

Shear Degradation of Polyisobutene

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Synopsis

A polyisobutene of $\bar{M}_w 1.98 \times 10^6$, $\bar{M}_w/\bar{M}_n 1.8$, was extruded in an Instron capillary rheometer. Shear degradation occurred at high shear stresses, approaching melt fracture, and was more prominent at lower extrusion temperatures for tests at 60–140°C. The capillary was 2.0 in. long with a length/diameter ratio of 66.7 and a 90° entrance angle. Repetitive extrusions at constant shear rate caused a decrease in a molecular weight and a simultaneous narrowing of the molecular weight distribution. Extrudate expansion was measured after each successive capillary pass for tests at 80°C. Extrudate swelling correlated well with $(\bar{M}_{z+1}) \bar{M}_z/\bar{M}_w$, except for the two first passes, where melt fracture was pronounced. The correlation with equilibrium extrudate expansion was almost as good for $(\bar{M}_z/\bar{M}_w)^{3.7}$ (Mill's correlation) and for \bar{M}_{z+1} alone. The efficiency of bond rupture is low, with the energy required to rupture 1 mole of bonds being about 200,000 kcal at 80°C.

INTRODUCTION

Macromolecules that are subjected to high shear may undergo chain rupture. This commonly involves the generation of macroradicals which either recombine or react further. The direction of secondary reactions is very much dependent on the environment and on polymer composition. In the absence of radical acceptors, a mechanical degradation cannot only result in a decrease in molecular weight caused by radical disproportionation, but also in polymer branching and crosslinking. For many polymer systems, there are great difficulties in distinguishing thermal and thermo-oxidative degradation from reactions caused by shear (mechanical degradation). As a result, studies on isolating mechanical degradation are generally conducted at relatively low temperatures. On the other hand, in commercial extrusion, polymers generally have to be exposed to elevated temperatures to sufficiently lower its melt viscosity.

Polyisobutene (PIB), however, is particularly well suited for such degradation studies as it can be extruded at relatively low temperatures. In addition, prior studies indicate that the radicals generated are readily deactivated.¹ Moreover, PIB is thus not prone to crosslinking reactions. Another advantage is the high resistivity of PIB toward oxidative degradation.^{1,2} Prior study of PIB reactions in shear has been generally conducted in solution

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rather than on the melts.¹ The degradation of PIB by shearing of its solutions was first reported by Bestul and co-workers. In one study, PIB solutions were recycled through a short capillary.³⁻⁸ After a large number of passes, a limiting molecular weight was reached. This complies with the concept of a limiting chain length for each polymer, a condition below which the applied forces under the shear conditions cause no further chain scission.

In a series of studies, PIB solutions were sheared in a specially designed concentric cylinder viscometer.⁹⁻¹² Extensive degradation of the polymer occurred at shear stresses in the order of 10^5 dynes/cm² for PIB of $M_v = 800,000$.⁸ Porter and Johnson⁹ applied a system of reduced variables for the equilibrium molecular weight obtained after shearing a series of PIB's. The variables which superimpose are stress, temperature, and polymer concentration.

Pohl and co-workers have investigated the mechanical degradation of PIB in the melt.^{13,14} They found that the extent of degradation, as observed by intrinsic viscosity, is sensitive to the initial PIB molecular weight and to the shear rate. A decrease in the melt temperature also resulted in increased degradation, especially in the lower range of extrusion temperatures. The shear stresses were not measured; the shear rates were 81 to 14,750 sec⁻¹. In a related study on PIB using a biconical rheometer, Pohl and Gogos found a continuous drop in melt viscosity, contradictory to the idea of a limiting molecular weight.¹⁴

As industrial recycling of polymer becomes more important, it is of interest to evaluate the changes in polymer structure that may occur during processing. As the rheological properties of a melt depends on molecular weight and distribution, an analysis of these parameters is critical. In this study, PIB was extruded in an Instron capillary rheometer, and the extent and origin of polymer degradation was analyzed. It is the object of this investigation to relate the changes in molecular weight and distribution, as measured by gel permeation chromatography, to the observed changes in rheological properties. An evaluation of the degradation mechanism has also been made.

