The Behavior of Polyisobutylene During Melt Shear

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INTRODUCTION

There has been a rapidly accelerating degree of attention paid to the behavior of molten polymer during shear. Considerable attention has been given to the behavior at very low shear rates, during which little chain rupture takes place. Careful rheological studies at low shear rates have been made by Flory[1] on polyesters, by Pollett[2] and by Marker, Early, and Aggarwal[3] on polyethylene, by Cox, Nielsen, and Keeney[4] on polystyrene, and by Allen, Gee, Lancely, and Mangoraj[5] on polyisobutylene. A considerable theoretical advance was made by F. Bueche and Harding[6] in applying viscosity behavior directly in the determination of "absolute" polymer molecular weights. In the higher shear ranges, studies by Tordella[7] have shown pictorial evidence of melt fracture. The operation of high shear to produce chain rupture in rubbers has been the subject of attention of Watson[8,9] and other British workers. There has been considerable Russian interest in the mechanical rupture of polymer chains since the early work of Frenkel.[10] Baramboĭm has reported both experimental and theoretical studies[11–13] on mechanical degradation produced by milling numerous solid polymers. Berlin[14] gave an extensive review of mechanochemical transformations and synthesis of polymers. The preparation of block and graft copolymers by intensive mechanical working was described by Kargin[15] et al. Photographic studies of mechanical rupture of polymer samples were reported by Gul' and Chernin.[16] The generation of heat in sheared polymer has been studied by Toor.[17,18]

Work in this country on the mechanical rupture of polymer chains has been done by Price[19] and co-workers to investigate the potential of the process for block and graft copolymerization. They found that almost every chain scission resulted in the inclusion of iodine on the chain when radioiodine is present during shear of a polymer solution. Rodriguez and Winding[20] have recently studied shear degradation of polyisobutylene dissolved in a variety of solvents.

Pohl and Lund,[21] using a capillary shear viscometer, studied the dependence of shear breakdown of polyisobutylene melts. The specific rate of bond rupture was found to be essentially independent of the molecular weight, whereas the rate of molecular size reduction was found to be dependent upon the original molecular weight. It seemed apparent from a study of the available literature that a need existed for some quantitative understanding of the melt viscosity and molecular weight changes which occur during melt shear. The present study is an effort to contribute to this area through the use of a biconical rheometer in which there is known mechanical shear exerted, and by which the apparent melt viscosity can be measured continuously during the shearing.

EXPERIMENTAL

In the following experiments, samples of molten polyisobutylene (PIB) were subjected to known shear rates for selected times, temperatures, and shear cessation intervals. From the torque measurements, the apparent melt viscosities were determined. The changes in degree of polymerization resulting from shear application were also followed by dilute solution measurements of viscosity.

I. Solution Viscosity Measurements

The intrinsic viscosity of the various samples of sheared polymer were determined in solutions in purified cyclohexane of boiling point range less than 1°C. Determinations were made at 30 ± 0.02°C. in an Ostwald-Fenske viscometer calibrated with suitable liquids of known viscosity to enable elimination of the kinetic correction. The viscosity of the polymer solutions in poises was calculated from the flow times and the expression:

$$\eta = at_s - b/t_s$$

where $a = 18.63 \times 10^{-3}$ and $b = 1.59$. In the series of polyisobutylene sample examined, the solution viscosities were determined at various concentrations, and the results were correlated with the aid of the Huggins[22] equation:

$$\eta_{sp} = [\eta]C + K'[\eta]^2 C^2$$

for which a value of $K' = 0.51$ was found to give reasonable agreement with the data obtained here for a wide range of molecular weights. From this, plots of η_{sp}/C vs. C were constructed to facilitate extrapolation of $[\eta]$ values. In this procedure the values of Table I were obtained for the several PIB samples examined. Molecular weights were calculated from the values of Fox and Flory[23] and Krigbaum and Flory[23] for the constants in the equation:

$$[\eta] = KM^a$$

where $a = 0.6897$ and $K = 2.7 \times 10^{-4}$.

TABLE I
Viscosity-Average Molecular Weights of Polyisobutylene Samples

Material[a]	$[\eta]_0$ at 30.0°C., dl./g.	Viscosity-average molecular weight
LM-MS	0.406	40,100
LM-MH	0.487	52,300
L-80	3.26	823,000
MD-331	10.03	4,200,000

[a] Vistanex, manufactured by Enjay Co., Inc.

II. The Biconical Rheometer

To minimize the uncertainty of shear rate as experienced in the capillary shear rheometer,[21]

and to permit long continued application of shear to a given sample, a biconical rheometer was constructed (Fig. 1). In it, because of its construction, the sample was exposed mechanically to essentially only one applied rate of shear throughout. Gaskins and Philippoff[25] have recently reviewed the merits of various types of rheometers. Approximately 5 g. of material was required for the sample. The biconical rotor was driven by a belt drive at selected speeds to provide various shear rates. The free-floating cup and cap, which ride on a plate supported by a bearing, enclosed the sample about the rotor. Four strain gages coupled to form a compression-extension-sensitive Wheatstone bridge, were mounted on a flexure bar attached to the free floating base and to the fixed base. The cup rotated, limited by the flexure bars.

The signal from the strain gage bridge was amplified and recorded during the run. Calibration of the torque strain was done with couples made with known weights prior to and following each of the runs. An electric heating jacket and enclosed thermocouples permitted runs at various known temperatures of the rheometer.

Loading of the sample into the apparatus was accomplished by injecting a plug of bubble-free polymer into the center of the cup, then firmly pressing the rotor into place, followed by the similar placing of the cap. The rotor was then chucked in the vertical drive. It was found necessary to use a lightly spring-loaded Teflon sleeve gasket on the rotor where it passed through the cap. This prevents bubble intake into the shearing polymer.

