Cold Milling of Polyisobutylene—A Molecular Weight Distribution Study

B. M. E. VAN DER HOFF and V. K. CHOPRA, *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

High molecular weight polyisobutylene samples were degraded by milling at 320 K. The degradation process was followed by determining the course of the changes in molecular weight distributions (MWD) that were obtained by gel permeation chromatography. After long milling times degradation stops or at least the rate of rupture becomes extremely small, the molecular weight approaching an apparent minimum value (M_m) of 0.4×10^6. The rate of degradation decreases in the course of the first ½ to 1 hr from an initial value to one constant up to at least 3 hr if the maximum shear rate is higher than about 6 s^{-1}. At lower shear rates the rate of scission is constant from the start. When milling is stopped for 24 hr, high initial rupture rate is observed on resumption of milling at high shear rate, again followed by a drop in rate to the same value as before the interruption. The initial rates are independent of shear rate, whereas the subsequent constant rates are proportional to the rate of shear. These observations are discussed in terms of an equilibrium between the formation of multimolecular "rheological units" and the tendency, due to thermal motion, to form a homogeneous entanglement network. The MWDs are compared with those calculated from a model based on a given relation between probability of scission (P) and molecular weight and an assumed probability distribution (Q) of rupture site along the length of the polymer molecules. The observed MWDs are incompatible with those calculated from models in which $M_m = 0$ or in which breakage near the center of the molecule is favored. They agree rather well with computed MWDs based on the assumptions that $P \propto$ MW and Q is the symmetrical beta function between points along the molecule M_m removed from the ends, where M_m is $(0.4-0.5) \times 10^6$. The mechanism of rupture appears to be the same for low and for high shear rates.

INTRODUCTION

In general, degradation is an impairment in physical or chemical properties of a material. In the field of rubber technology the term often refers to deterioration of mechanical properties due to a decrease in average molecular weight (MW) of the elastomer. Sometimes, degradation in this sense is necessary or desirable to render the polymer processible, as is the case for natural rubber and some emulsion polymers. However, in shaping operations of rubber articles, degradation is undesirable.

Degradation on milling or mastication has been known to occur ever since the macromolecular nature of rubbers was recognized.[1] Since that time a number of papers have appeared on shear scission which are referred to in a review paper on mechanochemistry by Casale, Porter, and Johnson.[2] In most of these, the course of degradation was followed by measurements of intrinsic viscosity. This method may lead to serious errors in conclusions about the mechanism of the degradation process because it provides only an average MW, which depends on the shape of the molecular weight distribution (MWD). This distribution usually changes appreciably during the degradation process.

Studies based on MWDs have been made of degradation of polymers.[2] Nearly

0021-8995/79/0023-2373$01.00

all of these concern degradation in solution. Reports on milling or mastication of bulk elastomers including analysis of the change in MWD have been published for cis-1,4 polybutadiene,[3] natural rubber,[4,5] cis-1,4 polyisoprene,[6] and for EPDM and SBR.[7] For each of these polymers there is evidence of reactions other than shear-induced scission, namely, recombination of radicals and polymers (branching and gel formation), oxygen-initiated degradation, or thermal scission. No comparable studies have been recorded for polyisobutylene (PIB) which "is particularly well suited for degradation study because it is of high chemical purity, structurally regular, linear, amorphous, nonpolar, has no tactic variations, and is not prone to chemical crosslinking or gelation." [2] Because of these properties PIB has been chosen for this study of shear scission on milling at low temperature.

Reliable MWDs can be obtained by means of gel permeation chromatography (GPC). This technique, used here, was not available at the time of most of the papers mentioned above. It is in principle possible to determine the probability distribution of scission of a macromolecule along its length from the changes in MWDs. In the research reported here, sufficient accuracy was achieved to make some conclusions with regard to this probability distribution.

The rate of scission was also measured. Its change with time has been associated with the change in flow regime often reported in papers on cold flow.[2,8] The latter is recurringly attributed to the formation of supermolecular "flow units." The MWD data provide some new information on these changes.

EXPERIMENTAL

Polymer

Three different PIB samples, courtesy of Imperial Oil Canada Ltd., marked LS-140, LS-120, and LS-100, were studied. They are designed here as polymers A, B, and C, respectively. Their number-average, weight-average, and z-average molecular weights (M_n, M_w, M_z) are as follows: polymer A—0.93, 1.72, 2.69 × 10^6; polymer B—0.75, 1.45, 2.29 × 10^6; polymer C—0.45, 0.86, 1.90 × 10^6.

