The Source of Degradation During Extrusion of Polystyrene

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Synopsis

The nature and magnitude of mechanical reactions of polystyrene in capillary flow has been examined in a model extrusion process. Studies on polystyrene quantify the sensitive increase in shear degradation tendency with increasing polymer molecular weight. A molecular weight spectrum caused by the shear stress profile was measured across the extrudate radius by the new technique of solvent coring. It was further determined that an appreciable fraction of the mechanical reaction is shear induced in the capillary reservoir. This is confirmed by precision determinations of molecular weights and distributions by gel permeation chromatography on samples taken from concentric layers in the capillary reservoir after 50% sample extrusion. These results, involving traces of oxygen as a chemical probe, describe the stress profile in the reservoir and in the capillary during the pressure extrusion of high molecular weight polystyrene. Thus, changes in molecular weight and distribution may be attributable to changes in different portions of the shear geometry rather than the uniform changes generally considered. Clear evidence is also presented showing the dramatic effects of oxygen on these shear-induced changes in molecular weight and distribution.

INTRODUCTION

Disturbances in the flow profiles of polymer melts have been widely reported. Flow irregularities have been found in melt extruders and in laboratory capillary rheometers. These disturbances have been classified by region of their occurrence such as in the capillary reservoir, the capillary entrance, within the capillary, and at the capillary exit—involving extrudate expansion and melt fracture.

Several approaches have been used to examine flow patterns in polymer melts in capillary rheometers. Cook et al.[1] loaded the reservoir with layers of differently colored polyethylene and acrylonitrile–butadiene–styrene polymers. After partial extrusion, a flow diagram was constructed by measuring the colored layers remaining in the reservoir. They reported evidence of backflow near the wall and flow contours much more pointed than the parabola expected for Newtonian flow. Others have used glass capillaries and tracer particles in extruded polymer systems. These pro-

files have been followed microscopically. For example, Bartos and Holomik[2] used a movie camera to record the movement of aluminum tracer particles as a means of examining the flow profile in capillary flow of viscoelastic materials.

In this paper, direct evidence is provided concerning the polymer flow pattern within the reservoir and the capillary of a pressure viscometer. This is the first such study, although the flow through tubes is a principal way of processing polymers. Moreover, degradation is common in such processes with one of the first demonstrations of capillary flow degradation of polymers (again on polystyrene) having been provided by Staudinger.[12] The extrusion tests were made using an Instron capillary rheometer. The polymer molecules themselves—through reaction with traces of oxygen—are used as a sensitive measure of profiles at high stress in this model extrusion process. This was possible by developing precise molecular weight measurements for samples from regions throughout the viscometer, i.e., reservoir, capillary, and entrace sections. The mechanically induced changes in molecular weight were monitored by calibrated gel permeation chromatography from samples obtained by mechanical sectioning and by the new technique of solvent coring.[3]

The polymer remaining in the capillary reservoir was also examined as a function of extrusion temperature. The polymer was removed from the viscometer as a solid plug and sectioned, and GPC measurements were made on each section. Positions of high shear stress were assigned to regions of high polymer degradation (i.e., decreased $\bar{M}_w$).

From previous studies on polystyrene, degradation is known to occur as a result of the high shear stresses in polymer melt flow.[4,5] The extent of this degradation is determined primarily by the applied shear stress, temperature, initial polymer molecular weight, and the presence of oxygen. Several high molecular weight polystyrenes with defined distributions were used for this study. The degradation effects increase sensitively with molecular weight. The reaction is caused by the extending forces on a network of entwined polymer chains with the activation energy reduced by oxygen and by heat at the highest temperatures. The mechanical forces which induce bond cleavage presumably lead to radical separation and thus degradation.

EXPERIMENTAL

Experiments were conducted using a conventional Instron capillary rheometer, Model TT-BM (Instron Equipment Corporation, Canton, Massachusetts) with a standard 0.375-in. diameter reservoir barrel. Shear rate was controlled by the selection of cross-head speed for the viscometer plunger. The resulting shear stress was recorded continuously with a load cell connected directly to the plunger. Selection of cross-head speed assures a constant and known average polymer flow rate after a brief induction period of a few seconds. The capillary itself consisted of a tungsten carbide orifice, 2.00 in. in length, with an L/D of 66.7. A long capillary

was selected so that most of the pressure drop would take place in the capillary. The capillary entrance involved a 90° occluded angle which tapered from the wall of the barrel to the center of the orifice. This same taper was present on the bottom end of the plunger.