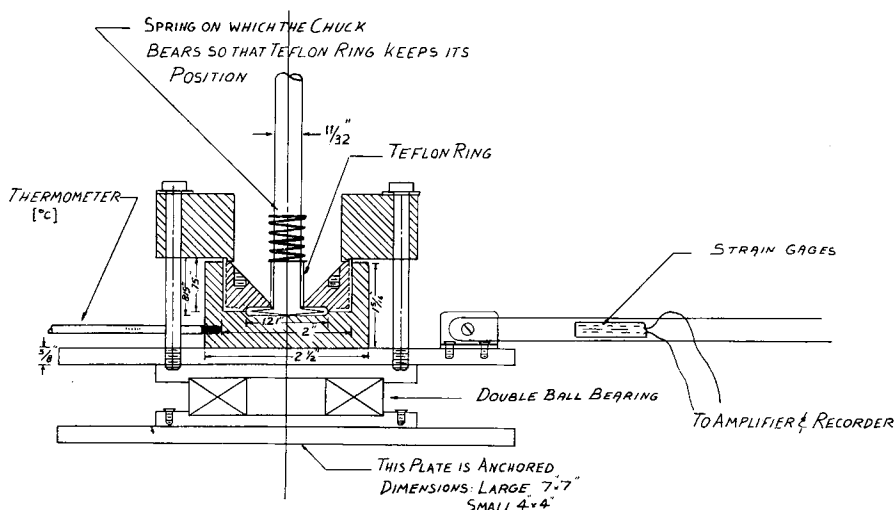The torque on the rotating biconical rheometer
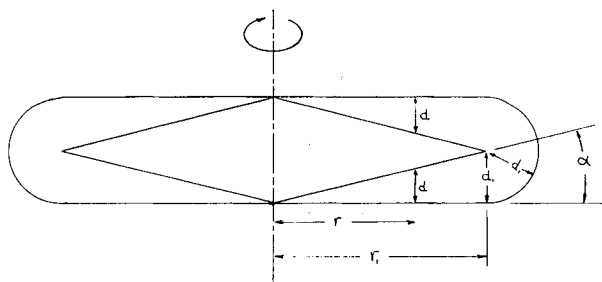

Fig. 1. Biconical rheometer.

Fig. 2. Geometrical factors in the biconical rheometer.

was interpreted in terms of the polymer melt viscosity by using the following equations. The increment drag force δF (see Fig. 2) is

$$\delta F = \eta \dot{\gamma} \delta A \tag{1}$$

where η is viscosity and the shear rate $\dot{\gamma}$ is given by

$$\dot{\gamma} = 2\pi \nu/d \tag{2}$$

where ν is the frequency of rotation in cycles per second, d is the distance between rotor face and base, the area increment δA, is given by $\delta A = 2\pi r \delta r$, and r is the radial distance from axis of rotation.

$$r/d = \cot (\alpha) \tag{3}$$

Therefore

$$\delta F = 4\pi^2 \eta \nu \cot (\alpha) \, r^2 \delta r \tag{4}$$

The torque moment u is then

$$u = \int_A r \delta F \tag{5}$$

where the integration is over both top and bottom surfaces.

$$u = \int_0^{r_1} 8\pi^2 \eta \nu \cot (\alpha) \, r^2 dr \tag{6}$$

$$u = (8/3)\pi^2 \eta r_1{}^3 \nu \cot (\alpha) \tag{7}$$

or

$$u = 4/3 \pi \eta r_1{}^3 \dot{\gamma}_1 = F_w L \tag{8}$$

where

$$\dot{\gamma}_1 = 2\pi r_1 \nu/d_1$$

and d_1 is the spacing between rotor and cup at some radial distance r_1, and F_w is the force exerted at the end of a lever arm of length L to balance the torque u created by the shearing of the polymer melt.

Also,

$$\eta_m = 3\mu/4\pi r_1{}^3 \dot{\gamma}_1 \tag{9}$$

EXPERIMENTAL RESULTS

A. Melt Viscosity Behavior During Shear

The molten PIB, after being loaded into the biconical rheometer, was subjected to shear at several temperatures, shear rates, and for selected intervals. The peculiar advantage of the present biconical rheometer is that it may be operated continuously or with desired interruption of shear. In this respect, shear studies on polymer melts are more fully made than in a capillary rheometer, where a steady state is not easily realized experimentally.[21,29] It is in just this aspect, the application, cessation, and reapplication of shear and the ability to operate at steady-state or at transition-state periods that the present results seem to demonstrate the somewhat remarkable properties of sheared polymer melts, The results of this study, shown partially in Figures 3, 4, and 5, are for a single polymer specimen, polyisobutylene sample LMMS obtained from Enjay Co., Inc.
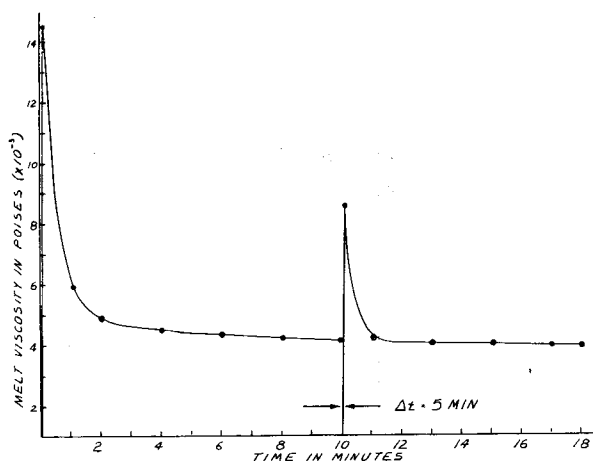

Fig. 3. Apparent melt viscosity vs. time of shearing at shear rate of 143 sec.[-1] and 26°C.
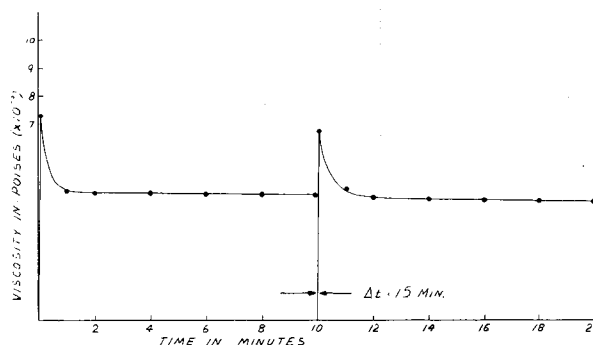

Fig. 4. Apparent melt viscosity vs. time of shearing at shear rate of 143 sec.[-1] and 46°C.