EXPERIMENTAL

Materials

The PIB used throughout was Vistanex L-140 which was provided by Enjay Chemical Co., New York, New York. It had a weight-average molecular weight of 1,980,000 as measured at University of Massachusetts by gel permeation chromatography. The heterogeneity index (\bar{M}_w/\bar{M}_n) was 1.8, see Table I.

Gel Permeation Chromatography

A Waters Associates GPC Model 200 equipped with an automatic injection system was used. The experimental conditions were as follows: solvent, tetrahydrofuran; temperature, 25°C; columns, 10^7 , 3×10^5 , 3×10^4 , and 3×10^3 Å; sample concentration, 1 mg/ml; flow rate, 1 ml/min. The GPC was calibrated with polystyrene standards with narrow distributions (Pressure

TABLE I
Molecular Weight Changes During Extrusion of Polyisobutene

Temperature, °C	Number of passes	Wall shear stress, (dynes/cm ²) × 10 ⁻⁶	Shear rate, sec ⁻¹	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	H	Scissions per molecule
—	—	—	—	1.11	1.98	1.8	—
60	1	5.2	22	0.91	1.77	2.0	0.22
70	1	5.8	448	0.97	1.78	1.8	0.14
75	1	5.7	448	0.88	1.73	2.0	0.26
80	1	5.5	224	0.97	1.75	1.8	0.14
80	2	4.9	224	0.89	1.63	1.8	0.24
80	3	4.4	224	0.80	1.41	1.8	0.38
80	4	4.1	224	0.77	1.28	1.7	0.44
80	5	4.0	224	0.74	1.32	1.8	0.49
80	6	3.8	224	0.73	1.17	1.6	0.51
80	7	3.6	224	0.66	1.08	1.6	0.69
80	8	3.5	224	0.67	1.05	1.6	0.64
80	9	3.4	224	0.68	1.01	1.5	0.62
80	10	3.2	224	0.63	0.97	1.5	0.75
95	1	4.6	44800	1.03	1.88	1.8	0.08
95	5	4.1	44800	0.91	1.66	1.8	0.21
95	10	3.6	44800	0.79	1.34	1.7	0.40
100	1	5.1	224000	0.98	1.79	1.8	0.13
120	1	1.7	4800	1.02	1.85	1.8	0.08
120	5	1.6	4800	0.98	1.72	1.8	0.13
120	10	1.6	4800	0.85	1.52	1.8	0.30
140	1	3.0	224000	1.05	1.93	1.8	0.05

Chemical Co., Pittsburgh, Pennsylvania, Waters Associates, Milford, Massachusetts, and Duke Standards, Palo Alto, California).

The concept of a universal GPC calibration proposed by Benoit et al.¹⁵ was applied. The intrinsic viscosities of the polystyrene standards were measured in tetrahydrofuran at 25°C.¹⁶ To transform the universal calibration to PIB calibration the following Mark-Houwink relationship was used¹⁷:

$$[\eta] = 3.95 \times 10^{-4} \times M^{0.65}$$

Molecular weights and MWD's were correlated for axial dispersion. The method employed has been described in a previous paper¹⁸ and is based on the Pierce and Armonas¹⁹ solution of Tung's integral equation for axial dispersion.²⁰

Extrusion

The extrusions were conducted using an Instron capillary rheometer, Model TT-CM (Instron Equipment Corp., Canton, Massachusetts). The capillary used had a tungsten carbide orifice and an L/D ratio of 66.7. It was 2 in. long with an entrance angle of 90°. The rheometer temperature was regulated by a proportional control device with ports for the thermocouple sensor at four positions along the capillary reservoir and barrel. Temperature variations with time along the barrel could be kept within 1°C. The

polymer was loaded in small portions into the barrel. After each loading, the sample was compacted by manual tamping. Approximately 4 g was used for each run. As the capillary reservoir had a 0.375-in (0.953 cm) diameter, this resulted in a PIB plug of about 6 cm in length. The complete loading procedure required about 20 min. In the temperature range of 60–140°C, no degradation was observed as a result of this pretreatment. Extrudate samples for GPC analysis were taken after approximately 50% extrusion. This constituted a representative part of the extrudate. The rheological data were not subject to any corrections.