The rheometer temperature was regulated by the standard proportional control device and was measurable at four positions along the barrel. Variations along the length were held to within 1°C. Test temperatures were 160°, 200°, 225°, and 250°C. Polystyrenes in general,[6] and these specific samples,[4] are known not to degrade thermally at temperatures below 265°C.

The test polymers for this study were the narrow-molecular-weight-distribution polystyrenes made by the Pressure Chemical Company by anionic polymerization. The sample principally used had a weight-average molecular weight ($\bar{M}_w$) of 1.8 million and a $\bar{M}_w/\bar{M}_n$ of 1.2. In addition, two lower molecular weight polystrene samples were also examined, $\bar{M}_w$ 670,000 (Pressure Chemical Company); and $\bar{M}_w$ 235,000 (Monsanto), which has a broad distribution and was supplied as pellets. The latter was compressed in the capillary reservoir by the same procedure as the powdered polystyrenes. This method minimizes the concentration of oxygen in the samples and provides a valid comparison between the samples, as given subsequently in Table II.

The narrow-distribution polystyrenes are supplied in the form of flocculent powders. In this form they are difficult to load directly into the heated viscometer without undue opportunity for oxidative and thermal degradation. All polymers were thus loaded first into the cold rheometer barrel (below 70°C) and the sample compacted by manual tamping. Further pressure (up to 1500 kg/cm²) was applied by the rheometer cross head and plunger to compress the polymer into a hard plug, free of voids. These plugs were of the exact dimensions and form as the viscometer reservoir. Prior to each experiment, a new plug was simply slipped into the heated reservoir. During some tests, the residual dissolved and entrapped oxygen was removed from these reservoir sample preforms and replaced by nitrogen. This was done by holding the preforms in a vaccuum chamber at 50°C. Occasionally the sample chamber was filled with pure nitrogen gas to atmospheric pressure and the gas again removed. This cycle was repeated many times during a 14-day period before the samples were sheared in the Instron rheometer.

Each preformed sample was held in the capillary reservoir for several minutes to allow for thermal equilibrium before extrusion was initiated. For each reservoir loading, the sample volume was noted and one half the volume extruded. Thus, each reservoir sample examined corresponds to 50% extrusion. After extrusion was stopped, the capillary was removed from the front end of the barrel and the residual plug in the reservoir was withdrawn as a single solid piece.

To obtain samples for molecular weight measurement, each solid plug from the reservoir was cut into sections. First, the entire length of plug

was sectioned into disks of $^{1}/_{8}$-in. to $^{1}/_{4}$-in. thickness. In other samples, molecular weight measurements were made on concentric layers across the reservoir diameter, i.e., starting at the barrel wall and tending toward the center axis. These sections were prepared using a mechanical lathe. The details for the new method called solvent microtoming, for sectioning the small diameter extrudate, have been recently described.[3]

Each of the vertical and lateral sections from the reservoir and the solvent microtoming portions of the extrudate was dissolved in tetrahydrofuran to a concentration of 1 mg polymer per ml tetrahydrofuran. Aliquots of 5-ml solutions were taken for molecular weight measurement using gel permeation chromatography.

All molecular weight and distribution analyses were evaluated using gel permeation chromatography. The instrument was a Model 200 GPC, made by Waters Associates, Framingham, Massachusetts. The operating temperature was 25°C and the column flow rate of THF was maintained at 1.0 ml/min. Separation was performed on four columns arranged in series, each 4 ft in length. The Corning porous glass bead column packings had average pore diameters of 274, 370, 790, and 1,400 Å, respectively. Calibration of the columns was performed using narrow-distribution polystyrene samples obtained from Pressure Chemical Company and from Waters Associates. All GPC results were corrected for axial peak spreading not due to the actual MWD by the use of Tung's[7] dispersion equation as modified by Pierce and Armonas.[8]

These analyses were made possible by the complete solubility of all shear-degraded polystyrenes. This feature is also consistent with an earlier study on polystyrene which showed that gel formation occurs at only above 10^4 atm. pressure.[10] In these studies, the maximum stress corresponded to about 10^3 atmosphere. The absence of gel, however, does not exclude the possibility of some chain branching as the result of degradation. For this study, this possibility is inconsequential although the apparent molecular weight distribution could be influenced by this feature. In this study, only weight averages were computed from GPC, and the total fraction of bonds broken was so low as to have no appreciable effect due to possible branching. In separate studies complete molecular weight distribution analyses for the same[5] and similar polymers have been developed in this laboratory (note Figs. 5–9 in ref. 4).

