

The Degradation of Polystyrene During Extrusion

KUNIO ARISAWA* and ROGER S. PORTER, *Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01002*

Synopsis

An investigation was made of the magnitude and mechanism of shear degradation of a narrow distribution, high molecular weight ($M_w = 670,000$) polystyrene. An Instron rheometer was used to perform the extrusion at temperatures from 164° to 250°C. The change in molecular weight distribution was studied by gel permeation chromatography. The maximum shear stress employed was 5.83 kg/cm². It was found that degradation could be induced at high stress at temperatures of 50°C lower than degradation of polystyrene would occur exclusively due to thermal forces. An activation energy for the degradation, calculated at constant shear rate, was +20.2 kcal/mole. The direction and magnitude of this value are consistent with degradation induced through a mechanical reduced activation for thermal degradation.

INTRODUCTION

In the field of polymer processing we commonly encounter the problem of how to estimate processing characteristics of polymer on the basis of acceptance tests of raw materials. Such tests include melt index, tensile strength, density, and ultimate elongation. The most important problem is evaluation of recoverable elasticity of molten plastics as it is manifested by extrusion. The elasticity is known to be related to the higher molecular weight moments in the form $\overline{M}_z\overline{M}_{z+1}/\overline{M}_w$.^{1,2} The molecular weight distribution (MWD) of molten polymer is therefore crucial in polymer processing. Moreover, there can be the practical requirement of recycling used plastics for economy with the inherent difficulties of predicting the extrusion performance of the recycled material, the original material, and their blends. It is obvious that consideration of MWD and its changes with extrusion can determine extrusion and elastic recovery characteristics of polymers.

From this perspective, we have investigated polymer degradation caused by a model extrusion process. For the purpose of simulating processing conditions an Instron capillary rheometer has been used to perform the tests of shear extrusion. MWD of the original and processed polymers were determined by gel permeation chromatography (GPC).

There have been several previous works in this general area of shear degradation of polymer systems. Bestul^{3,4} has shown that huge amounts

* Present address: The Furukawa Electric Company, 6-1 Nishihiranumacho, Nishiku, Yokohama, Japan.

of mechanical energy are required to break a carbon-carbon backbone (300,000 kcal/mole), because most of the energy is dissipated as internal frictional heat rather than bond breaking. He used solutions of polyisobutene and polystyrene. Molecular weight changes were measured by intrinsic viscosity.

Schott and Kaghan^{5,6} studied extensively the degradation of polyolefins using a commercial extruder. These authors recycled the extrudate and measured the change of melt index as a function of number of pass times and extrusion temperature and suggested that degradation due to shear occurred in addition to thermal degradation.

Formerly we have established the reduced variable treatment for shear degradation in laminar flow which is expressed as a function of shear stress or shear rate, temperature, and concentration.⁷ The change of equilibrium shear-degraded molecular weight has been well described by reduced variables only for the case of polyisobutene solutions sheared in a rotational viscometer. The molecular weight was estimated from viscosity measurements made in the same instrument in which the shear degradation tests were made.

Previously we have also shown the change of MWD by recovering the sheared solution of polyisobutene and found that the minimum molecular weight produced by shear degradation is close to the entanglement molecular weight of this system^{8,9} and that the minimum stress required to cause shear degradation at each temperature increases as the temperature is increased.

Apart from degradation during processing, several other studies have been reported concerning the MWD change due to degradation of polystyrene. Hendrickson¹⁰ has measured the rate of degradation of polystyrene caused by radiation, weathering, and peroxide. Recently, Smith¹¹ has studied the degradation of polystyrene due to ultrasonic waves. He has indicated that molecules are broken nearly at the center of the original molecule.

The purpose of our research series lies in understanding the mechanism of degradation under processing conditions and to see how entanglements may enter into the mechanism. As first approximations, one might expect that the polymer molecule in a high shear field might be broken owing to concentrated mechanical energy near the middle of the long molecules, at the locations of entanglement coupling, or midway between two adjacent entanglements. Which of these mechanisms is preferential may depend on the time scale of shear deformation, on temperature, on the probability for entanglement slippage, and on the strength of backbone chain. Bueche¹² has theoretically evaluated the mechanism of mechanical scission at the center of long molecules. Experimental confirmations, however, have not been general. In certain tests, Porter et al.⁸ found a minor peak near the region of entanglement molecular weight in the shear degradation of polyisobutene solutions. More confirmation is necessary, however, concerning the role of entanglements in shear degradation.

The previous work can be classified generally into two types; (1) experiments at low temperature using solutions and (2) experiments at high temperature using polymer melts. In high temperature experiments, degradation appears to be not due exclusively to shear. In the present work, an attempt is made to distinguish the mechanisms and their magnitudes in the high temperature shear degradation of polystyrene.

EXPERIMENTAL

The test sample was a widely available polystyrene standard (Pressure Chemical Company, Pittsburgh, Pennsylvania). The sample has a molecular weight (\bar{M}_w) of 670,000 and a MWD (\bar{M}_w/\bar{M}_n) of 1.15. Polystyrene was selected because it is known^{13,14} not to degrade thermally significantly at temperatures below 265°C. The choice of a narrow distribution polymer simplifies the analysis of MWD changes with degradation.