Extrudate Analysis

The extrudates at a set of extrusion conditions were observed in a scanning electron microscope, ETEC Corporation, Hayward, California. The extrudate diameter changes with time after emerging from the capillary due to recovery after flow. The equilibrium swelling of extrudates was attained as suggested to us by G. V. Vinogradov: The extrudate was heated in a water-alcohol mixture for 2 hr at 5°C above its extrusion temperature. The density of the mixture was chosen equal to that of the PIB, in order to exclude the effect of gravity on extrudate dimensions. Equilibrium swelling was achieved after 1.5 hr, the increase resulting from the hot bath treatment being less than 10%. The extrudate diameter was measured by a calibration scale in a light microscope, Vickers Instruments Ltd., England. The diameter was taken as the average of five to seven measurements at several locations along a representative portion of the extrudate.

RESULTS AND DISCUSSION

PIB of weight-average molecular weight 1.98×10^6 was extruded in an Instron capillary rheometer. The flow curves at a series of temperatures are shown in Figure 1. They are essentially power law behavior and illustrate extensive shear thinning. At 80°C, the shear stress increases linearly with shear rate, a power law region, and reaches very high values even at low rates. At higher temperatures, the shear stress is less dependent on shear rate. In Figure 2, the flow curves for first extrusion at 80° and 120°C are compared with the corresponding ones obtained for the 10th capillary pass (9th recycle). A large difference between the two curves was observed at 80°C, but at 120°C, only a miniscule difference was detected. Notice, however, that the shear stresses also were lower at 120°C. The corresponding changes in MWD at 120°C is not major, but a distinct shift toward lower molecular weights is observed. This small drop in molecular weight did not affect the flow curve at higher shear rates as shown in Figure 2. This is consistent with the fact that shear stress is insensitive to molecular weight at higher shear rates.

The extrusion experiments conducted at 80°C resulted in an appreciable drop in molecular weight, which in this case also affected the flow curve. As can be seen in Figure 3, the polydispersity decreases with an increasing number of passes. The molecular weight averages after one pass at 80°C are almost the same as after five passes at 120°C (see Table I).

A considerable swelling of the extrudate occurred at a series of extrusion

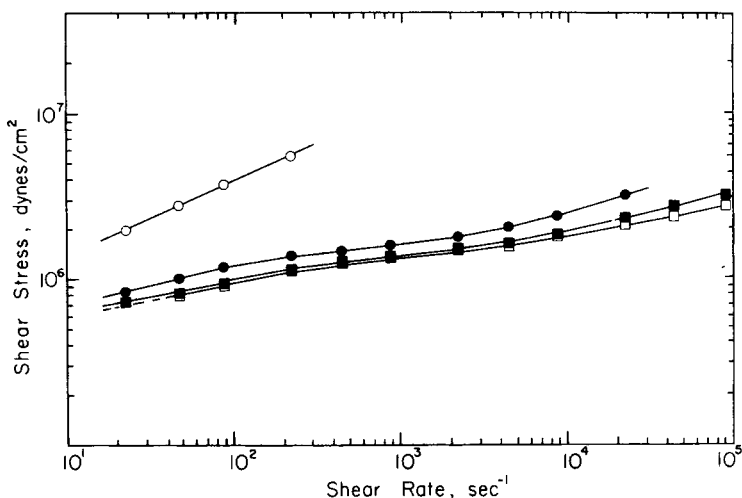
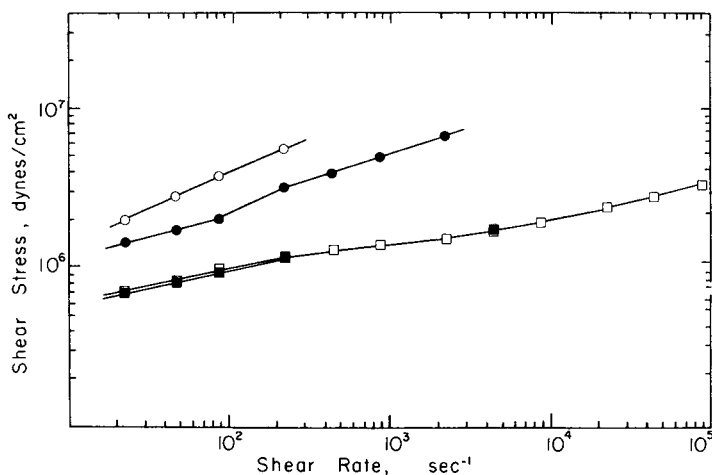


