

Shear Degradation of Polymer Solutions

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Synopsis

Shear degradation of polyisobutylene solutions was studied in laminar flow through capillaries. A special apparatus was designed with a view to a controlled shear history. The various effects of initial molecular weight, concentration, temperature, and shear stress at the wall on the final degradation product are combined in a single parameter representing the minimum force required for degrading a polymer sample to its final state.

This work is based on the M.Sc. Thesis of A. Kadim, submitted at the Department of Chemical Engineering, Technion—Israel Institute of Technology, Haifa, Israel.

INTRODUCTION

The degradation (depolymerization) of polymers induced by simple shear imposes severe limitations on uses whose effectiveness is controlled by the very high molecular weight. This type of instability has been encountered in such practical cases as viscosity index improvement of lubricating oils^{1,2} and drag reduction;³ it also impairs the reliability of polymer characterization at high shear.⁴ Hence the need for study of its factors and for effective means of control. In contrast to earlier studies,⁵⁻⁸ mostly carried out under conditions of turbulence induced by high-speed agitation or by ultrasonic waves, the authors attempted to keep to a well-defined laminar flow regime. A modified McKee consistometer⁹ was designed with a view to reliable data under various flow conditions and to a controlled shear history. No success, however, was achieved in the attempt to arrest degradation with the aid of external additives, and further effort is called for in understanding the role of the chemical and configurational structure of the polymer and its interaction with the solvent.

EXPERIMENTAL

The apparatus, designed for continuous automatic operation, consists of two identical stainless-steel thermostatic vessels connected by a horizontal capillary (Fig. 1). Transfer of the polymer solutions is affected by nitrogen gas pressure, the use of pumps or pistons being avoided in order to eliminate possible external sources of degradation. The vessels (A) are set in a thermoregulated bath (B) kept constant within $\pm 0.05^\circ\text{C}$. The capillary (C) ($l = 76.5$ mm, $d = 0.62$ or 0.33 mm) is insulated, and both pressure and temperature are measured with high accuracy at its ends. The automatic

control consists of an electronic regulator-counter (D) (Hengstler-FA-043D, with provision for presetting for any desired number of passes) operated by impulses from a photoresistor (G). The photoresistor in turn is connected with a rotameter measuring the flow rate of the nitrogen gas, which is introduced into the vessels through two sets ofasco 8262-B-95 electromagnetic valves (E and F), operating up to 134 atmospheres. At the end of

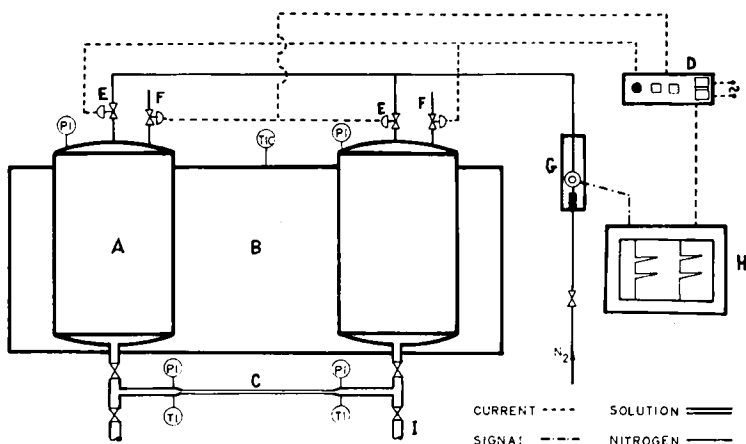


Fig. 1. Apparatus for shear degradation. For explanation see text.

each cycle, the float of the rotameter rises in response to the sudden increase in the flow rate of the nitrogen and the resulting impulse is transmitted to the regulator and to a Honeywell Recorder (H). The interval between two consecutive recorder readings is proportional to the duration of the cycle, which is gradually reduced in the course of the experiment; a

TABLE I
Data on Test Polymer

Type	Source	Molecular weight \bar{M}_v^a
PIB Oppanol B-200	BASF	6.4×10^6
PIB Oppanol B-100	BASF	1.3×10^6
PIB Vistanex L-120	Enjay	1.6×10^6

^a Viscometric average of molecular weight.

constant interval indicates equilibrium of the degradation process. Samples are drawn manually (through valve I) at different stages of each degradation run (maintained at constant temperature and constant shear stress at the capillary wall) and subjected to low-shear viscosity measurements in an Ostwald viscometer.