The test sample was degraded by shear through tungsten carbide capillaries of an Instron rheometer. The shear rate was controlled by the crosshead speed of the Instron while pressure was measured continuously with a load cell connected to the plunger of the rheometer. The dimensions of the capillaries used are shown in Table I.

Die A was used throughout unless otherwise stated. Die B was used in tests at lower temperatures because of a limitation of force applied to the plunger, which should not exceed 1400 kg/cm². Temperature was regulated by a proportional control device and can be measured at four different portions of the barrel. The variation of temperature along the barrel was within 1°C. The highest shear rate was 4750/sec, corresponding to the highest speed of the crosshead speed available, 5 cm/min. All reported shear rates are those calculated from volumetric flow and capillary geometry for values at the wall.

The test sample was placed in the capillary reservoir as rapidly as possible to reduce undesirable thermal degradation. Preformed and compacted samples were used to reduce inclusion of air voids. The sample introduction was usually completed within 20 min; the sample was then held for 3 min for thermal equilibrium before extrusion. It took approximately 4–5 min to run one extrusion.

The operating temperatures for the Instron rheometer were 164°, 184°, 204°, 224°, and 250°C. In the case of the run at 164°C, capillary die B

TABLE I
Tungsten Carbide Capillaries Used in
Shear Degradation Studies on Polystyrene

Die	Inlet angle ^a	Inner Diameter, in.	Length, in.	L/D
A	90°	0.020	1.0065	50.2
B	90°	0.030	2.0000	66.7

^a Different results may possibly be obtained for other entrance geometries.

was used and the shear rate was reduced to 140/sec because of the high stress. The recycling of extrudate was done repeatedly until sample amounts were less than needed for standard extrusion conditions.

The cold extruded sample was chopped into pellet form and again placed in the capillary barrel to carry out the next cycle. It took much less time, about 3 min, to feed the chopped sample into the barrel. A portion of the shear-degraded sample, approximately 0.05 g, was saved after every extrusion. This sample was dissolved in tetrahydrofuran (THF) for the MWD determination by GPC. The concentration was adjusted to 0.23–0.27 wt-%. The GPC of Waters Associates, Framingham, Massachusetts, Model 200, was used for evaluation of the change in MWD due to degradation. The GPC arrangement was a series of 4-ft columns with pore sizes of 10^6 , 10^5 , 10^4 , and 3×10^3 Å. The operating temperature was $25.0 \pm 0.5^\circ\text{C}$, the solvent was THF, and the flow rate was adjusted to 0.8–0.9 ml/min. The number of plate counts per foot was calculated from the elution curves of *o*-dichlorobenzene to be 600–700, corresponding to a total column plate count of 9,600–11,200.

In the course of repetitive extrusion, a control sample was also often taken from the residual sample in the barrel after extrusion. These samples were exposed to a less high shear field than the extruded sample, but were exposed to the heat for the equivalent time period. The MWD of these control samples was also measured by GPC.

Preliminary thermal degradation tests were performed using a Forma vacuum oven. The polystyrene powder sample was placed in a flask and was held for prescribed times in the oven under several conditions. The sample was heated under vacuum at a reduced pressure of 30 in. Hg referred to atmospheric pressure, in air and in nitrogen gas. The variation of temperature during the holding period was $\pm 5^\circ\text{C}$. These samples were also checked for changes in MWD by GPC.

GPC Correction

There have been several studies concerning the axial peak spreading not due to MWD.^{15–17} There is still considerable argument as to how to correct for this peak spreading. We have applied the solution of Tung's dispersion equation¹⁵ given by Pierce and Armonas.¹⁶ The procedure was as follows: The width of the curve was measured, which is defined as the width at the baseline of the curve between two tangents drawn on the points of inflection of the GPC curve and extended to the baseline. This calculation has been made for elution curves of several standard, narrow MWD samples of polystyrene.

If we assume that the shape of the GPC curve for narrow MWD polystyrene is Gaussian, we can calculate Tung's parameter h as follows:

$$h = 8/W^2 \quad (1)$$

The width W in count (5 ml) for each standard sample is shown in Table II. As shown in the last column of the table, the ratio of $W/(\bar{M}_w/\bar{M}_n)$ changes

TABLE II
Narrow Distribution Polystyrenes

M_w	M_w/M_n	W	$W/(M_w/M_n)$
1,800,000	1.20	4.61	3.84
860,000	1.15	3.19	2.78
670,000	1.15	3.17	2.76
411,000	1.06	2.85	2.69
160,000	1.06	2.85	2.69
20,400	1.06	2.34	2.21

little over the M_w range of interest. The near constancy of the ratio has been pointed out by Bly.¹⁷ We can therefore apply the Pierce correction equation¹⁶

$$W(v) = [h/(h - c)]^{1/2} F(v) \exp \{ -b^2/4(h - c) \}$$

where $W(v)$ is the corrected GPC curve and $F(v)$ is the original curve. Also

$$b = -(\partial \ln F / \partial v)$$

and

$$c = -1/2(\partial^2 \ln F / \partial v^2)$$

as far as the molecular weight range mentioned above is concerned. Moreover, we can expect from the data in Table II that the correction may at least be validly applied to the \bar{M}_w range from 10^2 – 10^5 . Recall that the original sample for this study has an \bar{M}_w of 670,000.