Fig. 1. Flow curves for polyisobutene ($\bar{M}_w = 1.98 \times 10^6$) at a set of extrusion temperatures: (○) 80°C; (●) 100°C; (■) 120°C; (□) 140°C.

conditions, and obvious signs of melt fracture were also observed. At 80°C, melt fracture appeared at 90 sec^{-1} and was considerable at 224 sec^{-1} , as can be seen in Figure 4. This figure shows the effect of the number of passes on extrudate swelling and on melt fracture. Extrudate dimensions were studied after one, five, and ten passes at 224 sec^{-1} . The extrudate obtained at the sixth pass was the first that showed no significant melt fracture. The sixth extrusion was performed at a shear stress of $3.8 \times 10^6 \text{ dynes/cm}^2$ (see Table I) and resulted in an extrudate of $\bar{M}_w = 1.2 \times 10^6$. Figure 4 shows qualitatively how the swelling decreases with an increasing number of passes. Figure 5



Temp., °C	Capillary passes
(○) 80	1
(●) 80	10
(□) 120	1
(■) 120	10

Fig. 2. Flow curves for repetitive extrusions of polyisobutene:

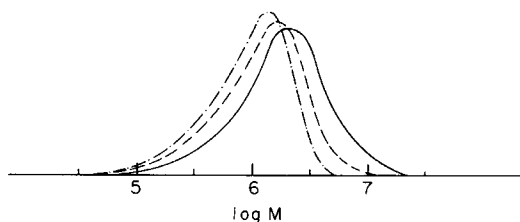


Fig. 3. Changes in MWD during repetitive extrusion of polyisobutene at 80°C. Capillary passes: (—) 0; (---) 5; (- · - · -) 10.

also shows D_E/D_0 as a function of $\bar{M}_{z+1} \times \bar{M}_z/\bar{M}_w$; D_E/D_0 is the diameter ratio for the extrudate at equilibrium swelling and that of the capillary. The correlation between the swelling and the higher molecular weight moments is very good, except for the first two extrudates (right-hand side of Fig. 5), where D_E/D_0 is lower. This deviation is probably due to the severe melt fracture occurring at these conditions, which limits elastic energy storage and makes it more difficult to estimate the average swelling. The loss of polymer adhesion to the capillary wall must inevitably lead to a limit in stored elasticity and in D_E/D_0 and thus a deviation from linearity at high values of $\bar{M}_{z+1} \times \bar{M}_z/\bar{M}_w$. Extrudate swelling was also plotted against \bar{M}_w , \bar{M}_z , \bar{M}_{z+1} , \bar{M}_z/\bar{M}_w , \bar{M}_{z+1}/\bar{M}_z , $(\bar{M}_z/\bar{M}_w)^2$, $(\bar{M}_z/\bar{M}_w)^{3.7}$, and $\bar{M}_{z+1} \times \bar{M}_z/\bar{M}_w^2$, respectively.²¹ Most of these plots showed S-shaped curves with deviations from linearity at low and high degrees of swelling. A linear relationship in the region of low to moderate swelling was observed only in correlations with \bar{M}_{z+1} and $(\bar{M}_z/\bar{M}_w)^{3.7}$ (Mills' correlation^{22,23}).

