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Effect of Polymer Molecular Variables on Drag Reduction

JACQUES L. ZAKIN
Department of Chemical Engineering
The Ohio State University
Columbus, Ohio 43210

and

DONALD L. HUNSTON*
Naval Research Laboratory
Chemistry Division
Washington, D.C. 20375

ABSTRACT

Drag reduction is the reduction in energy loss in turbulent flows caused by high polymer or other additives. Although the phenomenon was first observed independently by Mysels and by Toms over three decades ago, the complex interactions of the polymer molecules and the turbulent flow are still not well understood. This paper reviews some of the unusual flow characteristics of drag-reducing solutions, discusses potential applications, and points out the limitations posed by mechanical degradation. The effect of polymer molecular weight, molecular weight distribution, concentration, and solvency on drag reduction are shown for narrow molecular weight polystyrene samples and their mixtures.

Various hypotheses for predicting the onset of drag reduction are discussed and compared with measured onset values. The data are best fit by a time-scale hypothesis which depends on the ratio of a molecular relaxation time to a characteristic time of the flow (Deborah number).

*Present address: National Bureau of Standards, Gaithersburg, Md.

Two measures of the relative effectiveness of drag-reducing agents are discussed and results for a number of polymers in hydrocarbon solutions are given.

INTRODUCTION

About 30 years ago, Mysels [1, 2] and Toms [3] independently observed that the addition of aluminum disoaps and high molecular weight poly(methyl methacrylate), respectively, caused significant reactions in pressure drops in the turbulent flows of hydrocarbon liquids in tubes. In 1931, Forest and Guerson [4] had observed a similar effect in the flow of wood pulp fibers but little notice had been taken of it. In 1963, Savins first used the term "drag reduction" and pointed out the potential practical significance of its utilization.

During the past 15 years, interest has grown in this unusual phenomenon in which major effects, up to 90% reduction in turbulent energy loss, can be caused by only small amounts, a few parts per million, of high polymers. Researchers from fields as diverse as the structure of turbulence, rheology, hydraulics, and polymer chemistry have studied drag reduction. During this time, the journal and patent literature have mushroomed along with considerable unpublished industrial research and development results. A number of new types of drag reduction additives have been found, such as conventional aqueous soaps [5], so-called "complex soaps" [6], and nonionic surfactants [7, 8], as well as a greatly increased variety of high polymers, aluminum disoaps [9], and fibrous particulates [10]. However, the high polymer additives are by far the most effective and show the most potential for commercial application.

The first known application of the phenomenon was in the late fifties when high polymers were used as additives to fracturing fluids in oil fields in secondary recovery operations. In addition to their use in fracturing fluids, polymer drag reducers are being added to water pumped through fire hoses to produce a more coherent water stream and a greater effective fire hose range [11]. Moreover, the additive also can increase the throughput or reduce the size of hose needed for a given throughput. Polymeric drag reducers are being injected into storm sewers in Dallas and near Bristol, England [12] at times of peak loads during heavy storms to handle the increased run-off. They are also being field-tested in Czechoslovakia for hydrotransport of fly ash from power plants burning high ash coals [13]. Of special interest are recent successful tests of polymer injection into the Alyeska pipeline to increase the throughput of Alaskan crude [14]. Other potential applications include pipeline transport of slurries, high pressure jet cutting, hydraulic fluids, district heating, and nautical applications.

Because of the sensitivity of the most effective high polymer drag-reducing additives to mechanical degradation and the cost of the additives, they are not yet in widespread commercial use and applications have been limited to special situations.

LITERATURE REVIEW

A number of valuable general review papers on polymer drag reduction have been published [15-17]. They discuss the solution variables and the flow variables affecting drag reduction and mechanisms for drag reduction. Only a few of the specific research papers relating to the onset of drag reduction will be referred to here.

The variables affecting the onset of drag reduction were of particular interest to the early investigators. In 1965, three independent and almost simultaneous reports were written offering onset hypotheses.

Hershey [18] and Fabula et al. [19] proposed that molecules become active in reducing drag when their terminal relaxation times are equal to or greater than the characteristic time scale of the flow. The flow time scale was taken as η/σ_w, where η is solution viscosity and σ_w is the wall shear stress in tube flow. Since the flow time scale decreases as the flow rate increases, onset occurs when $\eta/\sigma_w^* = \tau_{1H}$, where τ_{1H} is the largest terminal relaxation time in the sample, i.e., for the highest molecular weight species present in the molecular weight distribution, τ_1 is the longest relaxation time for any species, and σ_w^* is the wall shear stress at which drag reduction begins (see, for example, Fig. 5).

Virk [20] proposed that the size of the molecules is the critical quantity and that onset occurs when the ratio of twice the radius of gyration R_g to the size of a characteristic length scale reaches a critical value.