The polymer used was polyisobutylene (PIB), known as an excellent drag reducer in kerosene³ but subject to chain scission (Table I).

Decalin solutions were carefully prepared over a range of concentration (0.264 to 1.05 g/dl). Molecular weights before and after degradation were determined through intrinsic viscosity measurements in an Ubbelohde viscometer. The flow behavior of the original solutions, as measured in a rotational viscometer (Epprecht Rheomat 15) and shown in Figure 2, is pseudoplastic in character.

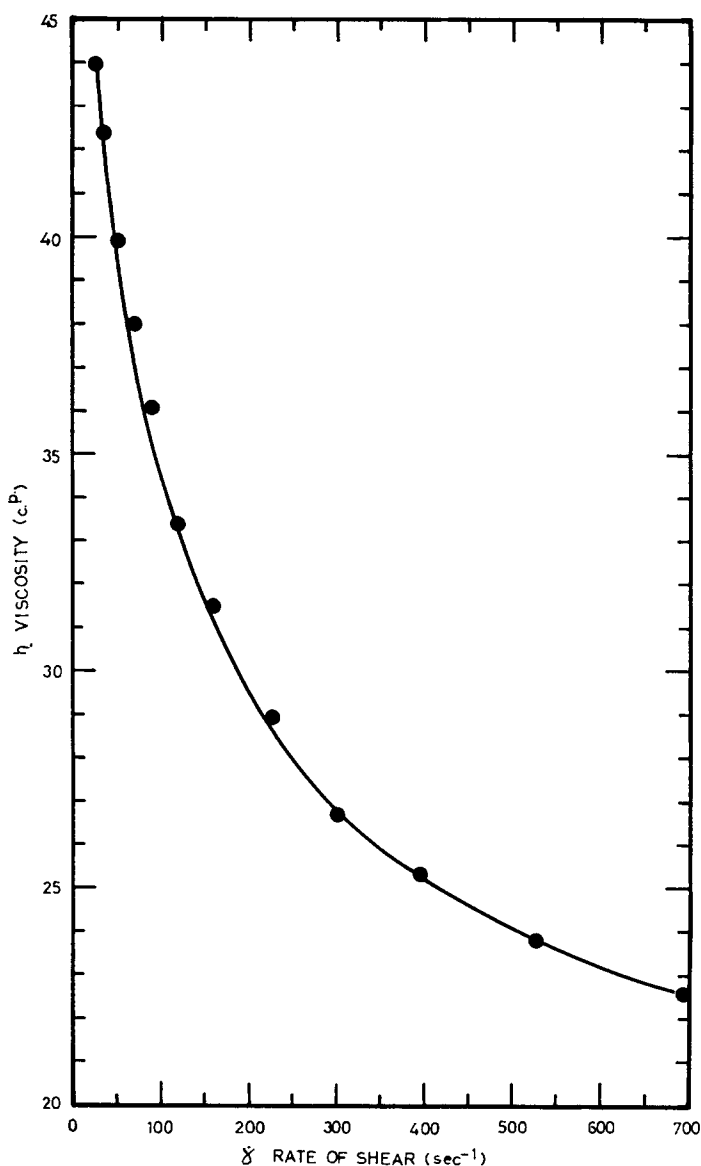


Fig. 2. Dependence of initial viscosity on shear rate. PIB B-200, $C = 0.525$ g/dl in Decalin.

RESULTS AND DISCUSSION

A typical shear history is shown in Figure 3. Following an initial steep drop, the viscosity (measured at low shear stress) tends to an asymptote after 100–150 passes (the latter figure was taken as the state of equilibrium), but its final value clearly depends on the prevailing shear stress (see Fig. 4).