Figure 6 shows the extrudates obtained at different shear rates during the tenth pass at 80°C. The extrudate to the left in Figure 6 may be compared

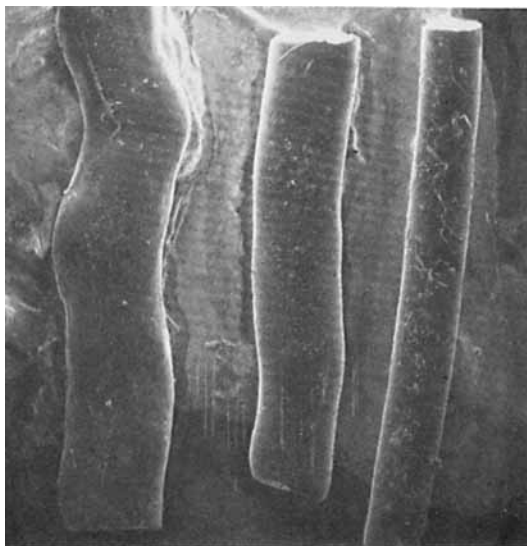


Fig. 4. Effect of the number of capillary passes on extrudate swelling and melt fracture. Polyisobutene extrudates obtained after 1, 5, and 10 passes at 80°C and 224 sec⁻¹ (from left).

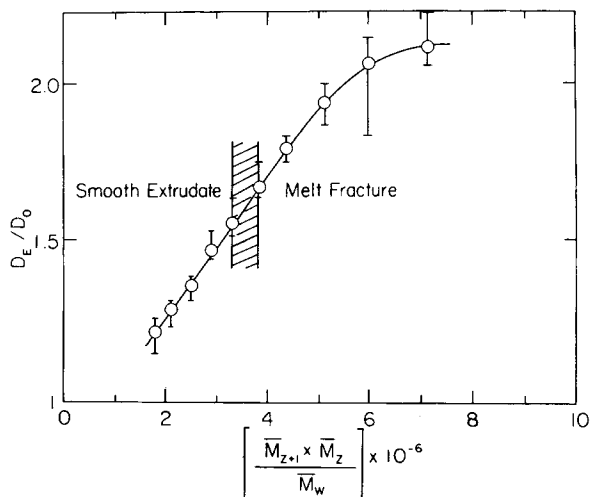


Fig. 5. Extrudate swelling (D_E/D_0) as a function of $\bar{M}_{z+1} \times \bar{M}_z/\bar{M}_w$. Repetitive extrusion of polyisobutene at 80°C .

with those to the left in Figure 4. Both extrudates were obtained at 224 s^{-1} . However, the shear stress was $6.5 \times 10^6 \text{ dynes/cm}^2$ during the first extrusion, compared to $3.2 \times 10^6 \text{ dynes/cm}^2$ during the tenth pass (cf. Table I). At higher extrusion temperatures, melt fracture was extensive as extrusions were