A more recent hypothesis, based on energy concepts [21, 22], suggests that the ratio of the rate of energy storage by the polymer molecules to the rate of convection of turbulent energy away from the wall must reach a critical value for onset to occur.

Table 1 lists the predictions for the average wall shear rate at onset for these hypotheses. In this table, σ_w^* is the wall shear stress at onset, η is the solution viscosity, $[\eta]$ is the intrinsic viscosity, M is molecular weight, C is polymer concentration, and K_1 and K_2 are constants. Since it is not easy to establish appropriate values of the quantities involved in these expressions for polydisperse samples, a

TABLE 1

Onset Predictions

Hypothesis	Predicted (σ_w^*/η)
Time [18, 19]	$1/\tau_1$
Size [20]	$K_1\eta/R_g^2$
Energy [21, 22]	$K_2/[\eta]^2\eta MC$

conclusive test of these predictions is difficult. The present experiments with "nearly monodisperse" polystyrene samples offer some unique advantages in this regard. Moreover, unlike many polymers, data for polystyrene can be obtained over a wide range of concentrations. This is important because the three formulations predict different concentration dependencies. Since the variation of onset point with concentration is small, data must be obtained over a wide range if an accurate assessment is to be obtained.

Recent papers on a time-based hypothesis for onset [23-26] also predict flow rate dependence. They suggest that only the "top part" of the molecular weight distribution can contribute to drag reduction. However, once the flow rate reaches a level at which all of these molecules become active in reducing drag, the effect levels off and further increases in flow rate produce little change in the drag reduction level. The nature of the flow rate dependence, therefore, is dependent on the shape of the "top part" of the molecular weight distribution.

EXPERIMENTAL

Drag reduction and gel permeation chromatograph (GPC) measurements were made on a series of monodisperse polystyrene samples in two "thermodynamically" good solvents, toluene and benzene, and in a thermodynamically "poor" solvent, a mixture of 58% toluene (by weight) and 42% 2, 2, 4-trimethylpentane (isooctane). The samples studied and their solution properties are shown in Table 2. The drag reduction apparatus has been described in a number of previous reports [27]. It employed a 1.58 mm diameter tube and covered a Reynolds number range for these solvents up to about 18, 000. Polymer degradation was done by using a high speed (3000 rpm) Virtis mixer. The degradation experimental methods have been described previously [28].

TABLE 2

Polystyrene Properties

Polymer source	Polystyrene sample	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$[\eta]$ (dl/g) Toluene	$[\eta]$ (dl/g) Mixed solvent
Duke Standards Co.	7M	7.1×10^6	1.1	10.4	2.4
Duke Standards Co.	4M	4.1×10^6	1.1	7.2	1.8
Pressure Chem. Co.	2M	2.4×10^6	1.2	5.0	1.4

The use of polystyrene in a study of this type has a great advantage since it has been extensively studied and can readily be characterized by GPC. Moreover, it is one of the few materials for which the τ_1 values calculated from molecular theories have been compared with experimental data for very dilute solutions [29]. The values of τ_1 used here were calculated from the molecular theory of Zimm as modified for nonhomogeneous molecular weight distributions [30]:

$$\tau_1 = [(\eta - \eta_0)M_i^2/2.369M_wCRT]$$

where η is solution viscosity, η_0 is solvent viscosity, M_i is the molecular weight of the highest species present, in this case taken as M_{Z+1}, C is polymer concentration, R is the gas constant, and T is absolute temperature. Since the viscosities of the degraded solutions were not measured, viscosities were estimated from the Huggins equation using intrinsic viscosities calculated from GPC values of $\overline{M}_w$ using the Mark-Houwink equation. The constants used in these equations were those for undegraded solutions. This is probably a good approximation since the shapes of the molecular weight distributions were not greatly changed by the degradation conditions used here (see Table 3).

TABLE 3

Degradation of 970 ppm 4M Polystyrene in Toluene

Degradation time (sec)	$\frac{\overline{M}_w/\overline{M}_n}{\overline{M}_w/\overline{M}_{no}}$
0	1.00
45	1.04
135	1.05
405	0.99

RESULTS AND DISCUSSION

Polymer Solution Variables Affecting the Level of Drag Reduction

Drag reduction is enhanced by high molecular weight.. It increases to a maximum with increase in concentration. Drag reduction effectiveness of a polymer is greater in thermodynamically "good" solvents and is smaller in "poor" solvents. These effects are illustrated in Figs. 1 and 2, where percent drag reduction at Reynolds number ~16,000 in the 1.58 mm tube is plotted against concentration in parts per million by weight. Figure 1 shows data for the three polystyrene samples in toluene at 25°C, a good solvent, and Fig. 2 shows data for the same three samples in a mixture of toluene and isooctane at 25°C. The mixture at 25°C is a "poor" solvent. Drag reduction increases rapidly at low concentration for all three molecular weights and approaches an asymptotic maximum value for these flow conditions at "high" concentrations. The asymptote value and the magnitude of "high" are dependent on molecular weight and solvency.