TABLE II

Experimental Data on Melt Viscosity and Degradation of Sheared Polyisobutylene

Run No.	Time, min.	Temp., °C.	F, g.	$\mu \times 10^{-3}$, dyne-cm.	$\dot{\gamma}$, sec.$^{-1}$	η_m, poise	$\Delta\eta_m$, poise	$\Delta u/u$, $\Delta\eta_m/\eta_m$	Rest interval, min.	$[\eta_0]$	$\dfrac{\Delta[\eta]}{[\eta_0]} \times 100$	MW_0	$\Delta(MW)/MW_0$	D.P.	$f \times 10^6$	$b \times 10^7$
N_{11}	0	46	630	401.3	143	3270.6			8	0.4058		40,100		716.07		
	3	48	620	394.9	143	3218.8	51.8	0.0159	5	0.3880	4.4	37,610	0.0621	671.61	4.672	1.5573
	5	48.5	617	393.0	143	3203.2	67.4	0.0206								
N_{12}	0	45.5	629	400.6	143	3265.0			8	0.4058		40,100		716.07		
	3	47.5	622	396.2	143	3229.0	36.0	0.0111								
	5	48.8	618	393.7	143	3209.0	56.0	0.0175	10	0.382	5.9	36,770	0.0830	656.61	6.323	1.0538
	10	50.8	603	384.1	143	3130.0	135	0.0413								
N_{13}	0	45.0	890	566.9	143	4620.0			8	0.4058		40,100		716.07		
	3	45.5	878	559.3	143	4558.0	62.0	0.0135								
	5	46.0	872	555.5	143	4527.0	93.0	0.0202								
	10	47.0	850	541.4	143	4413.0	207	0.0450	15							
	15	47.2	830	528.7	143	4309.0	311	0.0665								
	20	48.0	808	514.7	143	4195.0	425	0.0922		0.3795	6.4	36,350	0.0960	649.11	7.203	0.6002
N_{14}	0	47.5	576	366.9	366	1166.0			8							
	3	49.2	555	353.5	366	1124.0	42.0	0.0364	5							
	5	50.0	542	345.3	366	1097.0	69.0	0.0590								
N_{15}	0	25.9			143				8	0.4058		40,100		716.07		
	3	28.2			143											
	5	29.0			143					0.3840	5.3	37,000	0.0772	660.80	5.840	1.9467
N_{16}	0	24.5	970	617.9	143	5034.0			8	0.4058		40,100		716.07		
	3	26.5	930	592.4	143	4828.0	208	0.0412								
	5	27.5	910	579.6	143	4724.0	312	0.0618	5	0.375	7.6	35,750	0.1085	638.39	8.496	1.4160
	10	29.2	880	560.6	143	4558.0	478	0.0928								

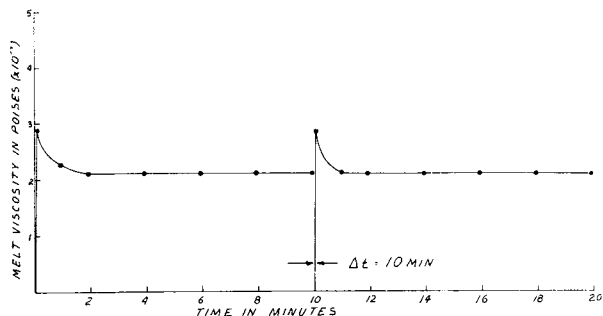|	i				N				q								
N_{17}	0	23.2	984	626.8	143	5109.0			8	0.4058		40,100		716.07		
	3	25.3	907	577.7	143	4708.0	401	0.0783								
	5	26.4	852	542.7	143	4423.0	686	0.1341	5							
	10	28.0	795	506.4	143	4127.0	982	0.1922								
	15	28.7	782	498.1	143	4060	1049	0.2052								
	20	30.0	725	461.8	143	3764	1345	0.2634		0.372	8.3	35,380	0.1177	631.78	9.315	0.7762
N_{18}	0	80.3	402.5	256.0	143	2089.0			8	0.4058		40,100		716.07		
	3	80.5	401	255.0	143	2082.0	7	0.0037								
	5	79.7	400	254.0	143	2077.0	12	0.0062	10	0.399	1.7	39,165	0.0233	631.78	1.667	0.5557
N_{19}	0	79.7	409	260.5	143	2133.0			8	0.4058		40,100		716.07		
	3	79.9	408	260.0	143	2118.0	5	0.0032								
	5	79.9	407	259.2	143	2113.0	10	0.0056								
	10	80.0	404	257.4	143	2097.0	26	0.0110	10							
	15	79.2	402	256.1	143	2087.0	36	0.0166								
	20	79.9	400	255.0	143	2077.0	46	0.0220		0.397	2.2	38,880	0.0304	624.29	2.191	0.1826
N_{20}	0	79.4	490	312.1	366	992.0	30	0.0306	8							
	1	80.0	475	302.6	366	962.0	50	0.0510								
	2	80.8	465	296.2	366	942.0	60	0.0612								
	3	81.2	460	293.0	366	932.0	67	0.0673								
	4	81.9	457	291.0	366	925.0	67	0.0673								
	5	82.4	457	291.0	366	925.0	67	0.0673								
N_{21}	0	58.0	940	599.0	143	4880.0			8	0.4058		40,100		716.07		
	1	58.5	950	605.0	143	4932.0	16	0.0032								
	3	59.2	937	597.0	143	4884.0	30	0.0053								
	5	60.0	935	596.0	143	4854.0	68	0.0138								
	10	62.0	927	590.0	143	4812.0				0.3840	5.3	37,000	0.0772	660.8	5.840	0.9733
N_{23}	0	60.2	914	582.0	143	4745.0			8	0.4058		40,100		716.07		
	1	59.4	920	586.0	143	4776.0										
	2	59.7	909	584.0	143	4760.0	37	0.0077								
	3	59.8	907	578.0	143	4708.0	63	0.0131								
	4	59.9	902	575.0	143	4682.0	73	0.0153								
	5	60.0	900	573.0	143	4672.0				0.391	3.6	38,035	0.0515	679.20	3.791	1.2637

Fig. 5. Apparent melt viscosity vs. time of shearing at shear
rate of 143 sec.$^{-1}$ and 80°C.

The initial high torque or apparent melt
viscosity drops rapidly to a steady-state value in
1–2 min. of continued shear. An interval of shear
cessation permits the polymer to make a consider-
able return to the original high torque or melt vis-
cosity, especially if the interval is long or the tem-
perature is high. During the steady-state period
there is a small and continuous drop in the already
reduced apparent melt viscosity. There are, then,
two observable viscosity drops during the shear of
such polymer melts: (1) a generally large, rapid,
and quasi-permanent one at the outset of intense
shearing action; (2) steady, monotonic, viscosity
drop, generally at a rather smaller rate, as shear is
continued. Further details of the behavior are
described in Table II.

The measured apparent melt viscosities η_m of
the various samples are shown in Figure 6 for the
several shear rates as a function of temperature.
The thermal activation energies calculated from
the slopes of these curves were 3.0 kcal./mole at
the 143 sec.$^{-1}$ shear rate, and 1.28 kcal./mole at the
366 sec.$^{-1}$ shear rate. The decrease in thermal
activation energy for viscous flow with increase in
rate of shear is to be expected if one regards the
flow processes for polymer chains under high shear
to involve the progressive chain disentanglement
and the selective grouping of holes in the fluid.
In this picture, if it is assumed that increase of
shear rate causes a decrease in average hole den-
sity near the center of the tumbling flow units and
a corresponding increase in hole density near the
periphery, the thermal activation energy required
for flow would be expected to be less where the
holes required for flow unit movement are already
numerous, i.e., at the higher shear rates.