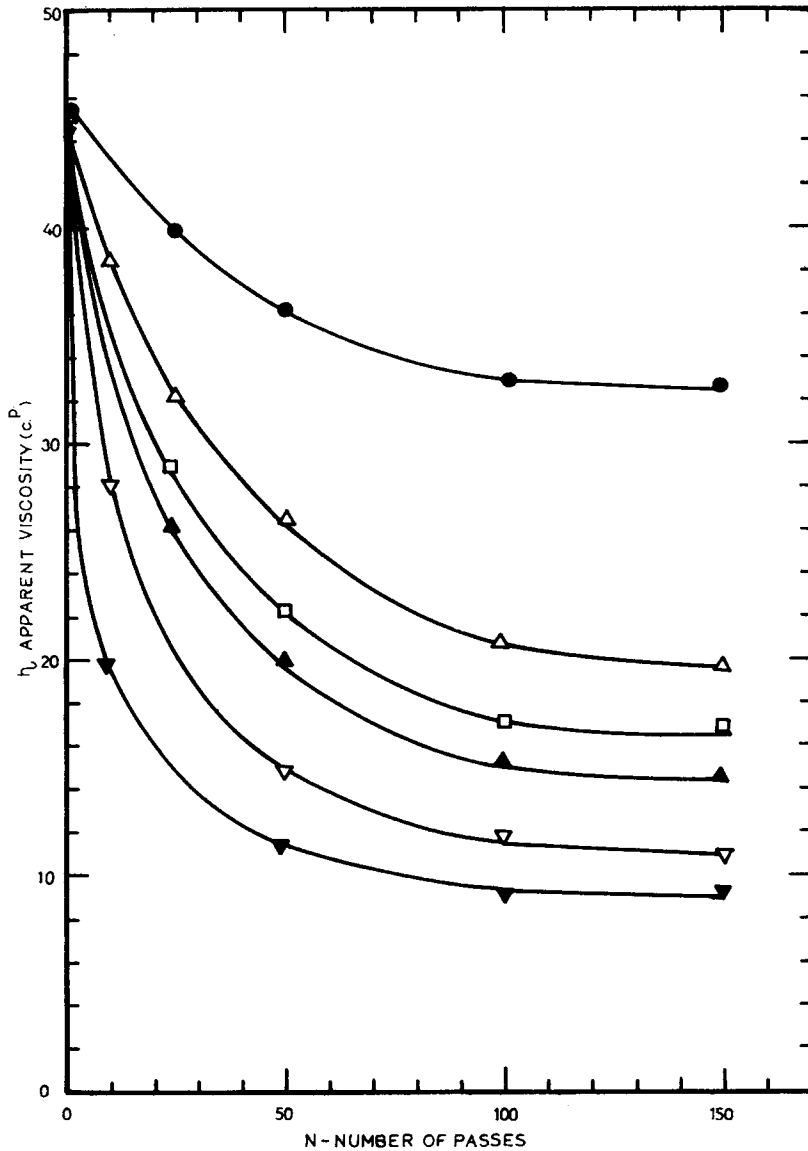


Fig. 3. Shear history. PIB B-200, $C = 0.525$ g/dl in Decalin, τ_w , in dynes/cm²:
 (●) 2800; (△) 4200; (□) 5600; (▲) 7000; (▽) 9500; (▼) 12500.