The large increases in drag reduction with increase in molecular weight are consistent with the fact that the molecular weights are less than one order of magnitude greater than the minimum molecular weight M_{min} required to observe drag reduction with polystyrene. $M_{w,\,min} \sim 10^6$ for the flow conditions of these experiments [31]. Previous studies [32] have shown that the maximum drag reducing ability of a polymer increases rapidly in the range from M_{min} to $10M_{min}$.

The effects of molecular weight distribution can be examined by considering 7M-2M mixtures. The data for mixtures containing either 58% 2M or 87% 2M in toluene lie close to the 7M results shown in Fig. 1 if the concentration of the 7M component is plotted as the abscissa. The presence of concentrations of 2M which, by themselves, would give significant drag reduction, had no measurable effect at these ratios of the two polymers. Hunston observed similar effects for 7M-2M polystyrene mixtures in benzene at concentrations of 30 to 89% of 2M [31].

Earlier investigators observed that drag reduction levels in poor solvents were lower than in good solvents at equal concentrations under similar flow conditions [33-36]. The data in Figs. 1 and 2. show clearly how concentration, molecular weight, and solvency are related to drag reduction efficiency for polystyrene. Above some limiting concentration for each molecular weight, drag reduction in the poor solvent is about two-thirds that in the good solvent at the same concentration and flow rate (approximately equal Reynolds

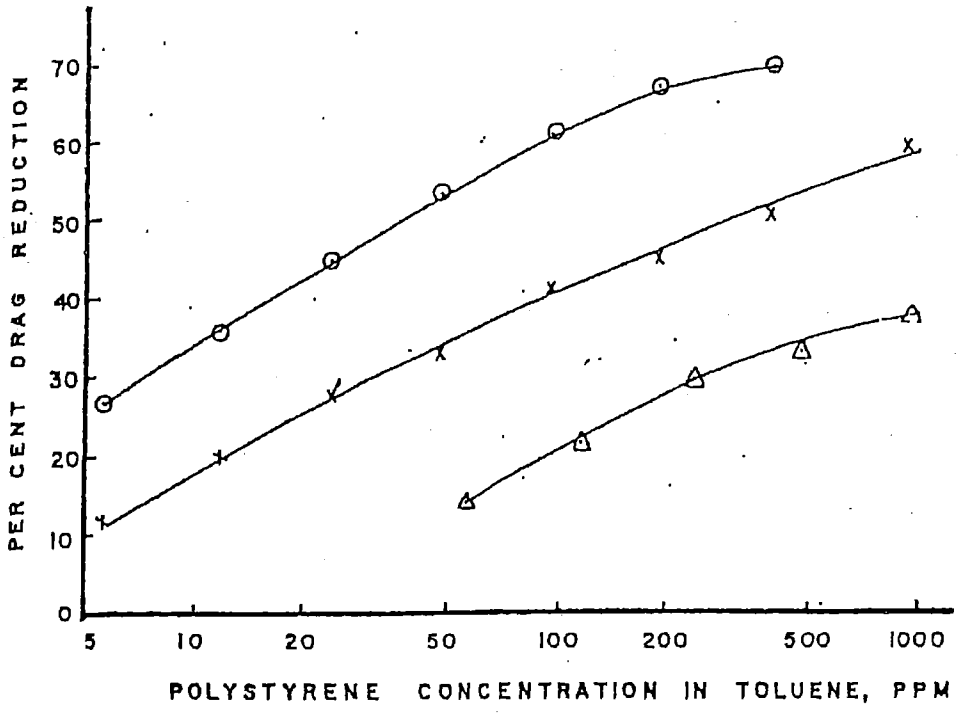

FIG. 1. Drag reduction vs. polymer concentration of various samples in good solvent in 1.58 mm tube, Reynolds number = 16,000: (O) 7M; (X) 4M; (Δ) 2M.