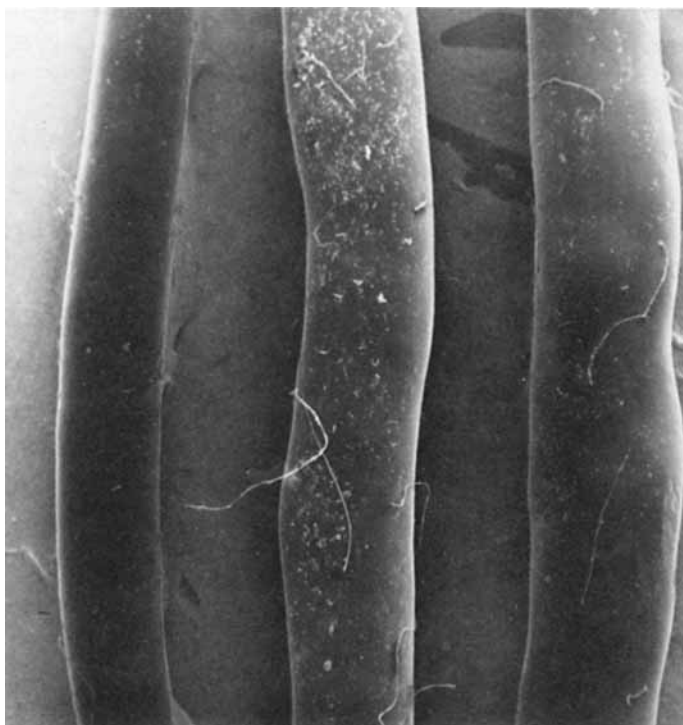


Fig. 6. Effect of shear rate on extrudate swelling and melt fracture. Polyisobutene extrudates obtained during the 10th capillary pass at 224, 448, and 896 sec^{-1} (from left).

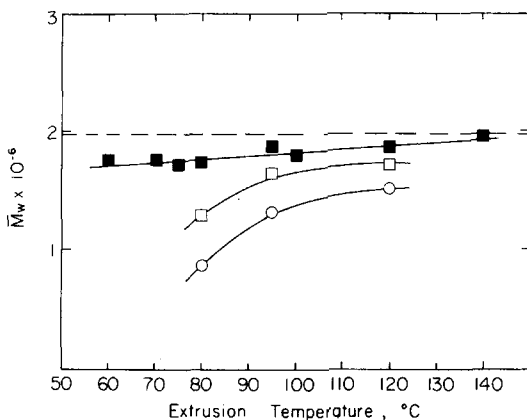


Fig. 7. Repetitive extrusion of polyisobutene \bar{M}_w as a function of extrusion temperature. Capillary passes: (■) 1; (□) 5; (○) 10.

carried out at very high shear rates, i.e., 4480 s^{-1} and above. The onset of melt fracture correlated with neither shear stress nor shear rate.

Bueche predicted that degradation induced by high shear stresses causes rupture near the middle of chains, where the extending forces are a maximum.²⁴ His theory assumes that chain entanglements are necessary for shear degradation. Thus mechanism can result in a decrease in heterogeneity index of a polydisperse polymer as the degradation proceeds. During the extrusion of PIB at 80°C, \bar{M}_w/\bar{M}_n decreased from 1.8 to 1.5 after ten passes. The changes in MWD are similar to those observed by Abdel-Alim and Hamielec²⁵ during shear of polyacrylamide solutions in a high-shear couette viscometer. In their case, they concluded that although a significant decrease in polydispersity was observed with increasing degradation, the rupture of polymer chains did not exclusively take place near the midchains. Their results agreed more with a theory predicting a Gaussian distribution for the location of rupture centered around the middle of the polymer chain. Degradation of polystyrene using ultrasonics has been shown to follow such a mechanism.²⁶

PIB exposed to mechanical degradation at low temperatures (-196°C) has

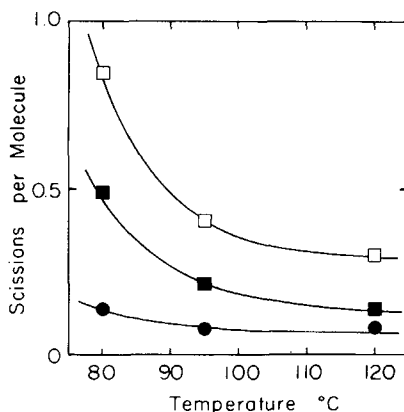


Fig. 8. Number of scissions per molecule as a function of extrusion temperature. Data after 1, 5, and 10 capillary passes. Capillary passes: (●) 1; (■) 5; (□) 10.