RESULTS

Preliminary tests were performed for possible polystyrene degradation during sample preparation and handling. The polystyrene ($\bar{M}_w$ 1.8 million) was carried through the entire procedure including compacting under high pressure followed by holding of the sample at 225°C but without extrusion. Measurements on the resulting samples revealed no significant change in $\bar{M}_w$ or MWD compared to the original polystyrene flakes. These findings are in agreement with an earlier report for a similar poly-
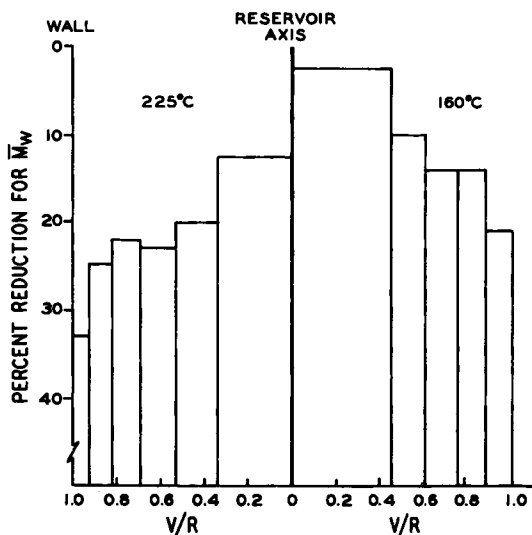
Fig. 1. Histogram of radial molecular weight profile across the barrel of the Instron capillary rheometer reservoir at 160°C and 225°C.

styrene which showed that no thermal degradation occurs in the rheometer reservoir even at temperatures as high as 250°C for hold periods of over 4 hr.[4] Polystyrene degradation was observed in the reservoir, however, after extrusion of part of the initial charge. The rheometer temperature was 225°C, and 50% of the initial charge was extruded with a shear rate at the capillary wall of 5460 sec^{-1}. The polymer remaining in the reservoir barrel was removed and sectioned for analysis. The polystyrene plug was cut to give six concentric layers over the entire length. The diameter of the plug was measured after each layer was removed. The weight-average molecular weight as well as the full MWD was determined for each layer by calibrated GPC.

The data were also obtained in an identical manner but at a rheometer temperature of 160°C. Molecular weight histograms shown in Figure 1 for both sets of data showing molecular weight as a function of radial position clearly reveal a molecular weight gradient across the entire reservoir diameter after 50% extrusion. This is consistent with a shear stress profile. The molecular weight and gradient are linear but are not the same at 160° and 225°C. Significantly greater molecular weight loss occurs at 225°C and with a steeper gradient. Studies of flow profiles in the reservoir made by others[1,2] show a convulsive oscillation of high stress which predominates near, but not at, the reservoir wall. This effect is caused by volume conservation in flow which necessitates the storage of elastic energy. These oscillating and high stress areas may be a principal reason for the marked degradation effects which are found with a gradient in the reservoir for conditions of calculated average shear stresses nominally much lower than in the capillary section.

TABLE I

Mechanochemistry of Polystyrene at 200°C. Molecular Weight Profile
Along the Length of the Barrel of the Capillary Reservoir

Section[a]	$M_w \times 10^{-6}$
1 (top-end section)	1.42
2	1.36
3	1.32
4	1.33
5	1.35
6 (tip section)	1.26

[a] Reservoir was cut into four equal disk sections plus tip and top-end sections.

TABLE II

Mechanochemistry of Polystyrene. Polystyrene Degradation within the
Capillary Reservoir During Extrusion for Different Weight-Average
Molecular Weight Polystyrene

Original M_w	M_w after extrusion[a]	$\bar{M}_w$ reduction, %
234,000	230,000	2
670,000	570,000	14
1,800,000	690,000	60

[a] Temperature 202° ± 2°C, stress at wall (2.5 ± 0.1) × 10⁶ dynes/cm².

To study flow irregularities that differ along the length of the reservoir, a third sample of the same polystyrene was extruded at an intermediate temperature, 200°C. The remaining 50% of the reservoir polymer was cut into six lateral sections. They are the orifice tip and the top-end section, and four disk-like, equal-length middle sections. These reservoir molecular weight profile data are presented in Table I. The data again show significant polymer shear reaction within the reservoir. Moreover, the extent of degradation is virtually the same along the reservoir length except perhaps for the extreme reservoir tip section where slightly greater degradation is observed adjacent to the capillary entrance.