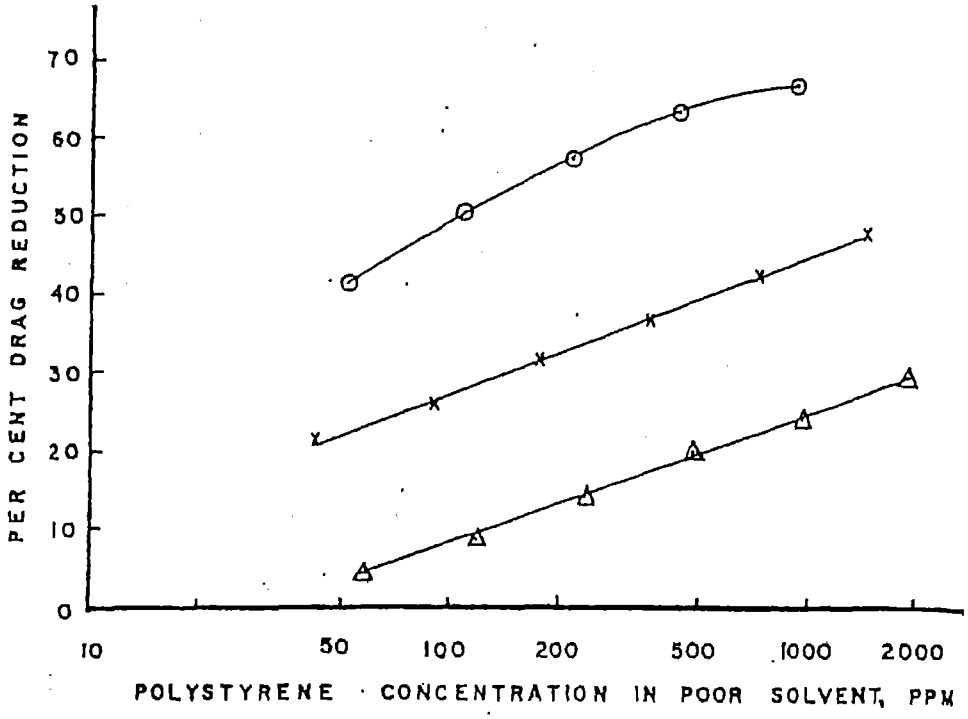

FIG. 2. Drag reduction vs. polymer concentration in poor solvent in 1.58 mm tube, Reynolds number = 17,000: (O) 7M; (X) 4M; (Δ) 2M.

numbers). Concentrations required for equal percent drag reduction are three to four times greater in the poor solvent. This is roughly equal to the ratios of intrinsic viscosity in the good solvent to those in the poor solvent. Thus, for a given polymer sample, $C[\eta]$ values (which are close to pervaded volume fractions) at equal levels of drag reduction are roughly constant, a result similar to previous observations [36].

Having observed the effects of polymer solution variables on the level of drag reduction under particular flow conditions, it is also of interest to examine their effects on the onset of drag reduction and on flow rate dependence above onset.

Onset

The estimation of onset points is subject to considerable error as it involves the determination of the point of intersection of two lines whose angle of intersection is small. The problem is accentuated at low concentrations as can be seen in the flow rate vs. wall shear

stress data traces in Fig. 3. Nevertheless, in these data and in a large number of other runs, little change in wall shear stress at onset was observed with increase in polymer concentration. This is consistent with the time-based onset hypothesis (Table 1) which predicts that σ_w^* will vary as $\eta/[(\eta - \eta_o)/C]$, which is a weak function of C at low concentrations.

The size-based onset hypothesis predicts that σ_w^* should be proportional to η^2/R_g^2. Since the numerator η^2 increases and the denominator R_g^2 decreases with concentration, this hypothesis predicts a stronger concentration dependence than observed experimentally. The energy-based onset hypothesis predicts that σ_w^* should be proportional to the reciprocal of concentration, a far stronger dependence on concentration than what is observed. Thus, only the time-based hypothesis appears to be consistent with the observed concentration effects.

Table 4 lists the values for the time scale onset ratio (Deborah number), $\tau_1 \sigma_w^*/\eta$, obtained for fresh and degraded solutions in the