For broader MWD, the spreading correction becomes less important. Therefore if the degraded sample has some portion of its molecular weight under 10^5 , the MWD will be wider than the original MWD, and the value of the correction parameter becomes less crucial. Tung¹⁵ has shown that the correction becomes less important in the case of broad molecular weight distribution compared with the case of narrow molecular weight distribution.

The elution peak width, W , for the original sample ($\bar{M}_w = 670,000$) was used to determine Tung's parameter, which gave an h value of 0.796. The correction was accomplished by dividing the GPC curve by units of 0.25 count from 24.25 counts to 36.00 counts. The total number of divisions was 48. After each correction, the peak area, considered to be the sum of corrected peak heights, was normalized to 1. Moreover, the correction was checked by substituting the corrected value into the original value through Tung's integral. The standard deviation between the substituted value and the original was acceptably small. For example, the ratio of standard deviation to maximum value in the curve was 3.53% in the case of a narrow MWD sample ($\bar{M}_w/\bar{M}_n = 1.16$) and in the case of broad MWD ($\bar{M}_w/\bar{M}_n = 4.80$) the ratio was 2.36%.

For calculation of MWDs after correction, we used the Yau and Fleming method,¹⁸ which takes the curvature of the calibration curve into consider-

ation. All the information required for one GPC curve was calculated by a computer to provide the \bar{M}_n , \bar{M}_w , MWD, and also the check of peak correction.

RESULTS

Preliminary tests for thermal degradation of polystyrene were performed in a vacuum oven at various temperatures. The tests were designed to distinguish thermal degradation from subsequently measured molecular

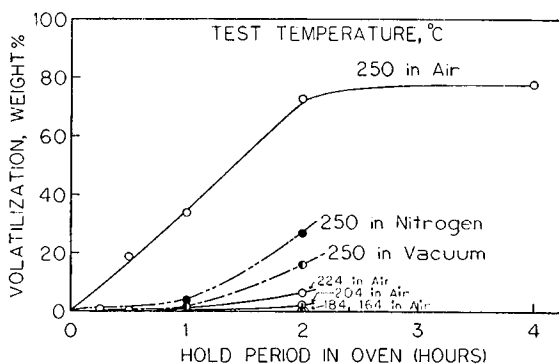


Fig. 1. Volatilization of polystyrene at different heating conditions.

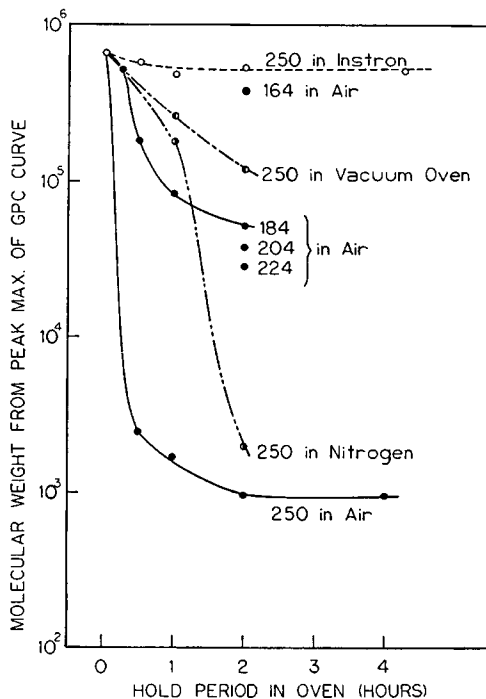


Fig. 2. Molecular weight changes for polystyrene at different heating conditions.

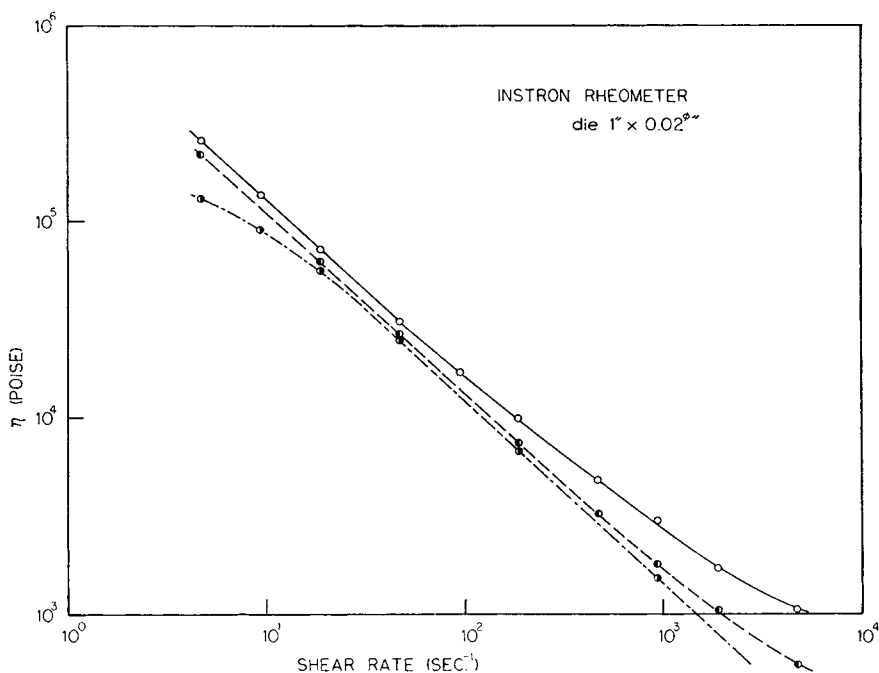


Fig. 3. Relationship between apparent viscosity and shear rate for polystyrene sample: (O) 184°C; (◐) 204°C; (●) 224°C.

weight changes due to shear. Figure 1 shows the per cent of sample volatilization as a function of the heating time at selected temperatures and conditions. Figure 2 indicates the corresponding change of molecular weight, as measured by GPC, for the same heating conditions used in Figure 1.