The effect of initial polystyrene molecular weight on the extent of polymer degradation within the reservoir was examined by extruding three different molecular weight polystyrene samples—all at about the same temperature and shear stress at the capillary wall. After 50% extrusion in these experiments, the entire reservoir was dissolved in THF and aliquots were taken for GPC analysis. These data are given in Table II. The results show the dramatic effect of polystyrene molecular weight on the extent of reservoir degradation. This feature is in accord with the mechanical mechanism where the highest molecular weight species are most subject to shear-induced degradation.

It has been classically considered that the maximum stresses on capillary flow, and consequently the principal source for polymer degradation, would be in the capillary itself. Indeed, Table III (at the top) illustrates that, for this particular experiment described above, there is a sizable reduction

TABLE III
Molecular Weight Profile Across an Extruded Strand of Polystyrene[a]

	$M_w \times 10^{-6}$	M_w/M_n
Unextruded polymer	1.71	1.19
Rheometer reservoir	1.53	1.22
Extruded strand	1.26	1.35

Strand layer	Strand diameter, %	$M_w \times 10^{-6}$	M_w/M_n
1	7	1.11	1.45
2	13	1.20	1.39
3	17	1.25	1.36
4	28	1.30	1.32
5	35	1.28	1.30

[a] Extrusion temperature, 160°C; shear rate, 27.5 sec^{-1}; shear stress, 1.96×10^6 dynes/cm^2; capillary, 0.03 in. $\times$ 2.0 in.

in molecular weight to capillary transit. This experiment was chosen for further examination because the maximum polymer reaction due to stress is expected at the lowest temperature, in this case, 160°C.

Speculation may be offered but no specific tests have been reported heretofore for a gradient of shear reacted polymer in mechanically degraded polymer. This possible feature of the polymer extrudate was examined using the recently published technique of solvent microtoming which avoids a cutting (bond breaking) procedure and allows sectioning of cylindrical cross sections of small diameter. Since this solution process has been shown to avoid selective extraction for just these polymers,[3] any molecular profiles across the sample may be specifically attributed to a mechanically induced reaction.

Table III (at the bottom) shows an evaluation of molecular weights across the shear reacted polystyrene of 1.8 million molecular weight. In our lab, the weight-average molecular weight of this sample was found to be 1.71 million. Progressively lower molecular weights were found for polymer in the capillary reservoir and in the extruded polymer. For the extruded polymer, progressively low molecular weights were found in each layer with increasing radial position (from the axis to the wall). The gradient is in molecular weight and distribution in the extrudate measurable and regular with the mechanical reaction occurring in the outer $\leq 37\%$ of the filament. The depth of this gradient indicates that it is not predominately, if at all, an effect of surface oxidation on exposure to air on extrusion. The possibility of oxygen migration already in the sample to the outer portion of the strand during extrusion is not excluded.

With the inference of effects of air on degradation, the influence of oxygen on the mechanical reaction was approached directly. An extensive procedure, described in the experimental section, was used for removing air from the original polystyrene. The additional precaution was taken of loading the polymer into the rheometer under purge of nitrogen gas. The shear

results on these samples are described on these samples in Figure 2 in terms of molecular weight reductions. The specific shear rate and shear stress conditions including absolute molecular weights for the correlation given in Figure 2 are listed in Table IV. The results on oxygen-free samples are
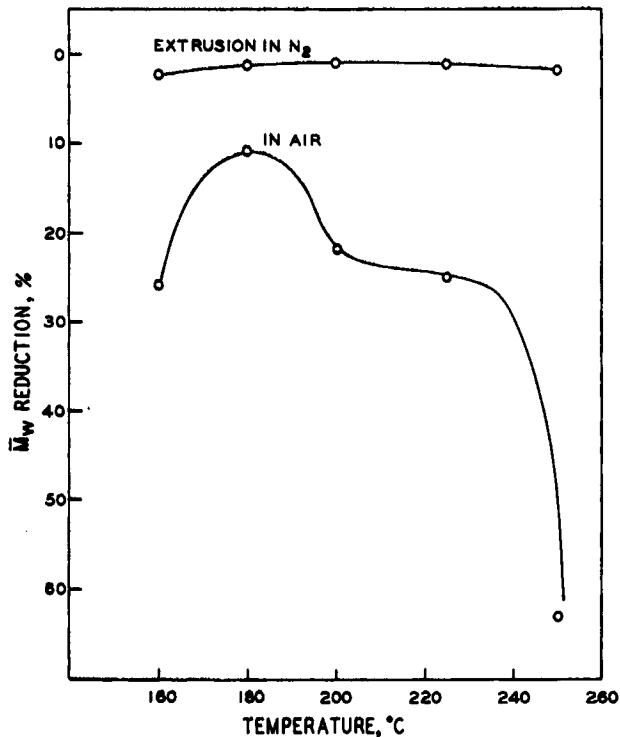