An alternate explanation, based upon the as-
sumption that no hole grouping occurs and that
just the existence of chain rupture brings about
the lowering of viscosity, is more difficult to ex-
press. It is possible, for example, that the in-
creased chain rupture brought about by low tem-
perature (and hence high viscosity) sufficiently
reduces the viscosity to bring about the observed
effect. Increasing the shear rate at the low tem-
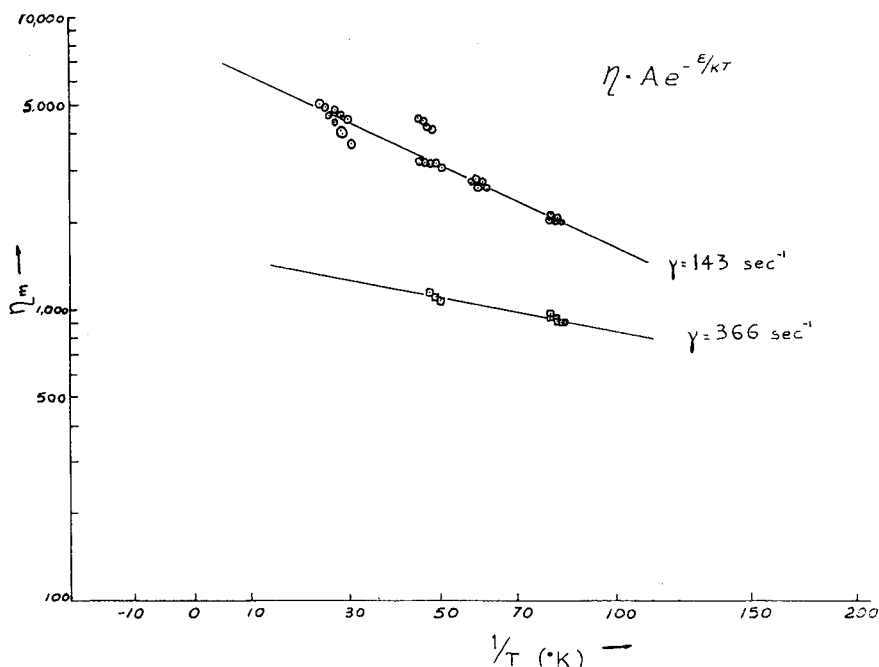
Fig. 6. Apparent melt viscosity of PIB sample LM-MS at shear rates of 143 and 366 sec.$^{-1}$ vs. reciprocal absolute
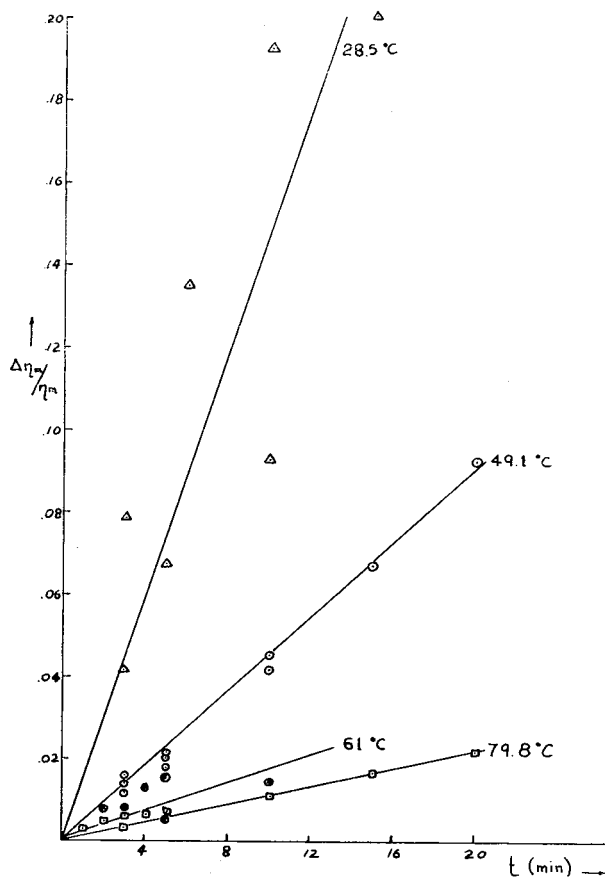temperature. Data collated from eight runs.

Fig. 7. The fractional change in apparent melt viscosity $\Delta\eta_m/\eta_m$ vs. time of shearing at various temperatures.
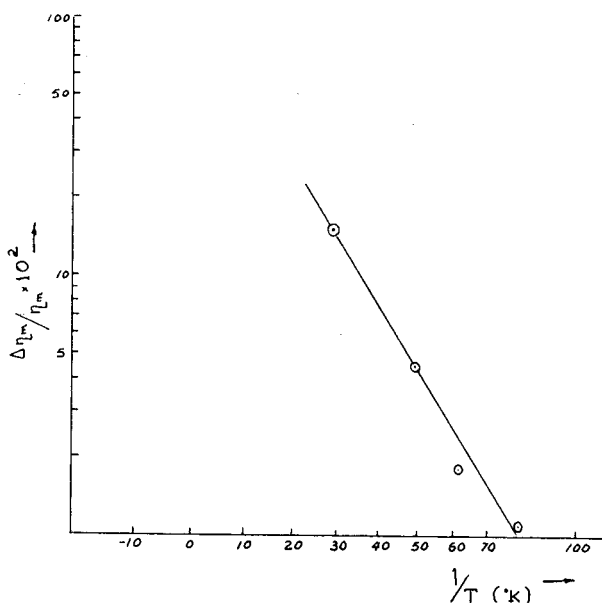
perature conditions would then bring about a disproportionately larger chain rupture and lower apparent melt viscosity than at high temperature conditions.

Let us now turn to a discussion of the long-term melt viscosity drop. As discussed earlier, the more or less steady drop in apparent melt viscosity which follows the initial large and rapid drop is referred to as the long-term melt viscosity drop due to continued shear. In Figure 7 are plotted the slopes of the apparent melt viscosity versus time curves for the various runs. The rate of viscosity fall with time is observed to be constant with duration of shear to within the limit of error of the measurements. A plot, as in Figure 8, of the rate versus reciprocal absolute temperature shows the rates to fit to a straight line from which the energy of activation of this process can be calculated to be -11.3 kcal./mole. Just how this varies with shear rate could not be ascertained from the data at hand, but it might be expected to be less at higher shear rates in the light of the previous discussion on viscosity behavior.