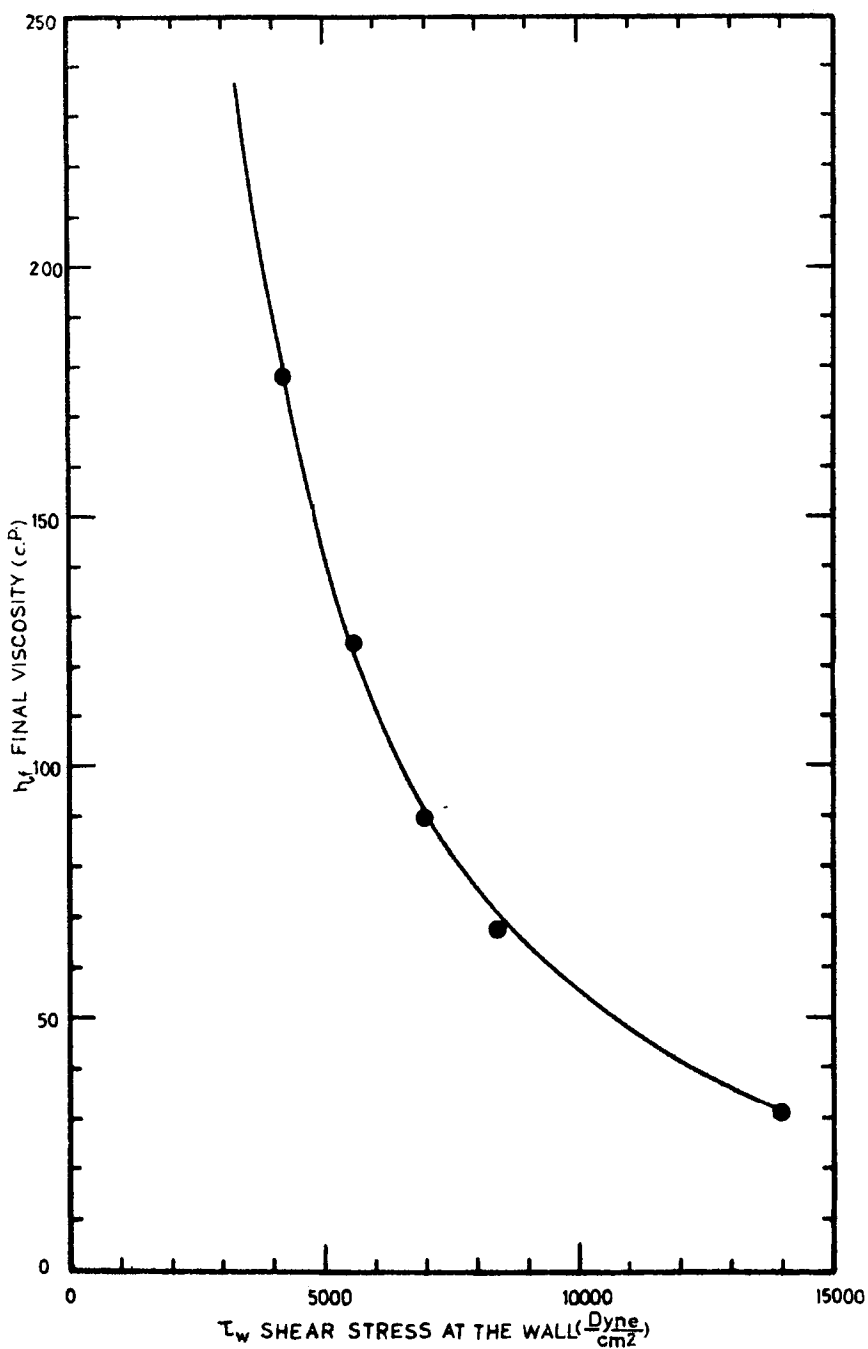


Fig. 4. Dependence of final viscosity on wall shear stress. PIB B-200, $C = 1.05$ g/dl in Decalin, $\eta_0 = 363$ cP.