As can be seen easily from Figures 1 and 2, the thermal degradation of the polystyrene sample in air proceeds markedly faster than under vacuum. In air, molecular weight changes appreciably only when the temperature exceeds 180°C. Under vacuum, the degradation is approximately ten times slower. The case where the air is replaced by nitrogen gas lies between these two conditions. This suggests that oxygen can play a major role in polystyrene degradation in the temperature range over 180°C. These differences in thermal degradation due to conditions could be explained by a mechanism of thermo-oxidative degradation¹³ of polystyrene.

However, the situation in the Instron rheometer, where the shear degradation studies were made, can be much different from that in the oven. In Figure 2, the dotted line indicates the change of molecular weight of the sample which was held in the Instron barrel for a maximum of 4.25 hr at 250°C. Significantly, no marked change of molecular weight was observed comparable to that in the oven. To be sure, air and thus oxygen are available to the test sample in the barrel of the Instron capillary rhe-

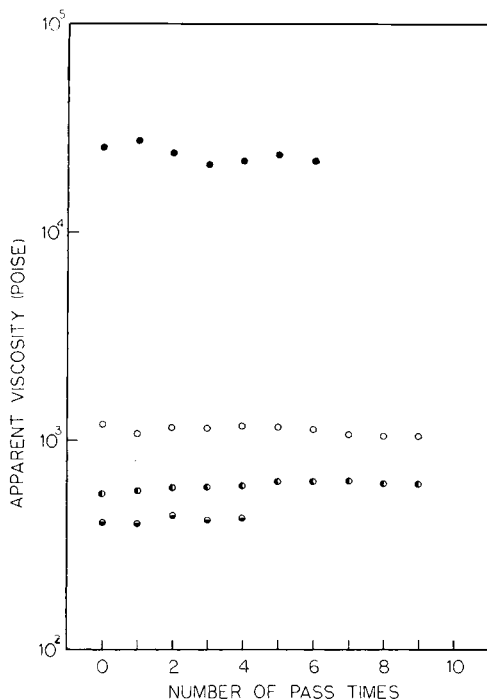


Fig. 4. Apparent viscosity change as a function of past time: (●) 164°C at 140/sec; (○) 184°C at 4750/sec; (●) 205°C at 4750/sec; (○) 224°C at 4750/sec.

ometer. In the barrel, however, the surface area of the sample that is in contact with air is likely to be much smaller than that in the oven. Therefore, only a small and measurable amount of degradation occurs in the Instron rheometer due to combined thermal and oxidative effects in the absence of shear at temperatures of 200°C and lower and over the time spans for shear degradation experiments. One can even say that the Instron rheometer is a convenient instrument to suppress oxidative degradation.

Figure 3 shows the apparent viscosity versus shear rate for the polystyrene sample measured with the Instron rheometer at several temperatures. The apparent viscosity shows a sharp decrease as the shear rate increases. At 184°C, one can see the appearance of a flat portion at the highest shear rate. This is due to a pressure effect.^{18a} One can also notice the approach to the low-shear limiting viscosity at the highest temperature, 224°C. The data in Figure 3 are for reversible viscosity changes due to shear. The shear degradation experiments were usually performed at the highest shear rate available, that is, 4750/sec.

Figure 4 shows the change of the apparent viscosity as a function of the number of passes through the Instron capillary. The apparent viscosity measured at high shear does not vary appreciably with the number of capillary passes. This is because apparent viscosity is insensitive to the

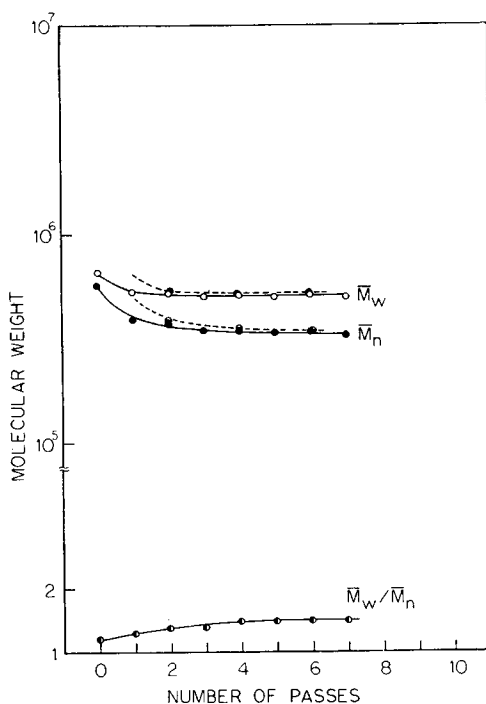


Fig. 5. Changes in polystyrene molecular weight with number of capillary passes, 164°C and 140/sec.

molecular weight at high shear rates. The phenomenon is general and has been cited by Katoaka and Ueda¹⁹ and has also been suggested by the study of molecular weight distribution by Poller and Kotliar.²⁰ Thus capillary pressure drop cannot be used to measure degradation.