B. Molecular Chain Rupture During Shear

From the intrinsic viscosity data obtained on polymer samples before and after shear, information was obtained as to the degree of permanent molecular size damage due to shear. The basic data obtained with the biconical rheometer are summarized in Table II. The relative changes in the intrinsic viscosity of this polymer when subject to shear of 143 sec.$^{-1}$ for various times and tem-

Fig. 8. The temperature dependence of the rate of change of the apparent melt viscosity during the pseudo-steady-state period.
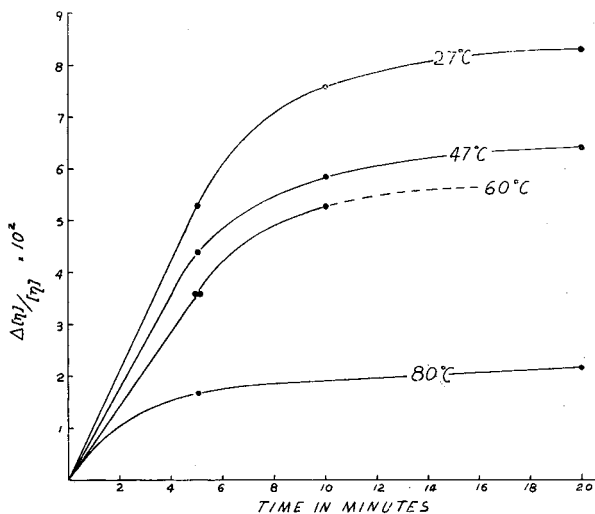

Fig. 9. The fractional change of the intrinsic viscosity of sheared PIB as a function of time of shear at various temperatures.
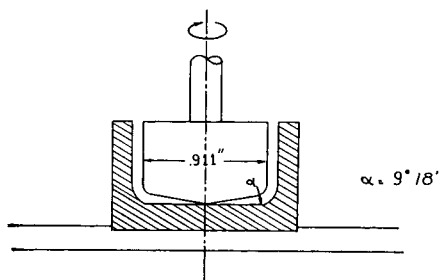
Fig. 10.   Single-cone rheometer.

peratures are shown in Figure 9. The greatest changes per unit time occur at the lowest temperatures. Furthermore, there is seen to be a decreasing rate of change with time of shear exposure. Analogous statements may be made about the viscosity-average molecular weight of the polymer.

In a preliminary attempt to investigate the effect of changes in shear rate upon the rate of degradation of this polymer, the following data were obtained with a single-cone rheometer used here in the early studies of shear behavior of polymer melts. The data are to be considered as rough approxi-
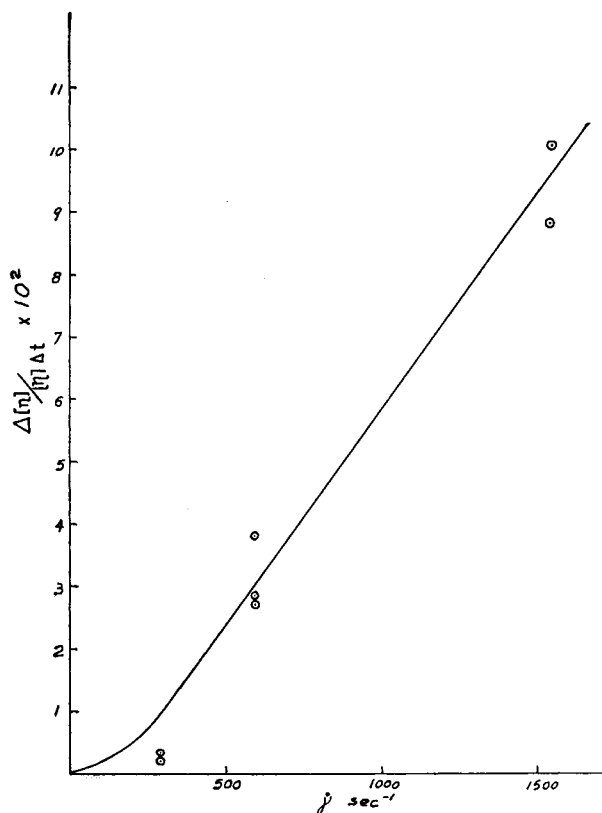
Fig. 11. Approximate data for the shear rate dependence of the molecular breakdown of molten PIB at 37°C. Data obtained with single-cone rheometer.
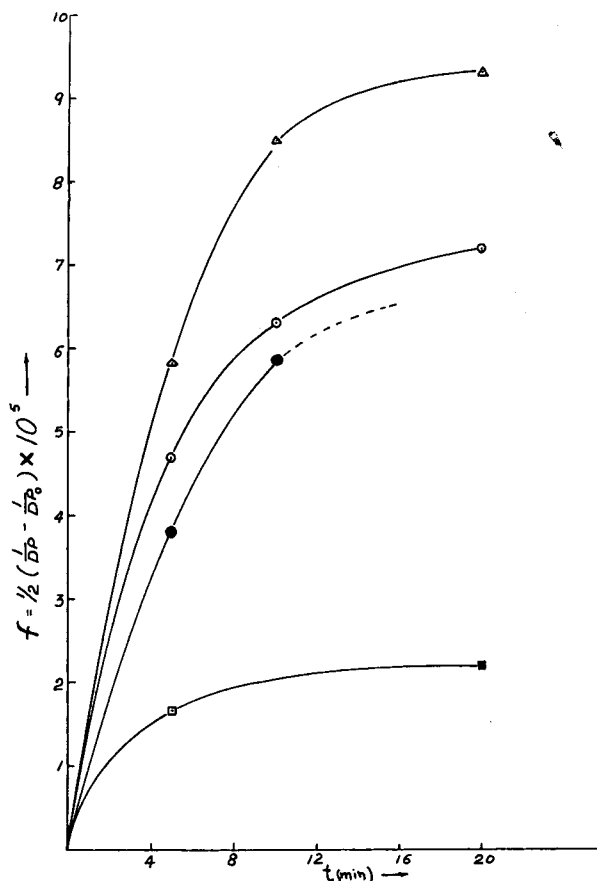
Fig. 12. Time dependence of the fraction of main chain bonds ruptured during shear at a shear rate of 143 sec.$^{-1}$ in molten PIB at: ($\triangle$) 28.5°C.; ($\bigcirc$) 49.1°C.; ($\bullet$) 60.0°C.; ($\square$) 80.0°C.

mations and are included only to serve as a preliminary guide to polymer melt behavior during various shear conditions. The form of the rheometer is sketched in Figure 10. The data observed are shown in Figure 11 and indicate that the rate of intrinsic viscosity change is proportional to the shear rate except at very low shear rates. These data would indicate that there may be a critical shear rate below which little detectable chain degradation takes place.