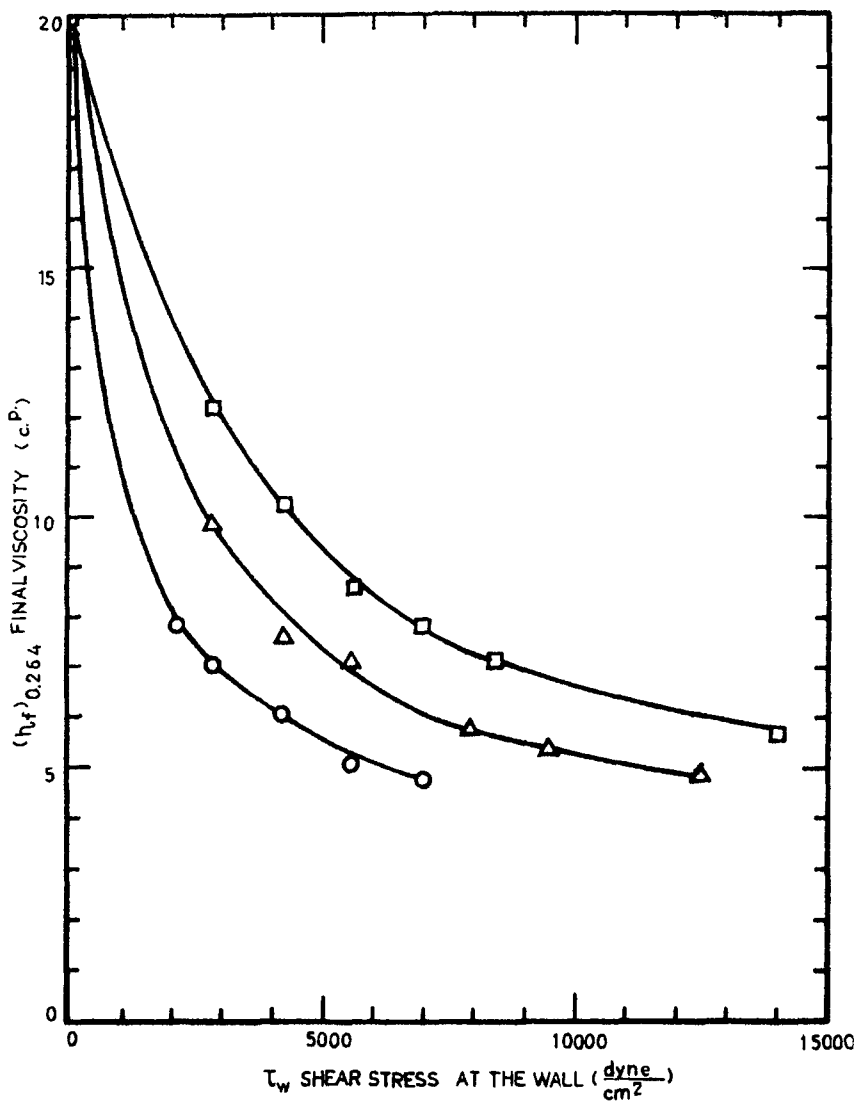


Fig. 5. Dependence of final viscosity on shear stress at various concentrations. PIB B-200, measured at 0.264 g/dl in Decalin, degraded at: (□) 1.050 g/dl; (Δ) 0.525 g/dl; (○) 0.264 g/dl.

The rate of degradation is also strongly dependent on the shear stress, increasing with the latter.

The specific effect of the polymer concentration is shown in Figure 5, in which final viscosities (measured after dilution to a single concentration) are plotted for solutions sheared at different concentrations. Figure 6 presents the same information in terms of the maximum relative reduction