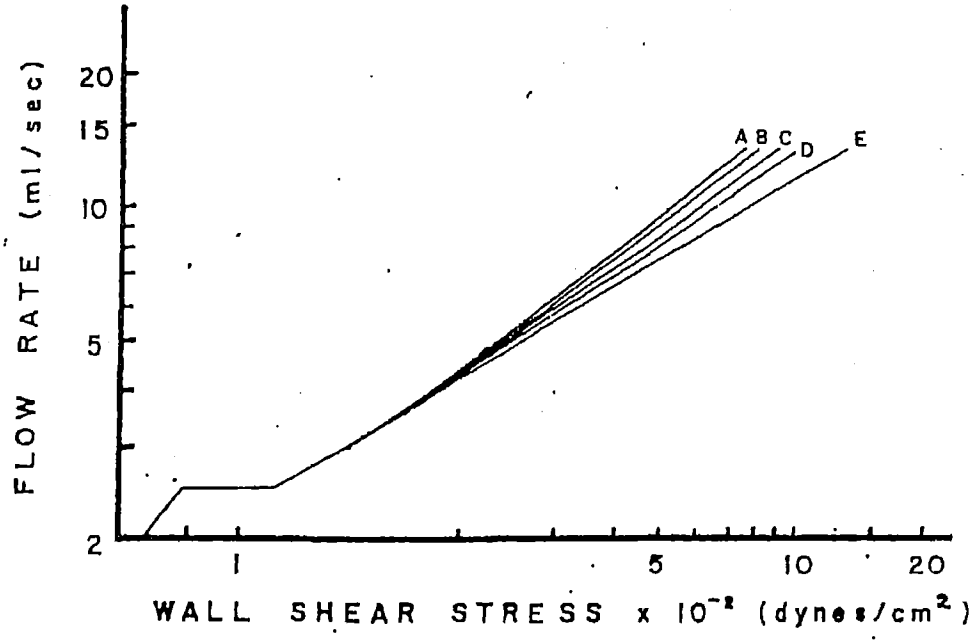

FIG. 3. Flow curves for fresh 4M polystyrene in toluene solutions in 1.58 mm tube: (A) 150 wppm; (B) 100-wppm; (C) 50 wppm; (D) 25 wppm, (E) solvent.

TABLE 4

Onset in Mixed Solvent

Polymer	Concentration (wppm)	Degradation time (sec)	Onset ratio $(\sigma_w^*/\eta)\tau_1$
7M	113	0	8.2
	226	0	10.5
4M	46.9	0	8.0
	93.8	0	7.2
	93.8	0	7.8
	188	0	7.6
	750	0	6.3
	1500	0	4.8
	1500	0	5.3
	1500	0	5.5
	150	0	7.3
	150	15	13.3
	150	45	15.3
2M	62.5	0	13.4
	125	0	11.2
	250	0	8.2
	500	0	7.0
	1000	0	6.0
	2000	0	5.1
	1000	0	5.8
	1000	30	6.7
	1000	90	6.5
	1000	270	5.4

mixed solvent which is a thermodynamically "poor" solvent for polystyrene. Within experimental error, the onset ratio is approximately constant showing only small variations over a wide range of concentrations and molecular weights. However, it has a value about one order of magnitude larger than that predicted by the time-based onset hypothesis. A weak concentration effect does appear to be present in the 4M and 2M results with a trend to lower values of the onset ratio as concentration increases.

Values of onset ratios in benzene and toluene, thermodynamically "good" solvents for polystyrene, are shown in Table 5. Although the

TABLE 5

Onset in Good Solvents

Polymer	Solvent	Concentration (wppm)	Degradation time (sec)	Onset ratio $(\sigma_w^*/\eta)\tau_1$
7M	Benzene	4.6	0	38.2
		5.7	0	38.2
		11.5	0	36.8
		11.5	0	35.9
		22.9	0	32.7
		28.6	0	32.2
		45.8	0	27.8
		57.3	0	29.9
		57.3	0	28.4
		68.7	0	28.2
		91.6	0	27.4
		91.6	0	25.3
		115	0	26.5
		115	0	26.9
7M	Toluene	63	0	31.9
		100	0	27.4
		100	405	17.4
42% 7M 58% 2M				
4M	Benzene	11.4	0	32.3
		11.4	0	27.7
		22.9	0	32.7
		28.6	0	27.9
		57.2	0	20.0
		57.2	0	21.9
		115	0	16.9
		115	0	19.1
		286	0	14.6
		286	0	15.6
		573	0	12.4
		573	0	13.9
4M	Toluene	6.3	0	38.2
		12.5	0	34.2
		50	0	20.8
		150	0	15.2
		150	45	13.4
		150	135	9.1
		150	405	11.8

TABLE 5 (Continued)

Polymer	Solvent	Concentration (wppm)	Degradation time (sec)	Onset ratio $(\sigma_w^*/\eta)\tau_1$
2M	Benzene	14.3	0	29.9
		26.8	0	22.9
		28.6	0	23.5
		53.7	0	22.0
		57.3	0	18.8
		71.6	0	20.7
		107	0	19.1
		115	0	16.8
		143	0	19.1
		215	0	16.3
		286	0	17.0
		429	0	14.9
		573	0	15.6
		573	0	11.9
		859	0	12.1
		1145	0	12.6
		1717	0	9.8
		2290	0	9.4
2M	Toluene	250	0	15.1

onset ratios in this table vary by a factor of about 4 (concentration ratios vary by up to 150 times), the variation is systematic and related almost entirely to concentration variables. At high concentrations, $C[\eta] \to 1$, where the polymer-polymer interactions cause shrinkage of the molecules in the good solvent to the point where the molecular pervaded volume approaches that characteristic of the poor solvent [37, 38], the onset ratio approaches the poor solvent value.