Turning again to the work done with the double-cone rheometer, it is observed that the changes in intrinsic viscosity permit one to calculate the changes in viscosity-average molecular weight of the variously sheared material. In the absence of specific data on the molecular weight distributions in each sample, it is recognized to be a considerable approximation to reinterpret the viscosity-average molecular weights obtained by intrinsic viscosity measurements as more than rough values of the number-average molecular weight by the use of the
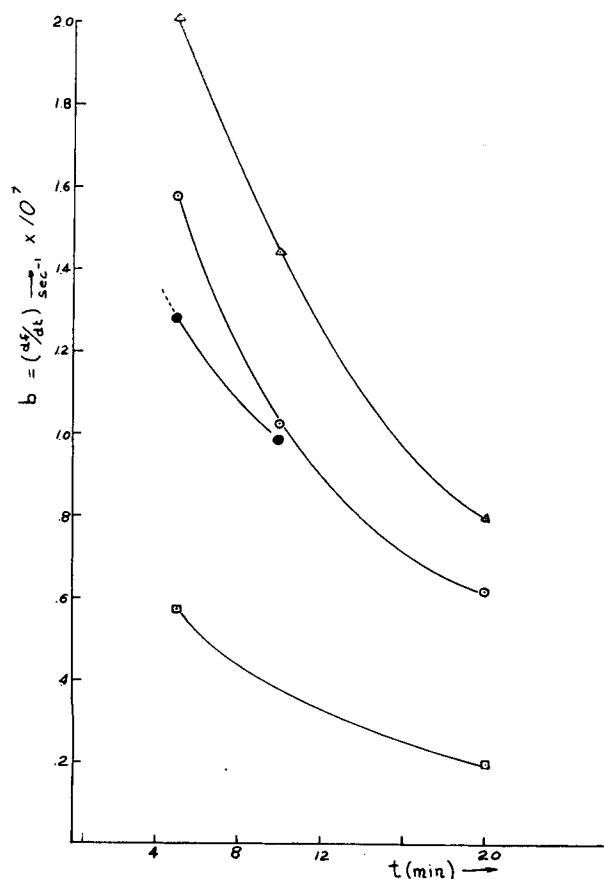
Fig. 13. The fractional rate of bond rupture (number of main chain bonds broken per main chain bond per second) as a function of time of shear at a shear rate of 143 sec.$^{-1}$ in molten PIB at: ($\triangle$) 28.5°C.; (O) 49.1°C.; (●) 60.0°C.; ($\square$) 80.0°C.

Flory-Fox and Flory-Krigbaum relations for intrinsic viscosity versus number-average molecular weight.[6,7] With this appreciation of the necessary approximation in mind, the values of the intrinsic viscosity were converted to bond rupture fractions f, where

$$f = \tfrac{1}{2}[(1/DP) - (1/DP_0)]$$

The fractional rate of bond rupture, $df/dt = b$, was also calculated. The results are shown in Figures 12 and 13. The data show the rate and amount of bond rupture to decrease with increasing time of shear and with increasing temperature of shear.

DISCUSSION

The rapid drop of the apparent melt viscosity of the molten polymer, followed by the appearance of a pseudo-steady state during which there is a relatively very low rate of change of apparent melt viscosity can be explained in terms of two types of hypothesis, a chemical one or a mechanical one. In the chemical type of hypothesis, it is said that the initial rapid drop in viscosity is due mainly to the rupture of main chain bonds and that a "stasis" results when the rupture rate of chain bonds equals the recombination rate of the active chain ends. There are three principal ways in which an organic polymer chain can rupture in the main chain: (1) to form free radicals in pairs; (2) to form free ion pairs (i.e., carbonium plus carbanion pairs); (3) to disproportionate. In the case of polyisobutylene, there might be a disproportionation such as

$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdots\cdots\cdots CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\longrightarrow$$

breaking bond⌐

$$-CH=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \ + \ CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-$$
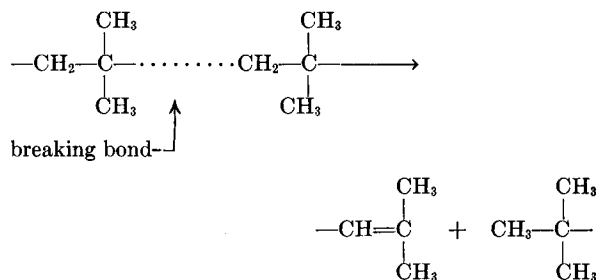
Of the three chemical modes of rupture, only the first two can bring about appreciable rapid recombination of the active chain ends. The last, disproportionation, presumably operates only to bring about permanent chain rupture and may be excluded from consideration as a mechanism for the reversibility of viscous behavior following the short shear cessation periods. We have recently obtained rather convincing proof that neither of the remaining chemical mechanisms, free radical formation or ion pair formation, contribute in a major manner to the observed reversibility of apparent viscosity during continued shear. This was done by observing the effects of added free radical or ion pair inhibitors, but the experiments will not be described further at this time.

In the mechanical action hypothesis, it is said that the observed drop in apparent viscosity during continued shear followed by a recovery upon cessation of shear is due to more or less reversible disentanglements of the segments[26] of neighboring polymer molecules or to orientation mechanisms.[27,28] There is still another mechanism by which the melt viscosity can be affected during the shearing process, one which does not seem to have been given much attention in the past. For brevity we may term it "fault flow." Fault flow is considered to arise when the holes within the liquid polymer are forced to take a nonrandom distribu-

tion by being made to gather at the periphery of the rotating molecular flow units. The nonrandom distribution of holes in the assembly of polymer chains is considered to come about because of the combined action of shear forces which buffet the various monomeric units into randomized motion to accomodate flow (much as in shear action in monomeric liquids) and the continued reminder exerted along the chain that the units are attached to each other. The net result of the combined actions, one randomized, the other having a centralized force effect, will, it is reasoned, result in the balling up of the chains. An analogy may be seen in the behavior of two mechanically observable macroscopic systems, a set of small separate balls and a set of balls linked together in long chains. As the separate balls are subjected to shear and agitation they merely roll and form randomly shifting holes in the mass. As the chains are subjected to lightly loaded shearing action, and agitation, the chains are seen to ball up and form tightly packed, larger, flattened spheroids which tend to disentangle and to become somewhat separated (but still interacting) entities as shearing action and agitation is continued. This migration of holes away from the centers of the chains and out to the peripheries would lead to the formation of denser, more viscous regions rotating within less dense, less viscous regions in which the concentration of holes would be rather higher. It is expected in this model of fault flow that the sizes of the rotating units would be dependent upon the shear rate, increasing as the shear rate increases. This expectation is based upon the fact that the polymer molecules are originally much entangled, and the view that as faster and faster response to shear is required, less respect would be paid to molecular niceties and more to existing weak points such as exist at normally random gatherings of holes, where high stress concentrations would be available to produce gross ruptures of the structure.