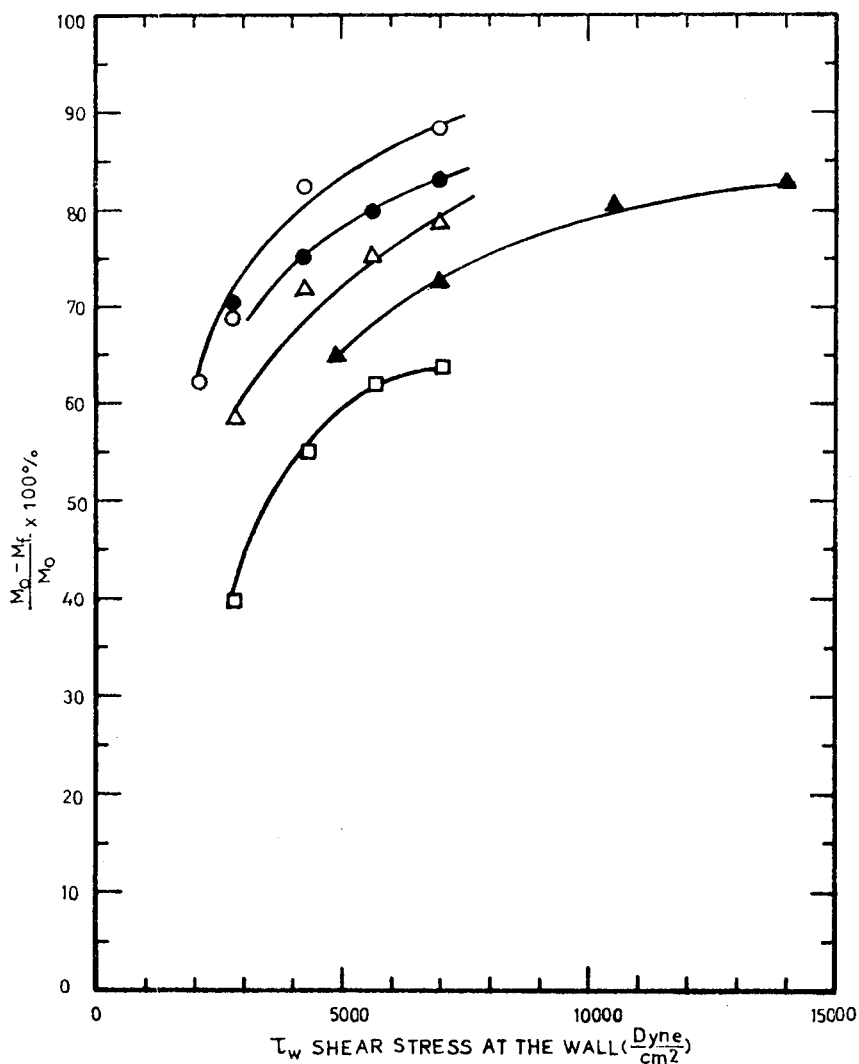


Fig. 6. Relative drop of molecular weight. PIB B-200 in Decalin: (○) 0.264 g/dl; (●) 0.350 g/dl; (△) 0.525 g/dl; (▲) 0.820 g/dl; (□) 1.050 g/dl.

in molecular weight versus concentration and shear stress (see also Table II).

With the shear stress kept constant, degradation was less effective as concentration increased—in apparent contradiction to other published results according to which degradation increased with concentration. In this case, however, it was the shear stress, not the rate of shear, which was kept constant. The significance of entanglement in shear degradation¹⁰ of dilute polymer solutions is uncertain, and the controlling factor is the shearing force per molecule; this accounts for the higher degradation in the

TABLE II
Final Molecular Weight of PIB B-200 Sheared at Different
Concentrations and Shear Stresses

Concentration, g/d	Shear stress τ_w , dyne/cm ²	Final molecular weight $\bar{M}_{v,f}$, $\times 10^{-6}$
0.264	2100	2.39
0.264	2800	1.98
0.264	4200	1.10
0.264	7000	0.75
0.350	2800	1.9
0.350	4200	1.62
0.350	5600	1.25
0.350	7000	1.10
0.525	2800	2.65
0.525	4200	1.80
0.525	5600	1.58
0.525	7000	1.35
0.820	4900	2.40
0.820	7000	1.75
0.820	10500	1.25
0.820	14000	1.10
1.05	2800	3.9
1.05	4200	2.9
1.05	5600	2.4
1.05	7000	2.3

more dilute solutions at same shear stress. A proper mathematical derivation is presented further below.

The tube diameter had essentially no effect on shear degradation at the same shear stress at the wall. This was also found to be the case with temperature (see Table III), in contradiction to the idea that low temperature

TABLE III
Effect of Temperature on Shear Degradation

Concentration, g/dl	Initial viscosity at 30°C, cP	Shear stress τ_w , dyne/cm ²	Temperature, °C	Num- ber of passes	Final viscosity at 30°C, cP
0.525	46	7000	30	50	19.0
0.525	46	7000	60	50	18.5
0.525	46	7000	30	150	14.4
0.525	46	7000	60	150	14.4
0.525	46	9500	30	70	13.1
0.525	46	9500	60	70	13.3
0.525	46	9500	30	150	11.3
0.525	46	9500	60	150	12.0
1.05	363	7000	30	100	9.4
1.05	363	7000	60	100	10.5
1.05	363	7000	30	150	9.0
1.05	363	7000	60	150	10.0

promotes shear degradation.¹¹ Here again, however, literature data refer to conditions of high-speed agitation, under which high temperature entails low viscosities with lower shear stresses as a result.

