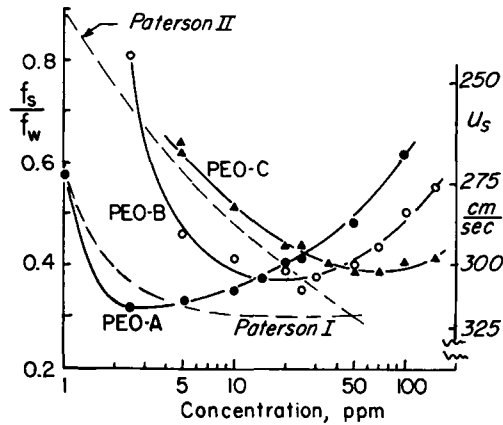


Fig. 2. For three samples of poly(ethylene oxide), optimum concentration increases greatly and minimum friction factor increases slightly with decreasing molecular weight (see Table II). Paterson's sample I had a molecular weight of about 8×10^6 , and II a, value of 1×10^6 .⁸

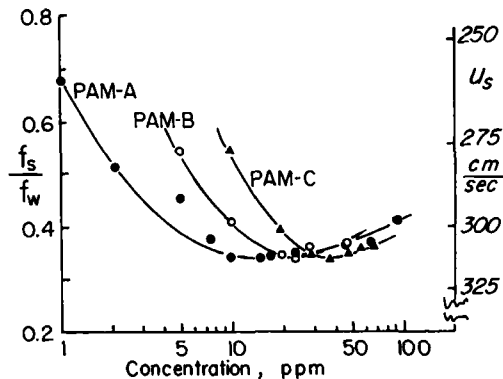


Fig. 3. Polyacrylamide samples show an increase in optimum concentration with decreasing molecular weight (refer to Table II).

of passes through the apparatus. In the present apparatus, the tube is 60 cm long, so that the residence time per pass is, on the average, about 0.2 to 0.3 sec. If we compare the two polymer types at about their optimum concentrations, it is apparent that, after the first pass, polyacrylamide at 10 ppm becomes superior to poly(ethylene oxide) at 2.5 ppm (Fig. 4). Even if we compare both polymers at 10 ppm, they become equivalent after a dozen passes (Fig. 4).

In some applications, a moderate amount of degradation may be no great detriment. However, flow through a fire hose or through a storm sewer system usually would involve residence times on the order of several seconds, so that even a single pass operation might suffer from the equivalent of several passes in the present apparatus.

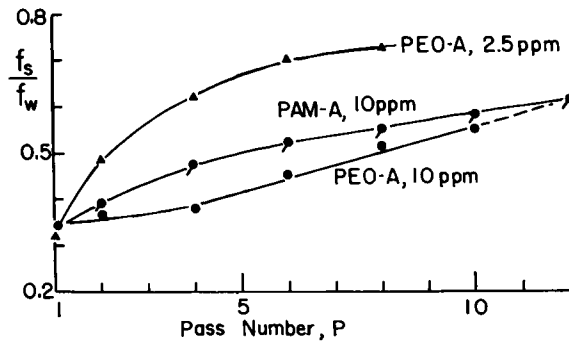


Fig. 4. At about equal initial effectiveness (center and top curves) or at equal concentration (center and bottom curves), polyacrylamide eventually becomes as good or better at reducing friction than poly(ethylene oxide) for the particular samples investigated.

If the degradation due to flow is decreasing molecular weight, the concentration dependence of drag reduction (Figs. 2 and 3) allows a qualitative prediction of some unusual behavior. If we start with the highest molecular weight polymer at a concentration *above* the optimum concentration, the first result of degradation at constant concentration should be to make the solution more effective. For example, PEO-A at a concentration of 50 ppm should degrade progressively through the molecular weights represented by PEO-B and PEO-C. These polymers are more effective at 50 ppm than PEO-A. The effectiveness should go through a maximum once the molecular weight has been reduced to a value for which 50 ppm is *below* the optimum concentration. This prediction is borne out in Figure 5. In Figures 5, 6, and 7, the ordinate is a measure of effectiveness of drag reduction, $1 - f_s/f_w$. For PEO-A at 50 ppm, effectiveness goes through a maximum after about 20 passes (Fig. 5).