Mill and Milling Procedure

The laboratory mill used consists of two steel rolls mounted, one before the other, on separate platforms movable with respect to one another. The diameter of the rolls is 3.2 cm. The rear roll, onto which the polymer bands, is provided with a guard at each end to prevent the polymer from being forced off the rolls. The guards consist of steel "fenders" lined with Teflon pressed onto the roll over about three quarters of the roll circumference. The distance between the fenders is 8.2 cm. The rolls are independently driven; their temperature can be regulated by means of built-in electric heating coils.

During operation the distance between the rolls was 0.5–0.6 mm. This distance was measured at both ends and in the center with feeler gauges used for setting spark plug gaps. The temperature of the polymer was measured by inserting a small thermocouple probe into the bank after temporarily stopping the mill. For the experiments reported here, this temperature was 320 K. In any run 6 g polymer was supplied to the mill about one fourth of which forms the bank.

The polymer flows upward roughly in the center of the bank. At the point where the polymer reaches the surface of the bank, the stream splits into two parts each flowing toward one of the rolls. This point oscillates irregularly between the rolls. The flow in the bank is turbulent. It is thus not possible to calculate a shear rate average. The shear rate ($\dot{\gamma}$) referred to in this report is the maximum theoretical rate at the narrowest point of the nip assuming uniform velocity of the polymer and no slip at the roll surfaces. Although under certain circumstances the same change in the difference of roll velocities and in the nip gap may not be equivalent,[9] the shear rate is calculated from $\dot{\gamma} = (u_1 - u_2)/d$, where u_1 and u_2 are the surface velocities of the fast and of the slow roll, respectively, and d is the gap width between the rolls. Samples of about 0.1 g degraded polymer were taken for MWD determination at regular time intervals.

MWD Determinations

The MWDs of the polymer samples were determined by GPC using a Waters Model ALC-301 apparatus. The following conditions pertain to sample analysis and chromatograph calibration: solvent, tetrahydrofuran (bp 338.0–338.5 K); polymer concentration, 2 kg/m^3; sample volume, 1 cm^3; flow rate, 1 cm^3/min; room temperature ± 0.5 K; column specifications, 5 Styragel columns with nominal pore sizes of 100, 10, 0.8, 0.3, 0.1 μm.

The chromatograph was calibrated using 12 narrow-MWD polystyrene samples (Pressure Chemical Co. and Waters Associates) having peak MWs from 900 to 2.3 × 10^6. The polystyrene calibration curve was determined following the procedure proposed by Boni et al.[10] From it the PIB calibration curve was obtained using the method developed by Rudin and Hoegy.[11] Before calculating MWDs from the chromatograms the latter were corrected for instrumental spreading using the iterative technique developed by Chang and Huang.[12] The spreading factor h needed for this correction was calculated using the method of Tung and Runyon.[13] The MWDs of polymers A and C, and to a lesser extent that of polymer B, indicate a small peak at their low molecular weight ends, < (0.1–0.3) × 10^6. Since the correction procedure for instrumental spreading applied here tends to exaggerate such small peaks due to its sensitivity to high values of the second derivative of MWDs[14] and because molecules in this MW range appear not to rupture (see next section), these secondary peaks were ignored in sketching the MWDs and in calculating the MW averages.

RESULTS AND DISCUSSION

Rate of Scission

It is well known that the molecular weight of polymers often decreases on milling. The lower the temperature or the higher the shear rate, the faster is the mechanical degradation. Typically, the MW of polyisobutylene A milled at 320 K and $\dot{\gamma} = 3.5$ s^{-1} decreases in the first hour to 0.6 times its original value and in the next 12 hr diminishes further by the same factor. On milling for an additional 12-hr period, the decrease is only 2%; degradation appears to have nearly stopped.

The scission of hydrocarbon polymers results in the formation of free radi-

cals.[15,16] These chemically active species can react with one another or react with oxygen to form stable compounds or with other radical acceptors. Since no gelation is observed, hydrocarbon radicals apparently do not react with PIBs. Interaction of polymer radicals can be recombination, which is undesirable in this investigation because it is the reverse of rupture; or disproportionation, which is the more likely reaction for PIB and which does not interfere with the phenomena under study. The commercial polymers used here contain 0.05 pph antioxidant, which acts as a radical scavenger. Experiments were conducted to ascertain whether enough antioxidant is present to prevent possible recombination. To polymer A, 1 pph Parabar 441 (2,6-di-t-butyl-p-cresol, Exxon Chemical Corp.) was added. This material (A') and polymer A were milled for 3 hr and M_n values were determined in each run for seven samples after 15, 30, 60, 90, 120, 150, and 180 min. The ratios $M_n(A)/M_n(A')$ were on the average 0.94, ranging from 1.00 to 0.89. If recombination had occurred in polymer A, these ratios should have been greater than unity. Instead, the ratio is found to be somewhat less than 1, probably due to the plasticizing effect of the antioxidant added. This result is in agreement with the findings of Baramboin and Santin.[17]

The degree of scission is determined by comparing the number-average molecular weight after time t of milling, $M_n(t)$, with that of the original polymer, $M_n(0)$. It is desirable to know the value of the latter fairly accurately. Therefore, the MWDs of each of the original polymers were determined four times. The values of $M_n(0)$, $M_w(0)$, and $M_z(0)$ for each of these distributions of polymer B are listed in Table I, which show that their reproducibility is good.