The explanation for the deviations observed in the good solvent may arise, at least in part, from failure of rheological theories to predict the terminal relaxation times in polymer solutions. The Zimm theory, which is utilized here, is known to describe the behavior in "poor" solvents quite well but it is less successful for "good" solvents. Moreover, recent studies at the University of Wisconsin have shown that the inclusion of concentration dependence via viscosity is not very accurate, particularly for a good solvent [39].

Flow Rate Dependence

As mentioned earlier, recent papers on time-based hypotheses assert that the flow rate dependence of drag reduction is related to the shape of the "top part" of the molecular weight distribution. Unfortunately, a quantitative statement for a mechanism as well as an exact definition of "top part" are not available at present. Nevertheless, several qualitative tests of the predictions are possible.

For a given polymer sample, the molecular weight of the largest molecule present in the distribution is determined by the kinetics of the polymerization. Thus, increasing the concentration of polymer in a solution cannot increase this top molecular weight. The number of activated molecules in the "top part" of the distribution, however, increases as the concentration is raised and thus the drag reduction level at each flow rate above the onset point will be increased. Consequently, the theory predicts that the drag reduction flow curves for a series of concentrations will display a fan-shaped appearance, i.e., the flow rate dependence will change markedly—increasing with increasing concentration—while the onset point exhibits a relatively small dependence on concentration. Figure 3 shows tracings of a set of flow curves for the 4M sample in toluene. The fanlike appearance seen here is typical of all the polystyrene results. Two effects of increasing concentration cause a shift in the onset point. First, the resultant increase in solution viscosity causes an increase in the relaxation time τ_1, and if the time-based onset hypothesis is correct, this would lead to a lower value of the onset wall shear rate. Second, the lower concentration solutions may contain a small number of very high molecular weight polymer molecules which are present in concentrations too low to have measurable effects as drag reducers. When the concentration is increased, these very high molecular weight species may reach a concentration at which they can lower the onset shear rate.

A second qualitative test of the theoretical flow rate predictions can be obtained by comparing samples where the molecular weight distribution is shifted to different molecular weights but the shape remains relatively constant. A unique opportunity to test such samples is provided by the degradation experiments.

GPC measurements on polystyrene samples of fixed concentration degraded by high speed stirring indicate that, although some change in shape of the molecular weight distribution was produced by the degradation, the primary effect is a shift to lower molecular weights (see Fig. 4 and Table 3). Figure 5 shows tracings of the flow curves for the same samples whose GPC curves are given in Fig. 4. The flow curves for these samples show a parallel shift corresponding to

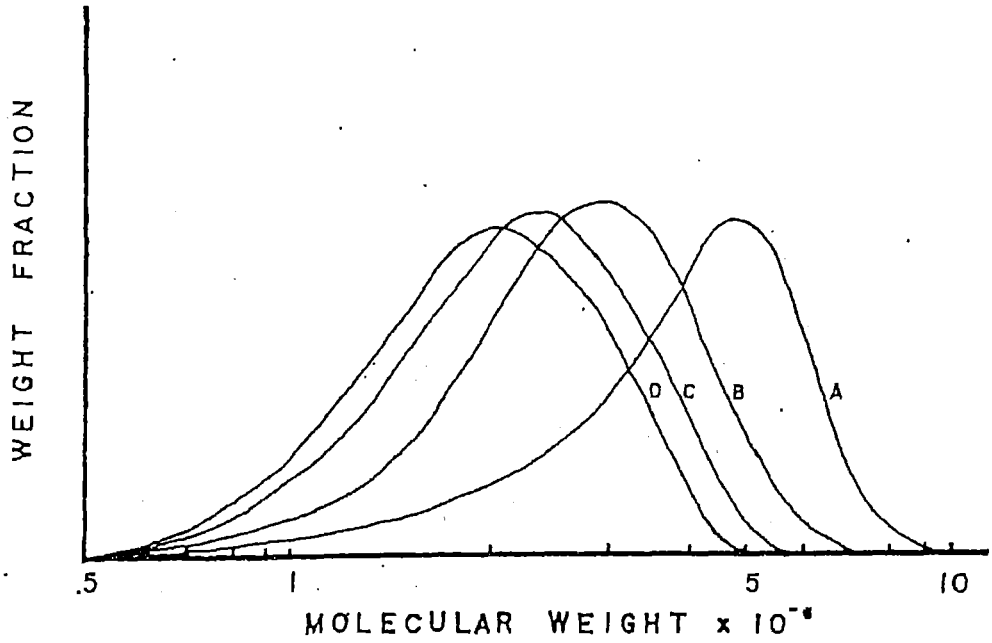

FIG. 4. Gel-permeation chromatograph curves for fresh and degraded 970 wppm 4M polystyrene in toluene solution for various degradation times: (A) 0; (B) 45 sec; (C) 135 sec; (D) 405 sec.

an increase in onset shear stress with very little change in flow rate dependence. Drag reduction measurements with degraded 2M and 7M samples gave similar results.