Figure 7 shows clearly that the final molecular weight of all three polymer samples converges to the same level, so that the initial molecular weight does not control the final state, although it does affect the rate of degradation.

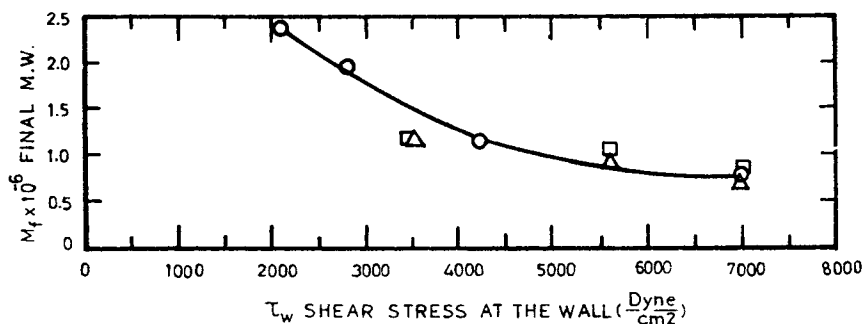


Fig. 7. Final molecular weight of three PIB samples, $C = 0.264$ g/dl in Decalin: (□) PIB L-120; (O) PIB B-200; (△) PIB B-100.

The theoretical analysis of the degradation process follows that of Harrington and Zimm,¹² who defined the average friction coefficient, the shear force per polymer chain in solution, as follows:

$$\bar{f} = \frac{\dot{\gamma}(\eta - \eta_s)}{nz} \quad (1)$$

where $\dot{\gamma}$ = rate of shear, η = viscosity, η_s = viscosity of solvent, n = number of polymer molecules per unit volume, and z = projected length of polymer chain perpendicular to flow.

Replacing n with $(C/M_f)N_A$ for the final value of molecular weight M_f , the rate of shear with the shear stress, and substituting the final value of the viscosity η_f , we obtain the critical force at the wall:

$$\bar{f}_{\text{crit}} = \frac{(\eta_f - \eta_s)}{\eta_f} \tau_w \frac{M_f}{CN_A z} \quad (2)$$

where N_A = Avogadro's number, C = concentration (g/cc), and τ_w = shear stress at the wall (dyne/cm²).

Physically, \bar{f}_{crit} represents the minimum force required for the proper final molecular weight to be reached in the degradation process under the experimental conditions. Assuming an average value for z , eq. (2) reduces to