The lines in Figure 1 present a typical set of MWDs of samples removed during milling of polymer B at a shear rate of 16.1 s^{-1}. For clarity, only four of the seven distributions of the degraded material are shown. The reproducibility of the degradation data can be judged from the distributions after 1 and 3 hr of milling for which weight fractions of a duplicate experiment are shown by symbols at regular MW intervals and at the peaks. (The complete distributions consist of 250 points.) Another indication of reproducibility is given by the sets of values of MW averages also listed in Table I for the same duplicate runs as those in Figure 1. Although there may be not inconsiderable uncertainty about the absolute values of the averages, the repeatability of the experiment is good.

It can be seen in Figure 1 that the MWD narrows considerably during milling, the high MW fractions disappearing fastest. In 3 hr of degradation the mass fractions with MWs of 3.0, 2.0, and 1.5 × 10^6 decrease to $\frac{1}{10}$, $\frac{1}{6}$, and $\frac{1}{3}$ times their original value, respectively.

In order to express the degradation during milling quantitatively, the degree

TABLE I
Molecular Weight Averages of Samples Taken During Replicate Milling Experiments

	Average molecular weights, (g/mol) × 10^{-6}							
	0 hr[b]				1 hr[b]		3 hr[b]	
M_n	0.73	0.75	0.80	0.74	0.52	0.49	0.40	0.39
M_w	1.44	1.45	1.54	1.41	0.87	0.82	0.62	0.59
M_z	2.27	2.30	2.37	2.20	1.30	1.22	0.86	0.80

[a] Polymer B; shear rate 16.1 s^{-1}.
[b] Milling time.
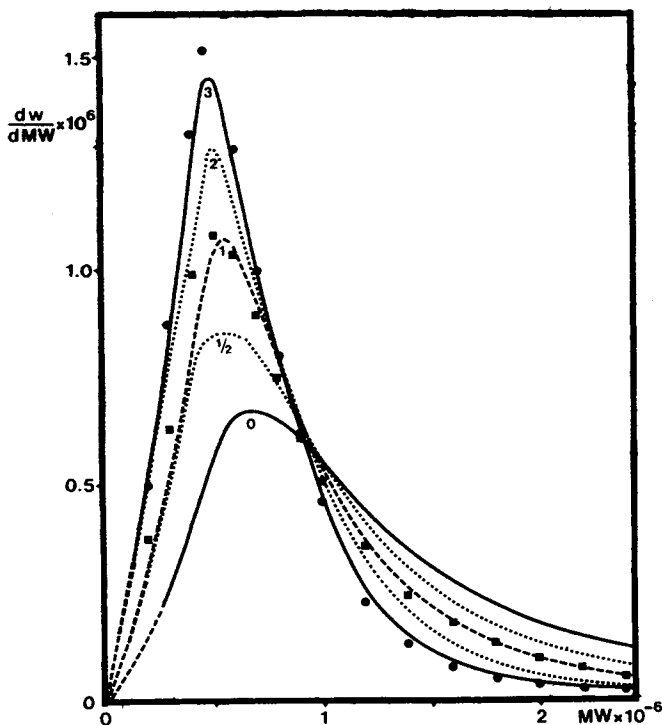
Fig. 1. Molecular weight distributions of original and degraded polymer B, shear rate 16.1 s^{-1}, 320 K: (—) original polymer; (⋯) $\frac{1}{2}$ hr milling; (- - -) and (■) 1 hr milling, duplicate runs; (⋯) 2 hr milling; (—) and (●) 3 hr milling, duplicate runs.

of scission (R_b) is defined as the ratio of the number of bonds broken to that of bonds present. Because in our experiments the maximum value of this ratio is 3×10^{-5}, R_b may be calculated from the number of bonds broken and those originally present. Thus,

$$R_b = \left[\frac{1}{M_n(t)} - \frac{1}{M_n(0)}\right]\frac{M_0}{n}$$

where M_0 is the MW of the monomer and n is the number of chain bonds per monomer unit.