A calibration curve for GPC was obtained by using narrow MWD polystyrenes, molecular weight 2000 to 1.8×10^6 . A minor change of flow rate causes a slight shift of calibration curve along the elution volume axis. To eliminate this effect, the original sample of M_w 670,000 was injected as a control in each GPC run, and the minor shift of the peak position of the control sample was used as the correction factor for flow rate variation.

Figures 5 to 9 show the weight-average molecular weight (\bar{M}_w) and the number average molecular weight (\bar{M}_n) and \bar{M}_w/\bar{M}_n as a function of number of passes through the capillary at each test temperature. A regular decrease in \bar{M}_w and \bar{M}_n and an increase in \bar{M}_w/\bar{M}_n is observed. Initially, \bar{M}_n decreases rapidly with a similar and lesser trend in \bar{M}_w . This leads in some cases to a pseudoequilibrium value of \bar{M}_w/\bar{M}_n as a function of capillary passes.

Figures 10 to 12 show the change in MWD as a function of number of capillary passes. The general behavior of MWD dependence on temperature and shear is as follows: At first, the peak shows a general spreading to lower molecular weight, producing a straight portion in the lower tail of

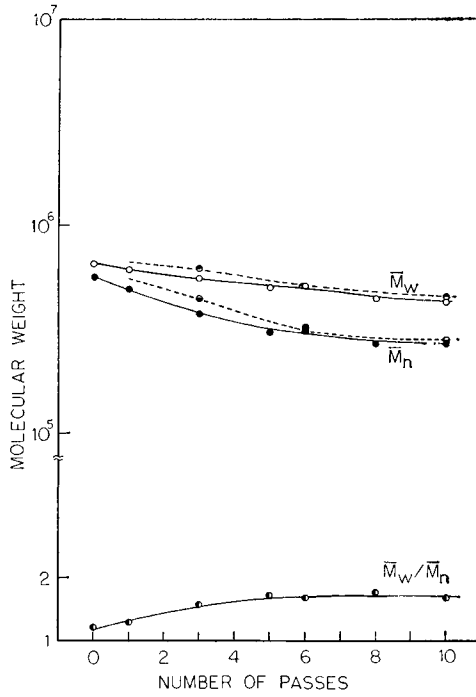


Fig. 6. Changes in polystyrene molecular weight with number of capillary passes, 184°C and 4750/sec.

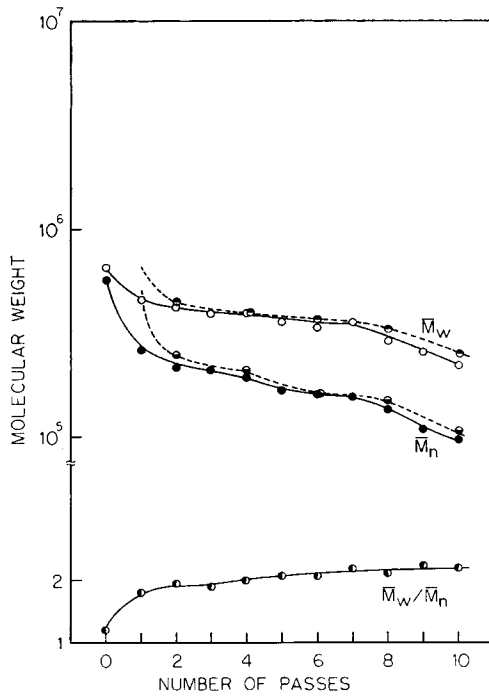


Fig. 7. Changes in polystyrene molecular weight with number of capillary passes, 204°C and 4750/sec.

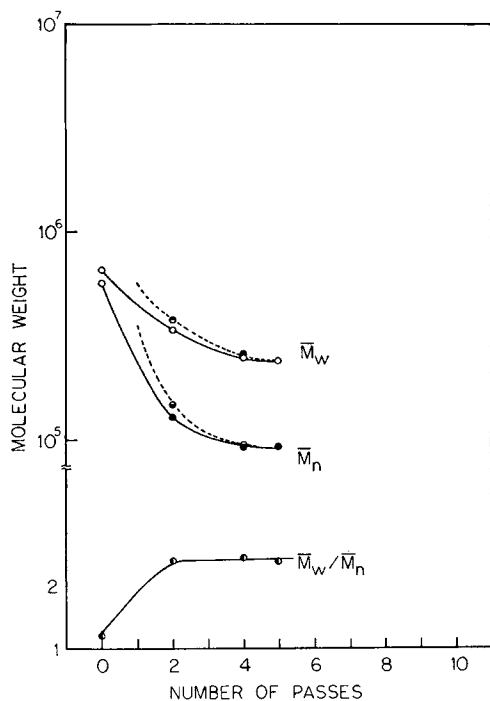


Fig. 8. Changes in polystyrene molecular weight with number of capillary passes, 224°C and 4750/sec.