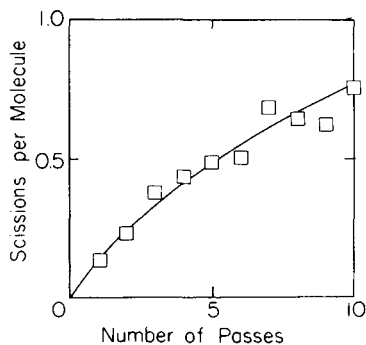
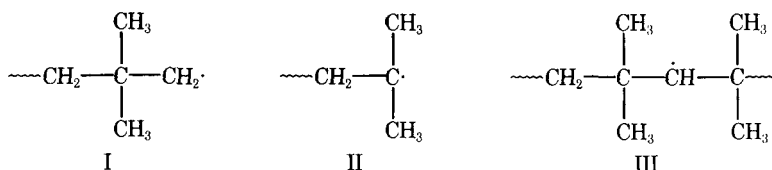


Fig. 9. Number of scissions per molecule as a function of number of capillary passes. Extrusion of polyisobutene at 80°C.

been shown to exhibit multiline ESR spectra.^{2,27} The spectra correspond to several macroradicals as follows:



Radicals I and II result from a chain scission. Radical III could be formed through hydrogen abstraction by an original radical. From III, methallyl radicals could be formed (activation energy 15 kcal/mole) which, by their high reactivity, can act as scavengers for other radicals.²⁸ At higher temperatures, an unzipping of the original scission products could be expected, as the ceiling temperature for PIB is between 50° and 80°C. However, due to the high reactivity of the original radicals, generally only a modest amount of monomer is formed during thermal degradation.²⁹

The following reactions will cause a drop in molecular weight: (1) an im-

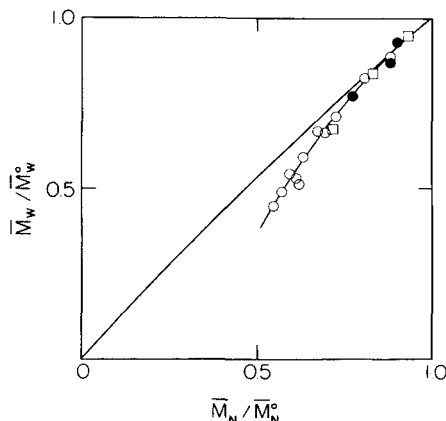


Fig. 10. Relative changes in weight-average molecular weight vs. relative changes in number-average molecular weight. Repetitive extrusions at 80°, 95°, and 120°C: (○) 80°C; (□) 95°C; (●) 120°C.

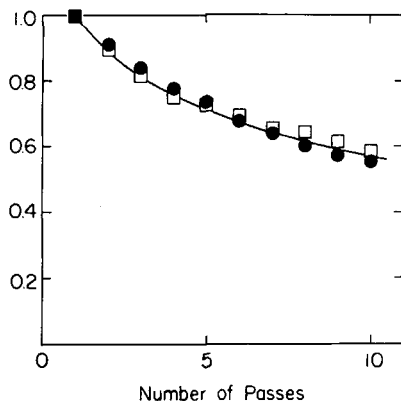


Fig. 11. Normalized shear stress and normalized chain scission vs. number of capillary passes. Repetitive extrusion of polyisobutene at 80°C: (□) normalized shear stress; (●) normalized chain scission.

mediate disproportionation, (2) a hydrogen abstraction by I and II, and (3) a hydrogen abstraction by a methallyl radical from II.

The \bar{M}_w after 1.5 and 10 passes through the Instron capillary rheometer is shown as a function of extrusion temperature in Figure 7 (cf. Table I). Data indicate that the degradation is more extensive at lower extrusion temperatures. However, the results are affected to some extent by the decrease in shear stress with number of passes. Thus, stress could not be kept strictly constant. The shear stress for the first pass was kept fairly constant, except at 120°C. At 140°C, no significant change in molecular weight was observed during extrusion. This is in agreement with results reported by Baramboim,³⁰ who found a minimum degradation for PIB in shear at 140°C. It is desirable to study the shear degradation using capillaries with different entrance angles and monitor the molecular weight of the polymer just before