The ratio R_b is plotted versus milling time in Figure 2 for various shear rates. The values of R_b are for the most averages of a number of runs (see legend). Since no systematic differences could be detected between R_b values of polymers A and B, the averages comprise data for both these polymers. Two runs with polymer C show consistently lower R_b values. Given the limited number and accuracy of the data at small times, it is not certain whether for the upper curves the rate of change of R_b is initially constant or gradually decreases over about $\frac{3}{4}$ hr to a steady value. We have chosen to represent the data by two straight lines for each shear rate greater than 8 s^{-1} and a single line for the two curves at lower shear rate.

It should be pointed out that the rate of degradation in the second period ($t > \sim\frac{3}{4}$ hr) cannot be constant indefinitely. After very long milling times, R_b changes very slowly, if indeed at all. However, an appreciable decrease in degradation rate does not occur before milling times of about 10 hr at $\dot{\gamma} = 16$ s^{-1} and longer at lower shear rates.
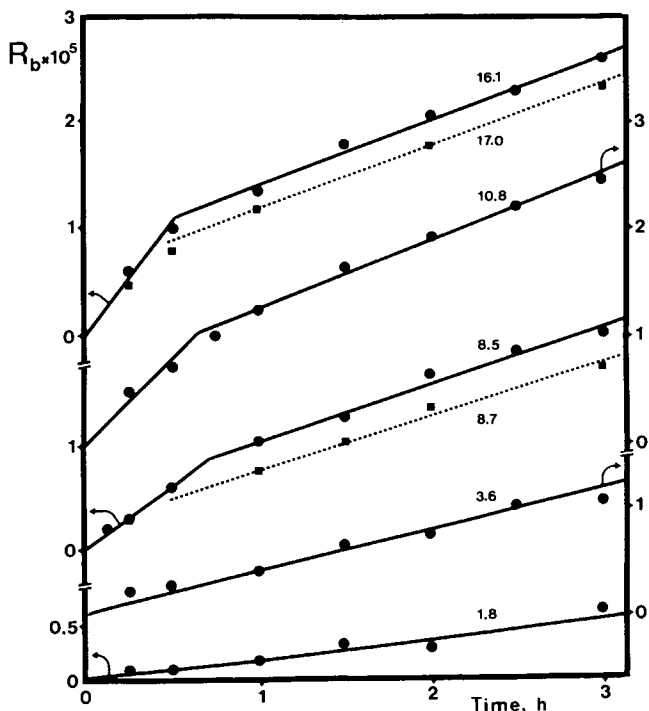
Fig. 2. Relative number of ruptures R_b as function of milling time, temperature 320 K, at shear rates of 1.8 to 17.0 s^{-1}; (●) (—) polymers A and B; (■) (⋯) polymer C. Number of experimental runs (top to bottom) 4, 1, 3, 2, 1, 2, and 1.

Whatever the detailed shape of the $R_b(t)$ curves in the initial period may be, a change in rate of degradation dR_b/dt occurs during or at the end of the initial period. To gain more information, the slopes of the straight lines in Figure 2 are plotted in Figure 3. It is seen that the initial high rate of scission is roughly proportional to the shear rate, while dR_b/dt in the second period is about constant, at best weakly dependent on MW, which varies by a factor 3 for different polymers after different milling times. It appears that during or after the initial period there is a distinct change in flow regime.

That the first period is relatively long precludes crystallization as a cause for
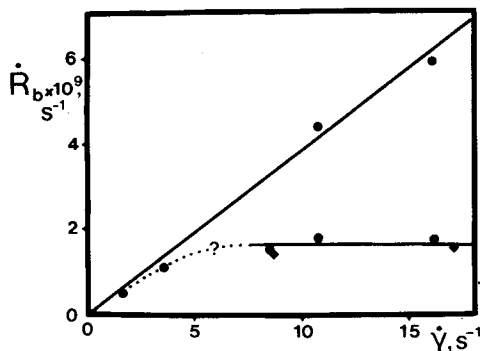

Fig. 3. Rate of rupture $\dot{R}_b$ as function of shear rate $\dot{\gamma}$. Temperature 320 K. ● Polymers A and B; ◆ Polymer C.

this change. The melting point of relaxed polyisobutylene is about 275 K according to one author[18] and 318 K according to others.[19] From the experimental data of Kato and Mark,[20] it is concluded that stress-induced crystallization at 320 K in elongation sets in at an extension ratio of about 3. In the nip of the mill, there will no doubt be regions in which chains are extended more than three times their relaxed length. This is about the same extension ratio at which natural rubber starts to crystallize some 25 K below its melting point in the relaxed state. It has recently been shown[21] that even for this structurally highly regular polymer, stress-induced crystallization does only set in after about 1 min, a time period independent of elongation. It is reasonable to assume that a delay time of this order also applies to stress-induced crystallization of PIB. Further, if crystallites are formed in the nip, they are likely to melt owing to stress relaxation in the band and, particularly, in the bank.