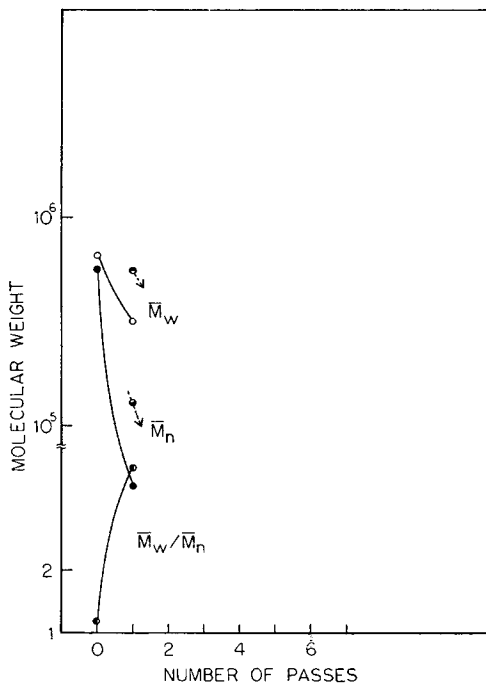


Fig. 9. Changes in polystyrene molecular weight with number of capillary passes, 250°C and 4750/sec.

MWD distribution, which leads to skewness. The second stage is characterized by a rapid change in the peak position with number of passes toward a lower \bar{M}_w and a decrease of skewness. As test temperature is increased, the second stage appears earlier.

In Figures 5 to 9, the \bar{M}_w and \bar{M}_n of the control sample is plotted by the dotted line. This sample was passed through the capillary ($n - 1$) times but was not extruded at n th trial, remaining in the barrel for GPC sampling. These control samples seem to have received the same thermal history as n -times extruded sample, yet were passed through the capillary only ($n - 1$) times. The difference between the two trials, therefore, can be attributed to the amounts of (shear degradation) at the n th trial.

DISCUSSION AND CONCLUSION

The change of MWD with number of pass times, shown in Figures 10 to 12, indicates the possibility of a minor degradation peak near an \bar{M}_w of 150,000. This minor peak seems to shift toward lower molecular weight as test temperature increases. It should be emphasized, however, that there is still uncertainty about this possible minor peak which only appears as a result of correction to the GPC curve.²¹ Apart from the minor peak, there are certain definite trends. The main peak position of the GPC curve moves gradually to lower molecular weight in the early stages of degradation. Subsequently it moves faster with the number of passes. This behavior is also recognized in the uncorrected GPC curve. The corrected and uncorrected curves also regain a symmetric bell-shaped form during the second stage of degradation.

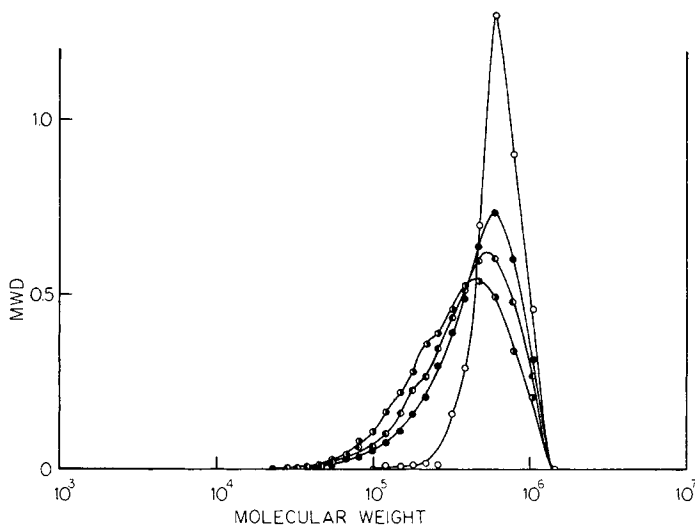


Fig. 10. Change of MWD of polystyrene at 184°C; (O) original sample; (●) after 3 passes; (⊙) after 6 passes; (⊚) after 10 passes.

One can notice both processes, the change of peak position movement and the skewness change, most clearly in Figure 11 at 204°C, corresponding to these two-step changes of MWD. There appears to be some pseudoequilibrium zone in \bar{M}_w and \bar{M}_n as shown in Figure 9, which becomes more definite at the lower test temperatures (see Fig. 8 for data at 184°C).

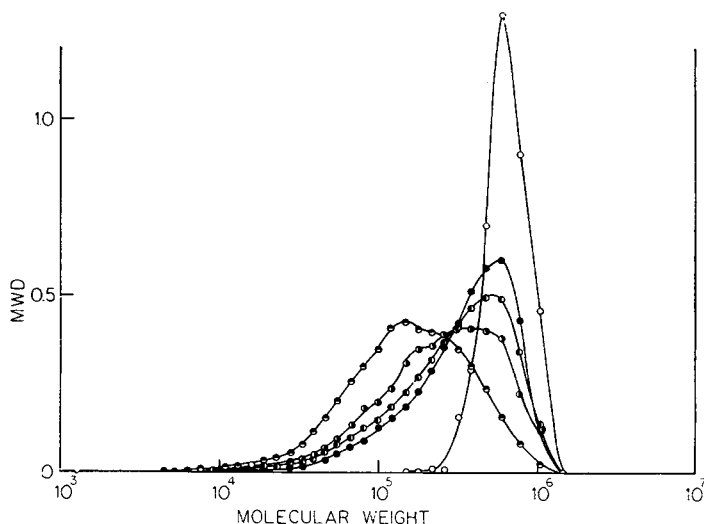


Fig. 11. Change of MWD of polystyrene at 204°C: (O) original sample; (●) after 2 passes; (⊙) after 4 passes; (⊕) after 10 passes.