We may summarize the two views of mechanical response mechanisms to shear as (1) disentanglement action without fault flow and (2) disentanglement action including fault flow. There appears to be no ready means to distinguish the two solely on the basis of flow studies at varying temperature, pressure, or shear rate. However, the first mechanism neither requires nor predicts any essentially prominent changes in local density, whereas the one including fault flow does. For this reason, a definitive experiment such as one showing up the existence or nonexistence of local density fluctu-

ations (i.e., those due to shear-induced hole aggregation about the peripheries of the rotating flow units) would be highly desirable.

It is rather easy to show on the basis of simple assumptions that the preferential clustering of holes, as by shearing action, should *not* in itself be expected to lead to large reduction in resistance to flow in nonpolymeric liquids. The argument is based upon two assumptions, both reasonable: first, that the fluidity of any portion of the liquid is proportional to the density (or concentration) of holes in it (this has been often shown, e.g., by Eyring et al.[26]) and second, that the fluidity of a mixture is reasonably represented by the sum of the partial fluidities, i.e., by a simple mixture law.

Following the first assumption, we have for ϕ_i, the fluidity of the ith portion of liquid containing a density ρ_i of holes,

$$\phi_i = (\rho_i/\rho_0)\phi_0$$

The fluidity of the original unsheared liquid is ϕ_0 and the original hole density is ρ_0.

The total overall concentration of holes remains fixed (no expansion), i.e.,

$$\rho_0 = v_0\rho_0 + v_1\rho_1 + v_2\rho_2 + \ldots + v_n\rho_n$$

where the v_i are the volume fractions of the various portions.

By the second assumption, additivity of the partial fluidities, we have, for a mixture of fluidity ϕ,

$$\phi = v_0\phi_0 + [(v_1\rho_1/\rho_0) + (v_2\rho_2/\rho_0)$$
$$+ \ldots + (v_n\rho_n/\rho_0)]\phi_0$$

$$\phi = (\phi_0/\rho_0)[v_0\rho_0 + v_1\rho_1 + v_2\rho_2 + \ldots + v_n\rho_n]$$

$$\therefore \phi = \phi_0$$

hence the fluidity of the mixture is unchanged by hole migration. It is felt that the two assumptions upon which this argument is based are at least fair approximations to the true state of affairs, at least in nonpolymeric liquids and hence one should see no major changes in fluidity due to hole density fluctuations as shear is applied. However, the disentanglement mechanisms in polymeric liquids are dependent upon shear rate, and the persistence of chain disentanglement between the rotating flow units is in reality a localization of holes in the region of high local flow. It seems clear that such localization of holes would affect the overall fluidity in such a direction as to increase the fluidity with increase of shear rate.

By way of emphasizing in a less qualitative way the expected behavior of a polymer melt which is exhibiting both disentanglement–reentanglement and fault flow one may represent the various factors in the following rather oversimplified manner. The molten polymer chains form a mass of entangled, rather spherical entities which, upon being sheared, develop regions containing a harder core surrounded by a more fluid portion as the holes are forced to gather at the periphery of the rotating flow units. The fluidity of the mass may be considered to arise from two portions: that due to the motion of (hard) spheres through a thin liquid, a case treated by Einstein[24] and others[30-32] and that due to the fluidity of the spheres themselves.

The Einstein relation for hard spheres in a thin liquid is

$$\eta_0 = \eta_1\left(1 + \left(\frac{5}{2}\right)V_2\right)$$

or the fluidity ϕ_0 due to the thin liquid containing hard spheres is

$$\phi_0 = 1/\eta_0 = 1/\eta_1\left(1 + \left(\frac{5}{2}\right)V_2\right)$$

where η_0 and η_1 are, respectively, the viscosity of liquid plus hard sphere mixture and the viscosity of the thin liquid and the volume fraction of the mixture occupied by the spheres V_2 is given by $V_2 = 1 - V_1$, where V_1 is the volume fraction of the mixture occupied by the thin liquid. In addition, we have fluidity due to the fact that the hard spheres are not hard. At low shear rates they will occupy the whole volume of the melt. To express these ideas we define as more or less appropriate representations, the fluidity due to the softness of the spheres ϕ_2 as $\phi_2 = a_2 e^{-b_2\dot{\gamma}}$ and $v_1 = f(1 - e^{-g\dot{\gamma}})$, where the factor f is about 0.1 because the volume fraction of the thin liquid is not expected to exceed 10% of the whole, and where a_2, b_2, f, and g are appropriate constants and $\dot{\gamma}$ is the shear rate.

The overall fluidity ϕ of the polymer melt is then that due to both types of fluidity. Using the mixture law, we have

$$\phi = V_1\phi_0 + V_2\phi_2$$

In the last equations, the reduced fluidity of the thin liquid, ϕ_0, is used rather than the fluidity of the thin liquid containing no sphere obstructions to its flow, ϕ_1. Furthermore, one would expect the fluidity, ϕ_1, of the thin liquid to be increasingly

large as the shear rate increases and more holes are forced into it. In consequence, we may set

$$\phi_1 = 1/\eta_1 = a_1 e^{b_1\dot{\gamma}}$$

Therefore, on combining these expressions, we find

$$\phi = [2V\phi_1 + (7 - 12V_1 + 5V^2)\phi_2]/7 - 5V_1$$

As $V_1 \sim 0.1$ as a maximum, we may drop the term, V_1^2, giving

$$\phi \cong [2V_1\phi_1 + (7 - 12V_1)\phi_2]/7 - 5V_1$$
$$\approx (2V_1\phi_1/7) + \phi_2$$
$$= {}^2/_7 f(1 - e^{-g\dot{\gamma}})a_1 e^{b_1\dot{\gamma}} + a_2 e^{-b_2\dot{\gamma}}$$

At very high shear rates ($\dot{\gamma} \to \infty$),

$$\phi_\infty = {}^2/_7 f\phi_1 \approx {}^2/_{70}\phi_1$$

or

$$\eta_{\dot{\gamma}=\infty} = 35\eta_1$$

At very low shear rates,

$$\phi_{\dot{\gamma}=0} = \phi_2$$

where ϕ_2 is the fluidity due to softness of polymer itself. Using such a picture, then, one would expect to see a polymer melt viscosity decreasing with increasing shear rate:

$$\eta_1 \leqq \eta \leqq 35\eta_1$$

and where η_1 is a low viscosity, representative of that of polymer of a very low degree of polymerization. It may be seen that the above equations and interpretation would serve to describe the observed behavior in general outline, and have, perhaps, a heuristic value, if not other.