During shearing of elastomers with high fractions of high MWs at low temperatures, an entanglement network is set up by the deformation. The relaxation times for disentanglement for the high molecular weight species are much longer than the reciprocal shear rates. If we disallow any disentanglement by slippage, the entanglement network, like a chemically crosslinked one, ruptures on continuous deformation. When, on a molecular scale, local high extensions are forced upon a small-volume element, there is a probability of breakage of a network chain situated along the shortest path through that element in the direction of the extension. As a result of the rupture of a single chain, neighboring chains will have to carry more of the local force. Thus, the probability of scission near a rupture site increases. Due to this propagation of ruptures, continued deformation of a chemically crosslinked material soon leads to catastrophic failure of the entire sample. The probability of propagation of scissions in a network held together by entanglements only likewise increases once rupture of chains has begun. At the same time, however, the probability of disentanglement also increases because of the possibility that the forces concentrate on an entanglement near the end of a polymer molecule. This last probability is enhanced by alignment of molecules in the direction of the force field. Thus, "internal rupture" [22] remains a localized phenomenon, melt fracture sets in and "rheological units" [23] are formed.

These flow units are envisaged to be small volumes of highly entangled polymer embedded in a matrix of less entangled macromolecules in which the flow deformation takes place. Flow units have been evoked from time to time in the literature to explain changes in flow regime. White[8] has reviewed this literature as part of a review paper on elastomer rheology and processing (for polyisobutylene, see in addition reference 24). Although the existence of flow units remains speculative, no other theory has yet proved adequate to explain observed "anomalous" [24] flow behavior.

Once the polymer leaves the nip of the mill and particularly in the bank, there is time for reentanglement of chains; the network becomes more homogeneous. This repair of the network is incomplete; a fraction of more stable units survive. It appears from the experimental data that it takes about $\frac{1}{2}$ to 1 hr to reach equilibrium between the processes of network fracture and repair.

It follows from the above description that, if the mill is stopped and the polymer allowed to relax over a considerable time period, the network should become homogeneous again; and, on resumption of milling, a high rate of scission

accompanying the reformation of flow units should occur. This is indeed observed, as shown by the data depicted in Figure 4. After 3 hr of degradation, the mill was stopped for 24 hr while the polymer was kept at 320 K. After restarting the mill, the rate of rupture is about as high as during the first initial period or higher. A rate about equal to the steady-state rate before the interruption is reached in approximately $1/4$ hr or less. This shorter time means that network homogenization is not complete or, more likely, that the rebuilt network is weaker because of the decrease in the fraction of very high molecular weight species.

Molecular Weight Distributions

So far, only M_n data have been considered. The MWDs, however, contain much more information. Use of all of this information requires the development of a detailed model based on the mechanisms of flow and of rupture. This is at present impossible. The only quantitative theory on flow behavior, based on a molecular model of rheological units due to Mooney,[25] is as yet not supported by experimental data and does not lend itself to further development to include rupture of chains. Therefore, we have adopted a simple model based on a general one developed by Glynn et al.[26] in which the course of degradation is described in terms of the probability $P(x)$ that a molecule with degree of polymerization x will break and the probability $Q(y,x)$ that on rupture of a molecule with degree of polymerization y a fragment with length x will result.

It is noted that the overall rate of scission in the milling experiments reported here is very low. At the highest shear rate, only a few tens of bonds per million are broken in the course of 3 hr of degradation during which time the polymer passes some 1200 times through the nip. It is therefore likely that bond rupture mainly occurs in an extremely small volume where the highest shear rates occur. Because the polymer is continuously being mixed by turbulent flow in the bank, the probability of a polymer molecule passing through this volume, and therefore its chance to rupture, is proportional to its degree of polymerization. In symbols,
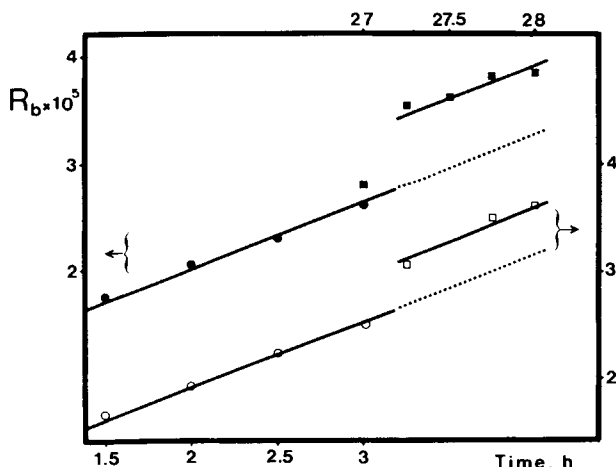

Fig. 4. Relative number of ruptures R_b as function of milling time. Polymer A: filled symbols, $\dot{\gamma} = 16.1$ s^{-1}; open symbols, $\dot{\gamma} = 10.8$ s^{-1}. After 3 hr of milling the mill was stopped for 24 hr. Temperature 320 K.