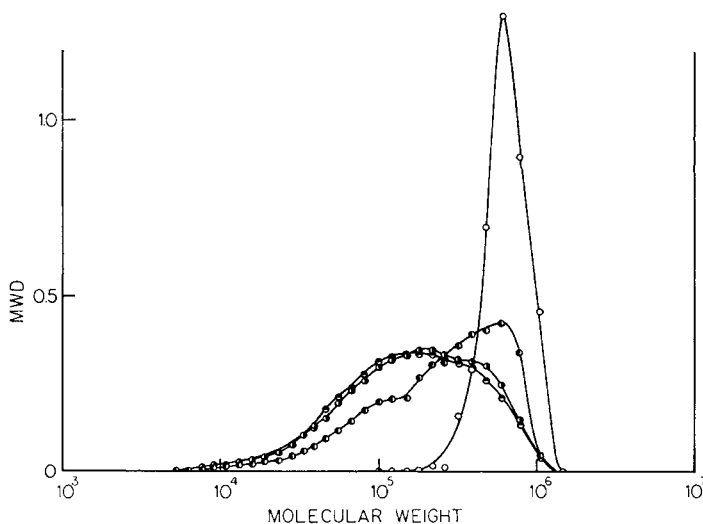


Fig. 12. Change of MWD of polystyrene at 224°C: (O) original sample; (●) after 2 passes; (⊙) after 4 passes; (⊕) after 5 passes.

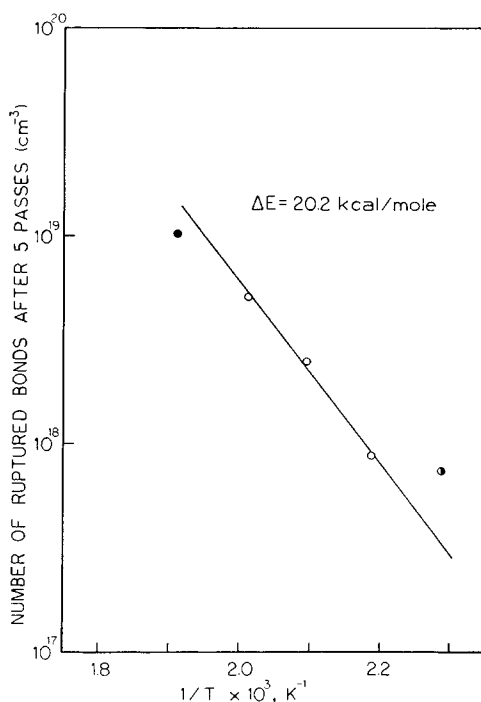


Fig. 13. Relationship between number of ruptured bonds and temperature after 5 passes (●) 1 pass at 4750/sec; (○) 5 passes at 4750/sec; (◐) 5 passes at 140/sec.

The number of ruptured bonds per unit volume was calculated by the following equation:

$$\text{bonds, no./cm}^3 = Na \times \text{density} \times [(1/\bar{M}_n) - (1/\bar{M}_n)_0] \quad (2)$$

where Na is the Avogadro number and \bar{M}_n is the number-average molecular weight of the original sample. The number of ruptured bonds after five extrusion passes is plotted as a function of reciprocal absolute temperature in Figure 13. Also shown are the data after one pass, samples at 250°C, and the data of five passes at 164°C, in which shear rate is much lower, 140/sec compared with 4750/sec. Considering that the 164°C value will decrease if it were measured at the same shear rate of 4750/sec and the number of ruptured bonds at 250°C would increase when five extrusion passes were done, the relationship can be well expressed by a single straight line determined by the middle three points obtained under the same shear conditions. The activation energy calculated from the slope is 20.2 kcal/mole. It is possible, and may even be more desirable, to calculate the activation energy at constant shear stress rather than at constant shear rate. This is impossible, however, with the data available.

One can calculate the mechanical energy required to cut a mole of bonds at each test temperature because the pressure exerted by the Instron rheometer is simply the mechanical energy applied per unit volume of extrudate

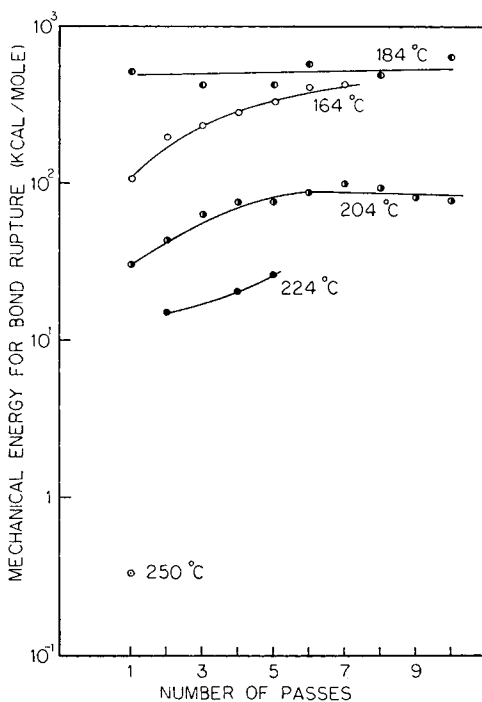


Fig. 14. Efficiency of polystyrene bond rupture by capillary shear.