Measures of Effectiveness of Polymer Additives

For low concentration solutions at a constant Reynolds number beyond the onset point, an empirical equation proposed by Virk et al. [40] and Little [32] can provide an approximate fit of the data. The equation is:

$$DR/DR_m = C/([C] + C)$$

where DR is percent drag reduction and C is concentration of polymer. Plotting C/DR versus C data for one size tube at a fixed Reynolds number, $1/DR_m$ is the slope and the limiting value of

(DR/C) as C approaches zero is $DR_m/[C]$. Values of the maximum percent drag reduction DR_m and the intrinsic concentration [C] are shown in Table 6 for several molecular weights of polystyrene in different solvents. They are empirical constants characteristic of each polymer-solvent system and the flow conditions. Generally, the larger the value of DR_m and the smaller the value of [C], the more effective the polymer as a drag-reducing additive in that solvent. As expected, polymer systems of high molecular weight and good solvency tend to show larger values of DR_m and smaller values of [C]. The addition of low molecular weight polymer in a mixture has little effect on DR_m. If [C] values are calculated based only on the high molecular weight species (7M) present; the low molecular weight species has no effect (see column 5). The results for the 13% 7M-87% 2M mixture in toluene are anomalous and may be in error.

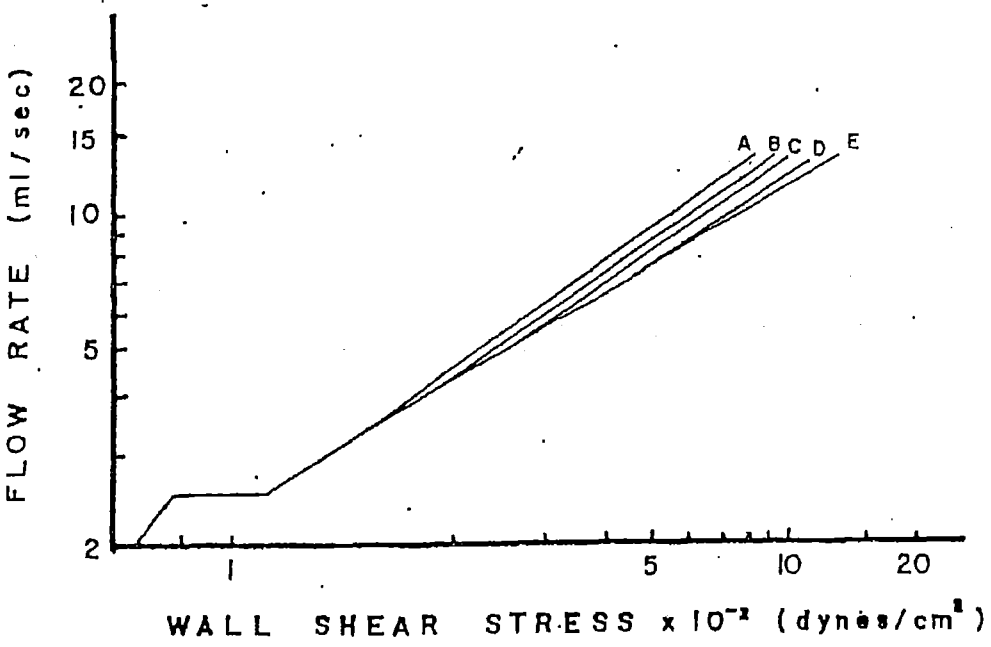

FIG. 5. Flow curves for fresh and degraded 4M polystyrene in toluene solutions in 1.58 mm tube. Degradation was carried out at 970 wppm. Flow curves are for solutions diluted to 150 wppm, with various degradation times: (A) 0; (B) 15 sec; (C) 45 sec; (D) 135 sec; (E) 405 sec and solvent.

TABLE 6

Drag Reduction Parameters

Polystyrene sample	Solvent	DR_m	[C] ppm	$[C]_{7M}$ (ppm)
2M	Toluene	44	125	a
2M	Benzene	42	90	a
2M	Mixed solvent	33	310	a
4M	Toluene	60	37	a
4M	Benzene	60	37	a
4M	Mixed solvent	50	70	a
7M	Toluene	75	13	a
7M	Benzene	73	12	a
7M	Mixed solvent	70	35	a
7% 7M / 93% 2M	Benzene	72	157	11
13% 7M / 87% 2M	Benzene	70	77	10
26% 7M / 74% 2M	Benzene	69	54	14
52% 7M / 48% 2M	Benzene	73	21	11
13% 7M / 87% 2M	Toluene	60	54	7
42% 7M / 58% 2M	Toluene	74	48	12

[a] Does not apply.