$P(x) = AF_n(x)$, where A is a normalizing factor and $F_n(x)$ is the number fraction of molecules with degree of polymerization x; P, A, and F_n are functions of the degree of degradation.

On the basis of the fact that after very long milling times degradation stops or at least its rate becomes extremely small, it is assumed that there is a maximum degree of polymerization, x_m, such that molecules with $x \leq x_m$ do not break.

The distribution $Q(y,x)$ describes the probability that a molecule y units long will break x units from its end. Obviously, $Q(y,x)$ must be symmetrical with respect to the center of the molecule. According to Bueche's theory[27] of rupture, Q is a Gaussian distribution. This function must necessarily be truncated because its domain is $-\infty$ to $+\infty$. It was found by mathematical experimentation that the course of the changes in MWDs calculated from the model is insensitive to the detailed form of the Q distribution, provided it is "hill" shaped. We have therefore preferred to assume for Q the positive part of the symmetrical beta distribution passing through $Q = 0$, $x = x_m/2$, and $x = y - (x_m/2)$, which needs no truncation. This function is given by

$$Q(y,x) = \left[\frac{x - x_m/2}{y - x_m} \left\{ 1 - \frac{x - x_m/2}{y - x_m} \right\} \right]^{\beta-1} \Bigg/ \sum_{x=x_m/2}^{y-x_m/2} \left[\frac{x - x_m/2}{y - x_m} \left\{ 1 - \frac{x - x_m/2}{y - x_m} \right\} \right]^{\beta-1}$$

For $\beta = 1$, Q is constant, i.e., scission occurs randomly along the chain between $x_m/2$ and $y - x_m/2$. When $\beta = \infty$, breakage takes place at the center of the chains only. From the initial distribution $F_n(0)$, $P(x) \propto x$, and the above $Q(y,x)$, the distribution $F_n(t)$ after t breaks per original molecule can be computed and from it the various MW averages (for computational aspects see reference 26).

The MWDs in this work have been obtained by GPC. With this technique the average MW with the highest accuracy is M_w. The averages M_n and M_z are less precisely known.[28] In order to extract as much information as possible from the MWDs obtained and taking the differences between the accuracies of the averages into account, an index q has been proposed[28] to compare the observed course of the degradation with the one calculated. This index is defined by

$$q = 1 - (R_n R_z / R_w^2)$$

where $R = M(t)/M(0)$.

In Figure 5, observed and calculated q values for polymer C are plotted versus $R_n = M_n(t)/M_n(0)$. The upper three lines are computed for $M_m = x_m M_0 = 0$. For random breakage, β indicates a weak preference for scission near the center of the molecule. The lower lines are calculated for random scission with $M_m = 0.4$ and 0.5×10^6. For polymers A and B many more data are available. Bearing in mind that q depends sensitively on all three MW averages, it is not surprising that there is considerable scatter of the experimental data in a plot of q versus R_n. In order to better visualize the fit of the experimental results to the calculated lines, the data were grouped in intervals of 0.05 of R_n and averaged. These mean values, representing each three to four data points, are shown in Figure 6 for polymers A and B, from which it may be concluded that the model of random scission with a minimum degradable molecular weight of $(0.4-0.5) \times 10^6$ agrees rather well with the experimental data. The course of the calculated lines $q = f(R_n)$ for given values of x_m is insensitive to the assumption that $P \propto x$. If $P \propto x^2$, the lines are only slightly higher than those shown in Figure 5.
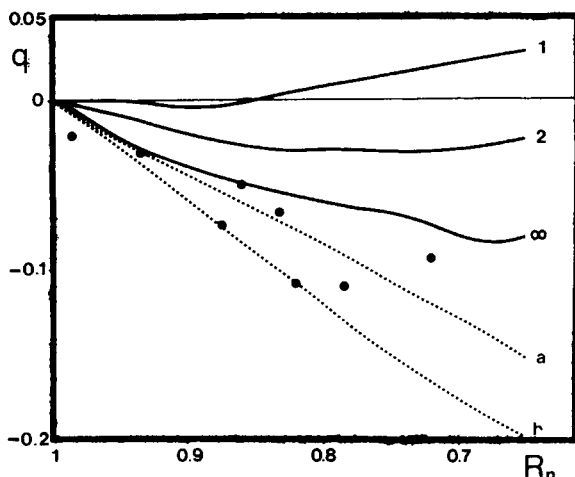
Fig. 5. Index q (see text) as function of relative number-average molecular weight $R_n = M_n(t)/M_n(0)$. Curves calculated: (—) $M_m = 0$, parameter β of beta function; (···) random breakage, (a) $M_m = 0.4 \times 10^6$, (b) $M_m = 0.5 \times 10^6$; (●) experimental, polymer C.
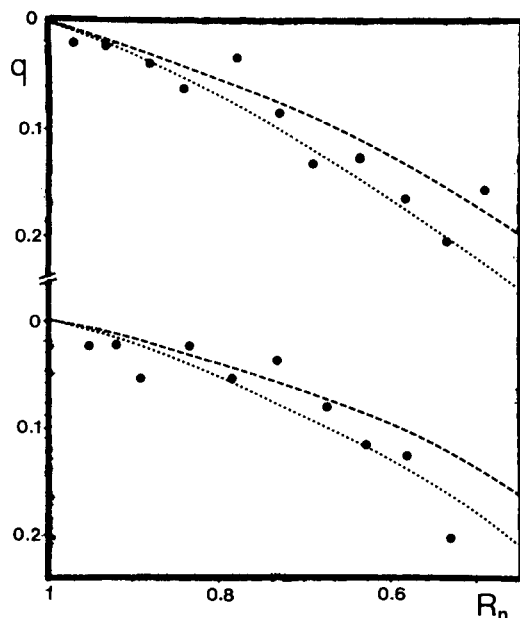