An advantage of plotting $\log(1 - f_s/f_w)$ versus \log pass number is the linearity that results. Also, the slope after maximum effectiveness is passed is very nearly the same for all starting concentrations. As a consequence, dividing the pass number by some power of concentration collapses the data into the form seen in Figure 7. The slope for poly(ethylene oxide) is -0.43 and for polyacrylamide, -0.28 . Since a higher power for concentration was used for polyacrylamide, the dependence of $1 - f_s/f_w$ on concentration is the same for both polymers at constant pass number.

Kenis also has studied the degradation in a somewhat different apparatus and comes up with similar results.¹³ When his data are plotted in the presently recommended coordinate system, we get a very similar picture of degradation (Fig. 8). This is of special interest since he worked with a different sample of poly(ethylene oxide) and at about four times the average velocity of the present work and at about one third the tube diameter. The important point here is that the concentration can be reduced out of the plot by this kind of group.

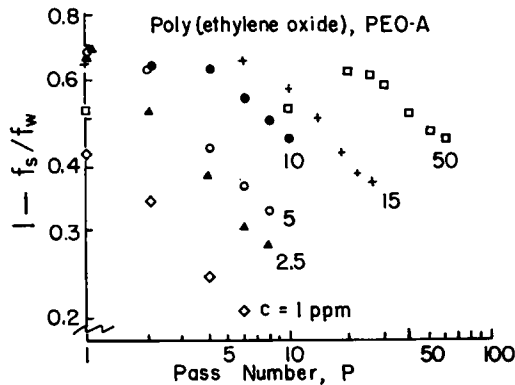


Fig. 5. Drag-reducing effectiveness $1 - f_s/f_w$, shows a regular pattern of degradation with successive passes through the apparatus.

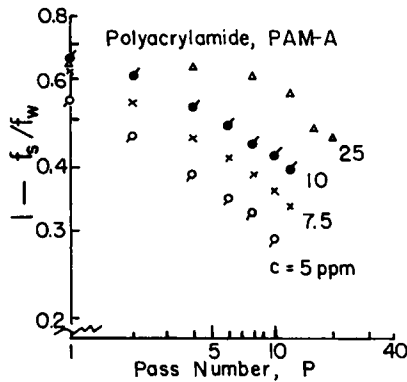


Fig. 6. A polyacrylamide sample shows the same pattern of degradation seen for poly(ethylene oxide) in the previous figure. The slope is less steep, however.

There are other conclusions which can be drawn from the superposed data in Figure 7. One can hypothesize, for example, that for both polymers a change in molecular weight takes place for the same number of passes independent of the concentration. That is, a plot of $\log(1 - f_s/f_w)$ versus \log concentration for various pass numbers would be a series of parallel lines with a positive slope of 0.43 shifting to higher concentrations at higher pass numbers. The fact that polyacrylamide appears to degrade more slowly in terms of $1 - f_s/f_w$ than poly(ethylene oxide) does not mean that the molecular weight is necessarily more stable. It may be a consequence of the molecular weight dependence of the friction reduction for each polymer. One measure of this is the dependence of the optimum concentration c_0 on molecular weight. It can be seen (Fig. 9) that larger changes in molecular weight of polyacrylamide can take place for the same change in c_0 than for poly(ethylene oxide).