during the capillary pass. Figure 14 shows the relationship between the mechanical energy required to break a mole of C-C bonds and the number of capillary passes at each test temperature. One can notice that the energy at 164°C is less than at 184°C in spite of the fact that the shear stress at 164°C is smaller than at 184°C. This would mean that the mechanical energy is more effective at 164°C. Bateman²² has suggested that in mechanical and thermal degradation of rubber, there exists the least effective temperature above which the thermal reaction prevails and below which the mechanical degradation governs the chemistry. In the case of polystyrene, the minimum effective temperature may lie in the neighborhood of 180°C.

Simha²³ has studied theoretically the change of the MWD due to scission which may be a model for random thermal degradation. The same result is also obtained through probability considerations by Coyne.²⁴ Figure 15 is a plot of the theoretical curve for change of \bar{M}_w and \bar{M}_n for the case of an original monodisperse sample. The ordinate is so adjusted that the original \bar{M}_w is 670,000 and the abscissa is an arbitrary unit of time.

There is some difference in MWD change between the theoretical monodisperse sample and the experimental results of narrow MWD sample. As for \bar{M}_n change, the monodisperse sample can reflect the behavior of the narrow MWD sample. One can recognize in Figure 15 that there is no

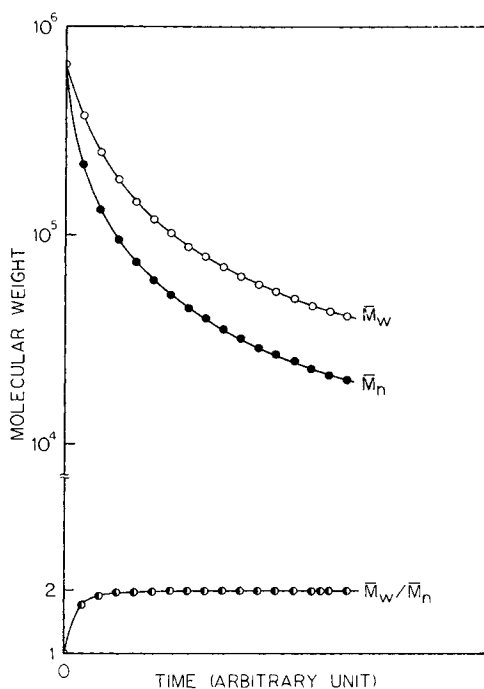


Fig. 15. Change of \bar{M}_w , \bar{M}_n , and \bar{M}_w/\bar{M}_n according to Simha.²³

flat zone of \bar{M}_n and the rate of degradation decreases during the course of degradation. This theoretically derived behavior of random scission may be compared with our results as shown, for instance, in Figure 9. Our results distinctly differ. This may be due to an initial random process which is followed in part by a radical attack of one chain on another, rather than a simple disproportionation. This can produce a broad MWD.

We have shown that there was little change in molecular weight in the case of purely thermal conditions in the Instron barrel. These are shown in the dotted line of Figure 2 and in the control sample in Figures 5 to 9. These portions of degradation are significantly different from purely thermal degradation, whereas the activation energy has a plus sign as shown in Figure 13.

One possible explanation is as follows: The shear mechanical energy, which is dissipated mainly as thermal energy, works in combination with random and oriented motions to cause the degradation. The purely thermal degradation prevails in the latter stages (see the figures) which is characterized by the faster movement of the peak position and the recovery of symmetric MWD shape. A true equilibrium portion is required by degradation exclusively due to shear, which appears to be the case for results at the lowest test temperature, 164°C. The nature of degradation is basically thermal, with a distinct reduction in temperature needed for reaction being provided by the mechanical energy stored by shear within

the polymer chains. This corresponds to a shear-induced change in the potential energy function for thermal bond rupture.²⁵

In Figure 14, one can notice that the mechanical energy is much higher at 164°C and at 184°C than C-C backbone energy of ca. 80 kcal/mole. This may mean the inefficiency of mechanical energy, but as the temperature increases, the efficiency increases due to the fact that thermal energy becomes more and more effective and dominant in the degradation process. Importantly, these results on polystyrene indicate that a static thermal stability test of plastic material to anticipate thermal stability during processing, which is the usual evaluation, can be misleading and that a dynamic test, including shear-induced thermal degradation, would be necessary to predict the precise features of processing. The results also indicate that the Barus effect, viz, extrudate expansion, may likely be significantly influenced by degradation because of the dependence of swell on the high moments of molecular weight.

Potentially significant variables yet to be fully investigated include the effect of entrance region geometry and shear intensity. Studies should also be made of polymer oxidation at the capillary exit. Variations in degradation with capillary length and axial position also require evaluation.

We would like to express gratitude to Dr. Tung of Dow Chemical Company and members of the Polymer Science and Engineering Program at the University of Massachusetts for their help with these studies.

We also wish to express our appreciation for the support of this study by the U.S. Army Research Office, Durham.

This paper is Part VII of a series of publications on Mechanochemistry of Polymers.

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Received September 3, 1969

Revised November 12, 1969