Fig. 6. Index q (see text) as function of relative number-average molecular weight R_n. Curves calculated: (●) experimental, upper half, polymer A; lower half, polymer B.

It is not unexpected that the data are not in accord with Bueche's theory[27] which would be represented by a line somewhat above the line for $\beta = \infty$ in Figure 5. This theory is based on slippage of chains through its entanglements. At the low milling temperature in our experiments, the polymers remain banded (i.e., stretched) around the roll. Therefore, the relaxation time is of the order of one revolution time (6–13 sec) or longer. These relaxation times are much too long to permit appreciable slippage during the very short time the polymer molecules are exposed to the maximum shear rate. Further, the theory is based on single-molecule "flow units," whereas it is likely that in flow during cold milling

multimolecular rheological units are formed. Also, Bueche does not consider the concept of minimum degradable length. He evaluates the forces arising from friction between an entanglement network chain and its contiguous material which forces are transmitted toward the center chain of the polymer molecule. Somewhere along the molecule there must be a segment such that the sum of the forces exerted by the contiguous chains between it and the nearest end of the molecule is insufficient to cause rupture.

In the above paragraphs a single, simple model has been assumed for degradation both in the initial and the second period with different scission rates. The accuracy of the index q attainable is not high enough to draw any conclusions from Figure 6 with regard to possibly different mechanisms operating in these two periods. In two runs at different shear rates, polymer A happens to have degraded to the same extent after different milling times, namely, 1 hr at 16.1 s^{-1} and 3 hr at 3.6 s^{-1}. In the run at the higher shear rate, the sample was taken at the end of the initial period; in the other, the rate of scission is constant throughout the run. The symbols in Figure 7 represent the observed MWDs of these two runs, and the solid line is the distribution calculated for random scission with $M_m = 0.4 \times 10^6$. The small difference between the two experimental MWDs is about the same as that between duplicate experiments on a single sample. The calculated MWD agrees fairly well with the observed distributions. It may therefore be tentatively concluded that the mechanisms of rupture in the periods with different flow regimes do not differ.

CONCLUSIONS

High molecular weight PIB degrades on milling at 320 K. After long times the molecular weight approaches an apparent minimum value of about 0.4×10^6.

An initial and a lower subsequent steady rate of scission are observed at shear rates higher than about 6 s^{-1}. At lower shear rates the rate of degradation is constant from the start. After the mill has been stopped for 24 hr the high initial
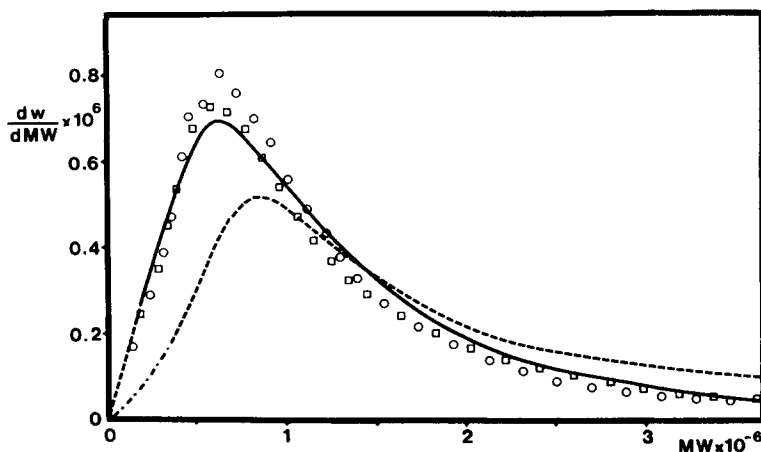