This approach appears to offer a convenient measure of polymer additive effectiveness in dilute solution to permit comparisons among different polymer-solvent systems. For example, poly(ethylene oxide) samples in water show values of DR_m up to 90% and values of

[C] less than unity [32]. However, values for only a few polymer types in aqueous systems have been reported.

Another measure of effectiveness based on more concentrated polymer solution behavior has been proposed by Patterson and Zakin. They suggested that the lowest polymer concentration C_c at which onset occurs in the laminar region (with no transition region observed) can be used as a measure of drag-reducing effectiveness in a particular flow system. This is illustrated in Fig. 6, where data for three concentrations of polyethylene oxide in benzene are shown as friction factor versus Reynolds number plots. At 200 wppm, typical "low concentration" onset is observed as departure from the turbulent (von Karman) line at a Reynolds number near 2700. At 1000 wppm, transition from laminar to turbulent behavior is seen, but the data points all lie below the von Karman line. At 2500 wppm however, the data show only a gradual departure from the laminar (Poiseuille) line. Thus, for this polyethylene oxide sample in benzene in this flow system (8.2 mm diameter tube), C_c lies between 1000 and 2500 wppm.

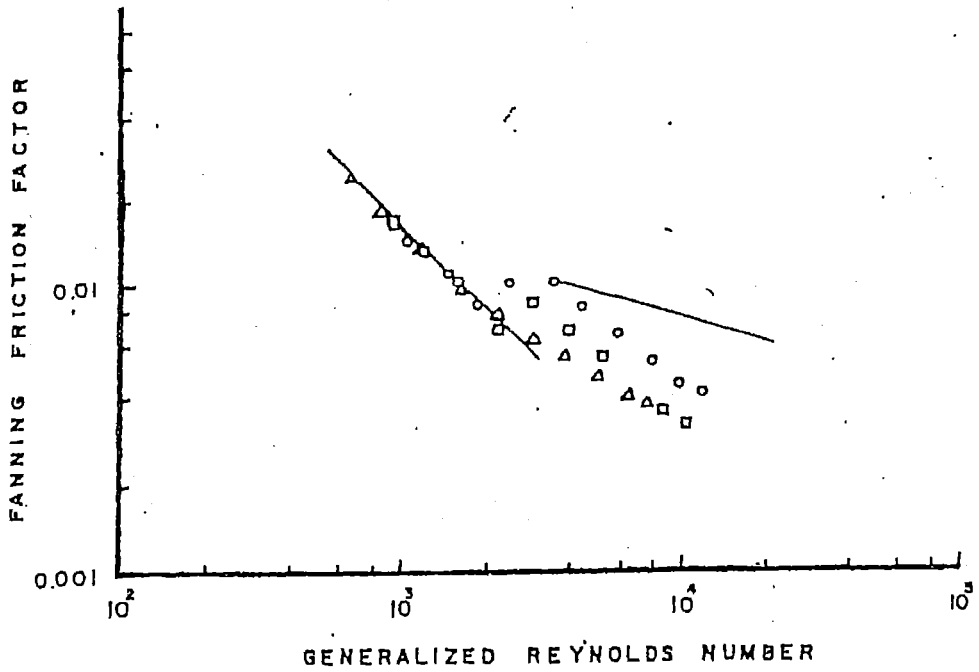

FIG. 6. Friction factor vs. Reynolds number curves for poly-(ethylene oxide) in benzene in 8.20 mm tube: (O) 200 wppm; (□) 1000 wppm; (Δ) 2500 wppm.

The products of C_c and intrinsic viscosity were compared for a series of polymers of different molecular structures in hydrocarbon solvents [41]. When comparisons were made for molecular chains containing equal numbers of chain entanglement units, M/M_c, the product $C_c [\eta]$ increased monotonically with β, the rigidity factor. (β is the ratio of the root-mean-square end-to-end distance under ideal conditions to the root mean square value assuming free rotation.) Comparisons made at equal numbers of chain units or equal degrees of polymerization gave anomalous results.

Poly(ethylene oxide) and polydimethylsiloxane, polymers with low values of β, are known to be much more efficient drag-reducing additives than poly(methyl methacrylate) or polystyrene which have high values. Polymers such as polybutadienes and polyisoprenes with intermediate values of β also show intermediate $C_c [\eta]$ values.

Unfortunately, no comparison of relative effectiveness of polymers using the two approaches is possible as the high concentration approach has been used exclusively in hydrocarbon solvents. To our knowledge, the [C] and DR_m data for polystyrene reported here are the only values in hydrocarbon solvents reported thus far.

Acknowledgment

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