Fig. 2. Polystyrene extrusion at constant shear stress. Molecular weight changes with temperature for polymer with and without all traces of oxygen removed.

TABLE IV
Effects of Oxygen and Temperature on Mechanochemistry.
Polystyrene Extrusion Conditions

Temp., °C	Atmosphere[a]	Shear rate, sec^{-1}	Shear stress, (dynes/cm^2) $\times 10^{-6}$	$M_w \times 10^{-6}$	M_w Change, %
160	N$_2$	27.5	1.96	1.67	−2.4
	Air			1.26	−26
180	N$_2$	136.5	1.82	1.69	−1.2
	Air			1.52	−11
200	N$_2$	1,365	1.92	1.72	0
	Air			1.34	−22
225	N$_2$	2,730	1.80	1.70	−1
	Air			1.29	−25
250	N$_2$	5,460	1.75	1.69	−1.8
	Air			0.625	−63

[a] Polystyrene sample conditioned in this atmosphere before extrusion.

compared in Figure 2 with tests on the same polystyrene containing the normal traces of oxygen present in polystyrene due to dissolved air. The differences, with and without oxygen, are dramatic. Molecular weight changes due to both reservoir and capillary shear are included for data on the first capillary pass of fresh polymer samples. Because of limited time exposure, a single pass for these samples does not lead to a limiting equilibrium molecular weight.[4,5] For the oxygen-free polymer, there is virtually no degradation for the most sensitive (highest molecular weight) polystyrene at the highest shear stress at all temperatures from 160° up to 250°C. Unlike the predominant mechanical mechanism, the oxidation and thermal decompositions both have a positive temperature coefficient. Oxygen itself is a potent free-radical scavenger and can lead to radical termination by formation of hydroperoxide. Whether oxygen in catalytic or stoichiometric amounts is required for these effects is not known at this time. What can now be said, however, is that air present in any conventional processing scheme for polystyrene may be expected to play a prominent role in degradation. Note, for example, in Figure 2 that traces of air also aid the reaction in the region of the negative temperature coefficient below 180°C. Indeed, the pattern is most reminiscent of the most well-studied polymer, natural rubber, where a condition for minimum reaction at high shear in oxygen is also observed. For polystyrene, the temperature of maximum shear stability is near 180°C, in contrast to natural rubber, where it is near 115°C.[11] These results are in agreement with the maximum stability temperature found in the degradation data as a function of molecular weight published earlier on yet an additional narrow distribution polystyrene, M_w 670,000.[4] The concept of a temperature for maximum shear stability may well apply generally to polymers. The use of trace oxygen to sense regions of high stress concentration through degradation may also be a useful general concept.

CONCLUSIONS

This work presents clear evidence that polymer degradation in a capillary melt viscometer can be caused by high shear stresses in the reservoir, in the capillary entrance region, and in the capillary itself. The first and last features are further illustrated by radical molecular weight gradients and the entrance effect by molecular weight analyses from the capillary entrance region after partial extrusion. Further, there is a general drop (12% at 225°C) in the reservoir molecular weight which may be caused by the traces of oxygen in contact with polystyrene at temperatures below its thermal decomposition temperature when under conditions of shear stress. This latter reaction is not observed without pressure and shear.[4] These results are consistent with practical extrusion behavior. It has been shown, for example, that degradation occurs under normal conditions of injection molding and that the amount from repeated injection molding is practically always greater than the degradation of the unsheared polymer.[9]

Through these studies some progress appears to have been made in distinguishing—in a model extrusion scheme—the contributions to polystyrene degradation attributable to oxygen, temperature, and shear and to the origin of these processes in various sections of an extruder.   Such reactions are important to the visions and particularly the elastic properties of polymers as they concern polymer processing, use, and recycle.   In some cases, changes in molecular weight and distribution across the sample may be desirable.   Natural rubber, of course, has been processed this way for over 100 years and vis-breaking is still a commercial process with polyethylene.

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