Fig. 7. Molecular weight distribution of original and degraded polymer A. Temperature 320 K: (- - -) original polymer; (O) time 1 hr, shear rate 16.1 s^{-1}, $R_b = 1.06 \times 10^{-5}$; (□ time 3 hr, shear rate 3.6 s^{-1}, $R_b = 1.06 \times 10^{-5}$; (—) calculated, $\beta = 1$, $M_m = 0.4 \times 10^6$, $R_b = 1.06 \times 10^{-5}$.

rate of rupture is observed again, followed by a drop in rate to the same value as before the interruption. The initial rates are independent of shear rate, whereas the subsequent constant rates are proportional to the rate of shear. These observations support the assumption of an equilibrium between the formation of multimolecular "flow units" and the tendency, due to thermal motion, to form a homogeneous entanglement network.

Comparison between observed MWDs and those calculated from a model leads to the conclusion that breakage occurs randomly between points along the molecule M_m removed from the ends, where M_m is $(0.4-0.5) \times 10^6$.

The mechanism of rupture appears to be the same for low and high shear rates.

References

1. H. Staudinger and W. Hever, *Ber.*, **67**, 1159 (1934).
2. A. Casale, R. S. Porter, and J. F. Johnson, *Rubber Chem. Technol.*, **44**, 535 (1971).
3. G. Kraus and K. W. Rollman, *J. Appl. Polym. Sci.*, **8**, 2585 (1964).
4. C. Booth, *Polymer*, **4**, 471 (1963).
5. D. J. Harmon and H. J. Jacobs, *J. Appl. Polym. Sci.*, **10**, 253 (1966).
6. N. F. Kovalev and I. M. Tsypkina, *Int. Polym. Sci. Technol.*, **1**, T/48 (1974).
7. K. Baranwal and H. L. Jacobs, *J. Appl. Polym. Sci.*, **13**, 797 (1969).
8. J. L. White, *Rubber Chem. Technol.*, **42**, 257 (1969).
9. H. Fujii, *Nippon Gomu Kyokaishi*, **38**, 1094 (1965).
10. K. A. Boni, F. A. Sliemers, and P. B. Stickney, Proc. Fourth International Seminar on Gel Permeation Chromatography, Miami Beach, Waters Associates, Framingham, Mass., 1967.
11. A. Rudin and H. L. W. Hoegy, *J. Polym. Sci. A* **1**, 217 (1972).
12. K. S. Chang and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **13**, 1459 (1969).
13. L. H. Tung and J. R. Runyon, *J. Appl. Polym. Sci.*, **13**, 2397 (1969).
14. P. A. R. Glynn and B. M. E. van der Hoff, *J. Macromol. Sci.-Chem. A* **7**, 1695 (1973).
15. M. Pike and W. F. Watson, *J. Polym. Sci.*, **9**, 229 (1952).
16. K. L. DeVries, *Rubber Chem. Technol.*, **48**, 445 (1975).
17. N. K. Baramboim and B. V. Santin, *Vysokomol. Soedin.*, **2**, 1196 (1960).
18. R. M. Kell, B. Bennet, and P. B. Stickney, *Rubber Chem. Technol.*, **31**, 499 (1958).
19. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1975.
20. B. M. Kato and J. E. Mark, *Rubber Chem. Technol.*, **49**, 85 (1976).
21. D. Göritz and F. H. Müller, *Kolloid-Z. Z. Polym.*, **251**, 892 (1973); *Rubber Chem. Technol.*, **49**, 210 (1976).
22. M. Mooney, *Rubber Chem. Technol.*, **37**, 503 (1964).
23. M. Mooney, *Rubber Chem. Technol.*, **28**, 488 (1955); *ibid.*, **30**, 460 (1957).
24. J. K. Lund and H. A. Pohl, *Can. J. Chem. Eng.*, **43**, 231 (1965); *Rubber Chem. Technol.*, **40**, 1492 (1967).
25. M. Mooney, *J. Appl. Phys.*, **27**, 691 (1956).
26. P. A. R. Glynn, B. M. E. van der Hoff, and P. M. Reilly, *J. Macromol. Sci.-Chem.*, **A6**, 1653 (1972).
27. F. Bueche, *J. Appl. Polym. Sci.*, **4**, 101 (1960); F. Buche, *Physical Properties of Polymers*, Wiley, New York, 1962.
28. B. M. E. van der Hoff and C. E. Gall, *J. Macromol. Sci.-Chem.*, *A* **11**, 1739 (1977).