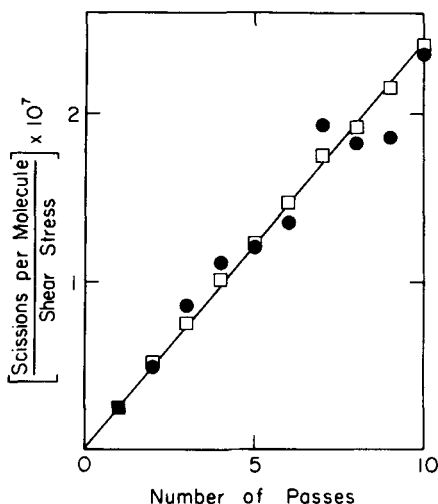


Fig. 12. Number of scissions divided by shear stress as a function of number of capillary passes. Repetitive extrusion of polyisobutene at 80°C: (●) primary data; (□) data obtained from a smoothed plot of \bar{M}_n vs. number of capillary passes.

and after passing the capillary. Due to the small changes in molecular weight per pass, we were not able to obtain such data. Experiments with capillaries of largely different lengths are also of interest.

The efficiency of bond rupture from the total energy input was calculated for the repetitive extrusion at 80°C. The calculation was carried out as suggested by Bestul.⁸ The degradation energy required to rupture 1 mole of bonds was approximately 200,000 kcal. For PIB solutions, Bestul estimated the corresponding energy required to be 521,000 kcal.⁸ This indicates a bond rupture efficiency twice as high in a PIB melt, where the energy dissipation could be expected to be lower. Still, the energy input is overwhelming, compared to about 80 kcal/mole needed for breaking carbon-carbon bonds.

The number of scissions per molecule is plotted as a function of extrusion temperature in Figure 8. This also shows the greater efficiency of bond rupture at the lowest extrusion temperatures. This observation is in agreement with the findings of Pohl et al.^{13,14} Chain scission is expected to increase with the amount of energy input or with rate of energy input. A prerequisite is that stress levels high enough for bond rupture are attained. In Figure 9, the number of scissions per molecule is plotted versus the number of capillary passes at 80°C. The efficiency of bond rupture per pass decreases with increasing passes. However, it may be noted that the shear stress is also decreasing with the number passes due to degradation. An analysis of the relative changes in number- and weight-average molecular weight as recently described by Scott has been proved to provide a versatile test for random chain scission.³¹ Data for a series of temperatures are shown in Figure 10. The heavy solid line represents the change predicted for a random scission assuming a Schulz-Zimm distribution for the original PIB. Data deviate considerably from the theoretical predictions, which indicate a nonrandom mechanism. This is in contrast to results reported in certain shear degradation and sonic degradation studies of PIB solutions, which were reported to follow a random scission process.^{10,11,31,32}

The shear stress and the number of scissions can be normalized with respect to the values measured for the first pass. Such a calculation was made for the extrusion of PIB at 80°C, as is shown in Figure 11. The relative changes in chain scission do follow the relative changes in shear stress very closely. This shows that shear stress, not shear rate, is the controlling factor in shear degradation. In Figure 12, the number of scissions divided by the shear stress is plotted versus the number of passes. The squares represent the smoothed data taken from a plot of \bar{M}_n versus the number of passes. The filled circles show the actual data points. It is evident that this kind of treatment gives the changes in the number of scissions at a normalized shear stress. The plot shows that in keeping stress and temperature constant, the number of chain scissions are proportional to the number of passes.

As shown in Table I, mechanical degradation results in a reduced shear stress for subsequent capillary passes at the same shear rate. The trend toward a limiting molecular weight with an increasing number of passes is in part a result of this stress decrease; the amount of high molecular weight material diminishes at the same time as the shear stress decreases. It is therefore obvious that the efficiency of chain rupture is lower the higher is the number of passes. The results shown in Figure 9 reflects this decreasing effi-

ciency. The deviation from random scission shown in Figure 10 could also be derived from the fact that shear stress decreases with increasing number of passes.

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