Many workers have speculated on the fundamental polymer parameters

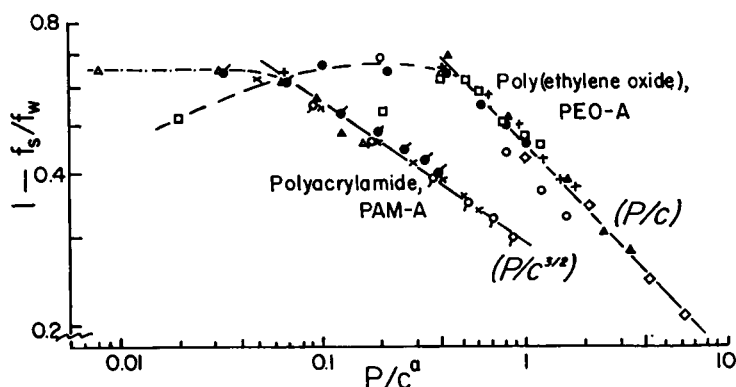


Fig. 7. The degradation behavior for both polymers can be collapsed to a single curve for each by dividing the pass number by a function of concentration.

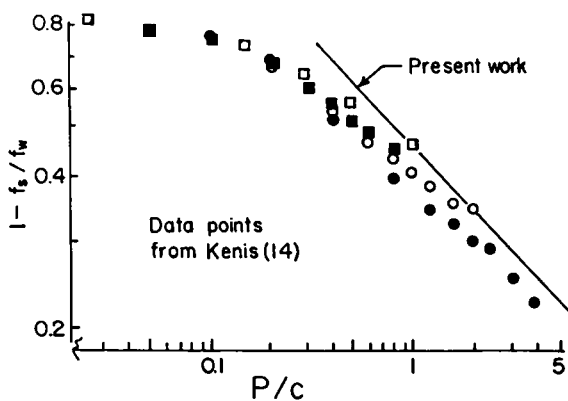


Fig. 8. Kenis' data¹³ can be superposed by using the ratio of pass number P to concentration c . His conditions are $u_s = 1,100$ cm/sec, $D = 0.117$ cm, $L = 41$ cm, and $c = 5$ (●), 10 (○), 20 (■), and 40 (□) g/kl.

that enhance friction reduction. Williams^{14,15} has been a strong proponent of the idea that effective drag reducers have a helical conformation in dilute solution. It is interesting in this respect that neutron inelastic scattering by poly(ethylene oxide) in aqueous solutions has been interpreted as indicating a helical structure for the polymer.¹⁶ Considering the probable atactic structure of polyacrylamide, it seems unlikely that any helical structure could be found for it. This might help explain why there is a difference in the molecular weight- c_0 plots for the two polymers. There is no corresponding difference in dilute solution viscosity. The Mark-Houwink exponents are similar:

$$[\eta] = 1.25 \times 10^{-4} M_v^{0.78} \text{ poly(ethylene oxide)}^{17} \quad 30^\circ\text{C} \quad (5)$$

$$[\eta] = 0.631 \times 10^{-4} M_v^{0.80} \text{ polyacrylamide}^{18} \quad 30^\circ\text{C} \quad (6)$$

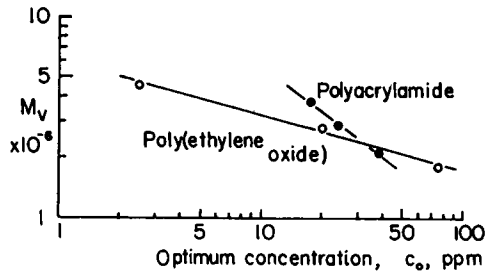


Fig. 9. The optimum concentration for polyacrylamide is less sensitive to molecular weight than it is for poly(ethylene oxide).

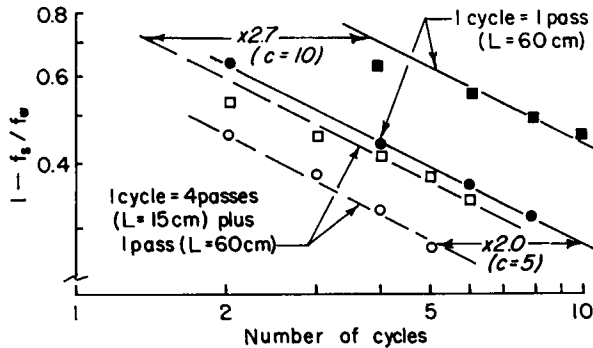


Fig. 10. Measurements of effectiveness were made using PEO-A in the long tube ($L = 60$ cm) alone or after each group of four passes in the short tube ($L = 15$ cm) at the same velocity.