$$\bar{f}_{\text{crit}} = K \cdot Y \quad (3)$$

where

$$Y = \frac{(\eta_f - \eta_s)\tau_w M_f}{\eta_f C} \quad (4)$$

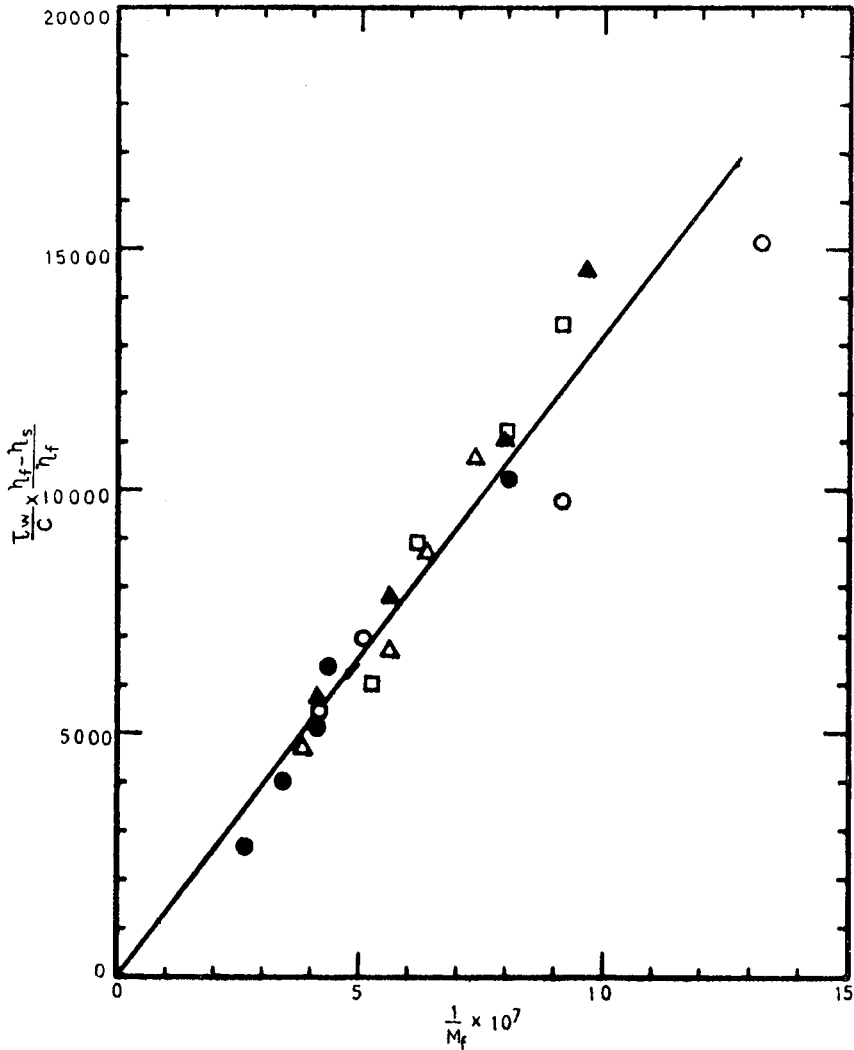


Fig. 8. Dependence of $\tau_w/C \times \eta_f - \eta_s/\eta_f$ on $1/M_f$, PIB B-200 in Decalin: (○) 0.264 gr/dl; (●) 1.050 gr/dl; (□) 0.350 gr/dl; (△) 0.525 gr/dl; (▲) 0.820 gr/dl.

For the same type of polymer and solvent, \bar{f}_{crit} is uniquely determined, and the combined parameter Y is assumed to be a constant. The straight line in Figure 8 ($X = [(\eta_f - \eta_s)/\eta_f](\tau_w/C)$ versus $1/M_f$) verifies our expectations: for every molecular weight, there exists a critical X below which

no degradation occurs; accordingly, X may serve as a criterion of shear degradation.

The parameter Y from eq. (4) can also be expressed for highly dilute solutions as follows:

$$Y = \left(\frac{\eta_{sp}}{C}\right) \left(\frac{\eta_s}{\eta_f}\right) \bar{M}_{vf} \tau_w \cong \frac{[\eta]_f}{\eta_r} \bar{M}_{vf} \tau_w \cong K_1 \bar{M}_{vf}^a + 1 \tau_w \quad (5)^*$$

where $\bar{M}_{v,f}$ = final viscosity-average molecular weight, and

$$[\eta]_f \cong \frac{\eta_{sp}}{C} = \frac{\eta_f - \eta_s}{\eta_s C} \quad (\text{intrinsic viscosity}) \quad (6)$$

$$[\eta]_f = K_1 \bar{M}_{vf}^a \quad (7)$$

$$\frac{\eta_f}{\eta_s} = \eta_r \rightarrow 1 \quad (\text{at high dilution}) \quad (8)$$

While Y is constant in the case of polyisobutylene in Decalin (its average value is 1.44×10^{10} , with C given in g/dl and τ_w in dyne/cm²), other combinations of polymers and solvents may yield different values. Further study is called for, and it is hoped that a systematic scale for polymer degradability will be achieved.

CONCLUSIONS

1. Polymer degradation in solution is controlled by the shear stress.
2. The higher the shear stress at the wall, the faster the degradation process and the lower the final viscosity at equilibrium.
3. At the same shear stress, the final molecular weight reached is independent of the initial molecular weight or temperature.
4. Increased polymer concentration at the same shear stress reduces the effectiveness of the degradation process.
5. The shear stress and the final polymer dimensions are combined in a single parameter which predicts the minimum force required for shear degradation.

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* Equation (5) is comparable to an equivalent expression for a constant parameter of the form τM^2 , involved in the shear degradation of melts.¹³

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