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Synopsis

Studies were made of the apparent melt viscosity and chain rupture of polyisobutylene melts during high mechanical shear at various temperatures, and for varied times of shearing action. A biconical rheometer was constructed and used for this study. It was observed that the torque developed in such a rheometer by the action of shear on molten polymer shows peculiarities. The initial high torque, or the apparent melt viscosity which may be derived from it, drops rapidly to a pseudo steady state value in about one or two minutes. An interval of shear cessation permits considerable return of the system to the original high value of the apparent melt viscosity, especially if the cessation interval is long (e.g., 10 min. at 45°C.). During the pseudosteady-state period there is a small and continuous drop in the already reduced torque or the apparent melt viscosity. Study of the chain rupture rate, made by examination of dilute solution viscosities, and the viscosity-average molecular weights determined from them, showed the rate of chain degradation to decrease as the temperature during the shearing operation is raised. The chain rupture rate decreases steadily as shearing is continued, and increases with increase of shear rate at a given temperature and time of shear application. The behavior of the apparent melt viscosity, decreasing sharply to a pseudosteady-state value shortly after intense shear begins, is presently pictured as due to two mechanisms, one chemical, the other mechanical, acting simultaneously. One process is considered to be the rapid breakdown of the chainlike molecules to smaller fragments forming mainly free radicals or ion pairs at their ends. These reactive ends begin immediately to recombine at a rate which increases with the rise in their concentration until the pseudoequilibrium state is reached. The second process is considered to arise from both chain disentanglement and the preferential migration of holes in the liquid away from the center of gravity of the chains to form regions of low viscosity which may be termed fault lines or regions.

Résumé

On a étudié la viscosité apparente à l'état fondu et la rupture de chaîne de polyisobutylènes fondus au cours de fortes tractions mécaniques à différentes températures et pour des temps variables de traction. On a construit un rhéomètre biconique en vue de cette étude. On a observé que la torsion développée dans un tel rhéomètre par l'action de la traction sur des polymères fondus offrait des particularités. La forte torsion initiale ou la viscosité apparente qui peut en être dérivée tombe rapidement jusqu'à une valeur d'état pseudo-stationnaire en une ou deux minutes. Un temps d'arrêt de traction permet un retour considérable du système en arrière jusqu'à la valeur initiale élevée de la viscosité apparente a l'état fondu spécialement si le temps d'arrêt est long, par exemple de dix minutes à 45°C. Durant la période d'état pseudo-stationnaire il y a une diminution petite et continue de la torsion déjà réduite ou de la viscosité apparente à l'état fondu. L'étude de la vitesse de rupture de chaîne effectuée au dépens des viscosités de solutions diluées et les poids moléculaires moyens viscosimétriques déterminés par leur intermédiaire ont montré que la vitess⹁ de dégradation de chaîne diminue quand la température s'élève au cours de l'opération de traction. La vitesse de rupture de chaîne diminue uniformément quand on continue la traction, et elle augmente pour une augmentation de la vitesse de traction à une température donnée et le temps d'application de la traction. Le comportement de la viscosité apparente à l'état fondu décroissant fortement jusqu'à une valeur d'un état pseudo-stationnaire peu après l'application d'une force de traction élevée, est actuellement représentée comme résultant de deux mécanismes, l'un chimique, l'autre mécanique agissant simultanément. L'un des processus consiste dans la rapide desagrégation des chaînes moléculaires en petits fragments formant principalement des radicaux libres ou des paires d'ions à leurs extrémités; les extrémités réactionnelles commencent immédiatement à se recombiner à une vitesse augmentant avec l'élévation de leur concentration, jusqu'à ce que l'état de pseudo-équilibre soit atteint. Le deuxième processus résulte à la fois du déroulement des chaînes et de la migration préférentielle des lacunes dans le liquide loin des centres de gravité des chaînes.

Zusammenfassung

Eine Untersuchung der scheinbaren Schmelzviskosität und Kettenspaltung von Polyisobutylenschmelzen während einer hohen Scherbeanspruchung wurde bei verscheidenen Temperaturen und bei variierter Dauer der Schereinwirkung durchgeführt. Ein bikonisches Rheometer wurde konstruiert und in dieser Arbeit verwendet. Es wurde beobachtet, dass der in einem solchen Rheometer durch die Einwirkung der Scherung aufgeschmolzenes Polymeres entwickelte Drehungswiderstand Besonderheiten zeigt. Der hohe Anfangswiderstand oder die daraus abgeleitete scheinbare Schmelzviskosität fällt rasch in etwa ein oder zwei Minuten, auf einen pseudo-stationären Wert ab. Ein scherungsloses, Intervall führt in dem System zu einer beträchtlichen Rückbildung des ursprünglichen hohen Wertes der scheinbaren Schmelzviskosität, besonders wenn das Unterbrechungsintervall lang (z.B. 10 Min. bei 45°C) ist. Während der pseudo-stationären Periode findet eine kleine und kontinuierliche Abnahme des schin schon herabgestzten Widerstands oder der scheinbaren Schmelzviskosität statt. Eine Untersuchung der Kettenspaltungsgeschwindigkeit durch Messung der Viskosität in verdünnter Lösung und des daraus bestimmten Viskositätsmittelswerts des Molekulargewichts zeigte, dass die Geschwindigkeit des Kettenabbaus mit einer Temperaturerhöhung während der Scherbeanspruchung abnimmt. Die Kettenspaltungsgeschwindigkeit nimmt bei fortgesetzter Scherung stetig ab und bei Zunahme der Scherungsgeschwindigkeit bei einer bestimmten Temperatur und Dauer der Scherbeanspruchung zu. Das Verhalten der scheinbaren Schmelzviskosität, nämlich die scharfe Abnahme zu einem pseudo-stationären Wert kurz nach Beginn einer intensiven Scherung, wird hier auf zwei Mechanismen zurückgeführt, einen chemischen und einen mechanischen, die gleichzeitig wirksam sind. Als der eine Prozess wird die rasche Bildung von kleineren Bruchstücken aus den Kettenmolekeln angenommen, bei welcher hauptsächlich freie Radikale oder Ionenpaare an den Enden der Bruchstücke entstehen. Diese reaktionsfähigen Enden beginnen untmittelbar mit einer Geschwindigkeit, die mit ihrem Konzentrationsanstieg zunimmt, zu rekombinieren, bis der Pseudo-Gleichgewichtszustand erreicht wird. Ein zweiter Prozess wird offenbar sowohl durch eine Entschlingung der Ketten als auch durch die bevorzugte Wanderung von Löchern in der Flüssigkeit weg vom Kettenschwerpunkt verursacht, wodurch Bereiche mit niedriger Viskosität entstehen, die als Fehllinien oder-bereiche beziechnet werden können.