where $[\eta]$ is the intrinsic viscosity in dl/g and M_v is the viscosity-average molecular weight. Of course, the calculated hydrodynamic volume, $[\eta]M$, is larger for poly(ethylene oxide) than for polyacrylamide at the same molecular weight. Although the hydration of the polymer might make the actual hydrodynamic volume somewhat larger, especially for the polyacrylamide, it is not likely to be different enough to explain the difference in slope in Figure 9.

One further question remains. Is the change in effectiveness of the degradation of molecular weight happening in the tube or is it something which is happening also possibly outside the tube in end effects or in the handling of the solution in the recycling process? To study this, two concentrations of poly(ethylene oxide) were tested in a duplicate system using a tube which was one fourth the length of the original tube. The system was adjusted so that the velocity would be the same in both lengths. After four passes in the shorter tube, the solution was measured once in the longer tube. One cycle now means one pass in the long tube plus four passes in the short tube. At a concentration of 5 parts per million, the indication is that one pass through the long tube plus four passes through the short tube is equivalent to two passes through the

long tube; or, in other words, four passes through a length of 15 cm is equivalent to one pass through a length of 60 cm (Fig. 10). This would indicate that all of the degradation is taking place in the tube and almost none of it can be ascribed to end effects or degradation taking place on splashing into the beaker or being poured back into the reservoir and other operations. On the other hand, at a concentration of 10 parts per million the equivalence between the two procedures was 2.7 rather than 2.0, indicating that four passes through the short tube is equivalent to 1.7 passes through the long tube (Fig. 10). This would be an indication that there are indeed, in this case, degradation processes taking place outside the tube: entrance effects, end effects, splashing, other turbulent degradation mechanisms.

References

1. A. G. Fabula, *Proc. Fourth Intern. Congr. on Rheology*, Part 3, E. H. Lee, Ed., Interscience, New York, 1965, p. 455.
2. G. K. Patterson, J. L. Zakin, and J. M. Rodriguez, *Ind. Eng. Chem.*, **61**, 22 (1969).
3. F. Rodriguez and C. C. Winding, *Ind. Eng. Chem.*, **51**, 1281 (1959).
4. M. T. Shaw and F. Rodriguez, *J. Appl. Polym. Sci.*, **11**, 991 (1967).
5. R. E. Harrington, *J. Polym. Sci. A-1*, **4**, 489 (1966).
6. J. W. Hoyt, U.S. Patent 3,420,096 (1969).
7. J. G. Knudsen and D. L. Katz, *Fluid Dynamics and Heat Transfer*, McGraw-Hill, New York, 1958, p. 153.
8. R. W. Paterson and F. H. Abernathy, *J. Fluid Mech.*, **43**, 689 (1970).
9. G. Astarita, G. Greco, Jr., and L. Nicodemo, *A.I.Ch.E.J.*, **15**, 564 (1969).
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell, 1963, p. 635.
11. M. R. Raju and E. W. Merrill, *Polymer Letters*, **2**, 13 (1964).
12. P. J. Flory, *op. cit.*, p. 310.
13. P. R. Kenis, *J. Appl. Polym. Sci.*, **15**, 607 (1971).
14. J. H. Hand and M. C. Williams, *J. Appl. Polym. Sci.*, **13**, 2499 (1969).
15. J. H. Hand and M. C. Williams, *Nature*, **227**, 369 (July 25, 1970).
16. P. G. Assarsson, P. S. Leung, and G. J. Safford, *Polymer Preprints*, **10**, 1241 (1969).
17. F. E. Bailey, Jr., J. L. Kucera, and L. G. Imhof, *J. Polym. Sci.*, **32**, 517 (1958).
18. W. Scholtan, *Makromol. Chem.*, **14**, 169 (1954).

Received June 17, 1971

Revised July 16, 1971