

## Polystyrene Degradation in Model Extrusion Experiments

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### Synopsis

An investigation has been made of the magnitude and the source of degradation of polystyrene in model extrusion experiments. A preformed solid plug of a narrow-distribution, high molecular weight polystyrene ( $\bar{M}_w = 2 \times 10^6$ ) was used for each experiment. The extrusions were performed with an Instron capillary rheometer at constant temperatures from 160° to 220°C. The molecular weight changes occurring in the capillary reservoir during the pass of the capillary and in the hot extrudate were evaluated. Molecular weights and distributions were obtained by gel permeation chromatography. A significant degradation was observed in the capillary reservoir. The degree of degradation was independent of polymer flow. The polystyrene near the walls reacted more extensively than that closer to the axis, but a constant degradation was observed along the axis. The molecular weight profile across the capillary reservoir was attributed to a selective thermo-oxidative degradation (160° and 190°C). Changes in molecular weight due to mechanical degradation in the capillary were observed only at 160°C. This reaction was referred to as a mechano-oxidative process, as no degradation could be detected in the absence of oxygen. At 160°C, selective migration of macromolecules (fractionation) during extrusion did not occur to any significant extent, nor could any thermo-oxidative degradation of the extrudate be detected. When a small amount of antioxidant (Ionol) was added to the polystyrene, no selective degradation did occur at the walls of the capillary reservoir during extrusion at 160° and 190°C.

### INTRODUCTION

It is well known that migration of particles occur in suspensions during Poiseuille flow in tubes.<sup>1-4</sup> The suspended particles migrate from the wall towards the center of the tube, that is, from regions of higher to lower shear gradient. A similar effect has also been postulated for polymer melts flowing through a capillary viscometer.<sup>5,6</sup> In such a case, a fractionation of polymer molecules with respect to molecular weight would occur along the capillary radius. Large molecules near the wall require a large amount of free energy of elastic deformation, while very small molecules do not. A "pseudothermodynamic" force is thus acting in a way that tends to increase the concentration of very small molecules at the wall and of the larger ones close to the tube axis. Very few experiments have been performed to test this concept.

Schreiber and Storey<sup>7</sup> extruded polyethylene through capillaries of different lengths at 190°C. They reported reductions in the molecular weight of

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the surface layer compared to the whole extrudate. The migration was observed for a branched polyethylene and a 50:50 mixture of two linear polyethylenes. A linear polyethylene fraction did not exhibit any fractionation.

Whitlock and Porter<sup>8</sup> did not observe any effects of fractionation during capillary extrusion of a polystyrene of  $\bar{M}_w = 234,000$  at a series of conditions. In another investigation, a tendency toward lower molecular weight polystyrene at the extrudate surface was observed.<sup>9</sup> These experiments were carried out using a narrow molecular weight distribution polystyrene of a molecular weight around 2,000,000. In this case, the results cannot be attributed to the effects of migration as even the polystyrene in the rheometer reservoir was degraded.

The theory predicting fractionation along the capillary radius has also been suggested to account for the fact that extrusion lubricants tend to concentrate at the die wall.<sup>5,6</sup> The incompatibility of lubricant and polymer may be a driving force here. A similar effect has been observed for quite a different system. Mason and co-workers<sup>1,3,4,10</sup> studied the effect of tubular flow on suspensions of rigid particles in a series of liquids. They observed that in a pseudoplastic liquid, the particles tend to concentrate at the wall, the reverse of migration in a simple (Newtonian) fluid.<sup>10</sup> By analogy, a migration to the wall of rigid particles, e.g., fillers, may be possible in extruded polymer melts which are generally shear thinning. Information on such systems is, however, very limited.

The existence of low molecular weight polymer in the outer layer of an extrudate does not conclusively prove that migration of molecules has occurred. At high shear stresses, e.g., polymer molecules could be ruptured at the highest shear stress, which is at the capillary wall. This will result in a molecular weight profile across the extrudate which could be confused with that from migration. It has been shown in an earlier model extrusion experiment that polystyrene of the same high molecular weight studied here does degrade under high shear stresses.<sup>9,11</sup>

Regions of high shear stresses may occur not only at the capillary wall, but also in the capillary entrance region, which is still another possible source of polymer degradation. Up to now, there is little conclusive evidence concerning the origin of degradation in capillary flow. However, for polymer solutions, it has been shown that the degradation occurs mainly in the capillary entrance region.<sup>12</sup>

In addition, investigations of polymers in the molten state are often complicated by thermal decomposition. Polystyrene melts generally exhibit good thermal stability below 250°C, but it has been shown that the presence of oxygen effectively lowers the decomposition temperature.<sup>9,11</sup> As many processing parameters are closely related to polymer molecular weight distribution (MWD), a change in MWD due to polymer degradation may drastically change the processing conditions. The possibility of different sources of degradation in extrusion can, of course, also complicate the interpretation of the resulting flow curves. Furthermore, for any polymer melt, where changes in MWD occur during processing or rheometer testing, the elastic properties of the polymer melt are also changed. As elasticity depends on high molecular weight moments, ( $\bar{M}_z$  and  $\bar{M}_{z+1}$ ); scission reactions have a great effect. Radicals formed during the processing may result in branching and/or cross-

linking as well as a molecular weight reduction. This is, of course, a drawback in most cases. However, the formation of radicals can be advantageous for the mechanical synthesis of block and graft copolymers during processing.<sup>13</sup>

It is the object of this investigation to elucidate the effect of flow and atmosphere (oxygen) on the magnitude and mechanism of the degradation of polystyrene in model extrusion experiments with and without an antioxidant. A specific condition of the oxidation kinetics is, however, beyond the scope of this study.

## EXPERIMENTAL

### Materials

The polymer tested was a high molecular weight polystyrene standard prepared by the Pressure Chemical Co., Pittsburgh, Pennsylvania, by anionic polymerization. It has a reported weight-average molecular weight  $\bar{M}_w$  of 2,000,000 and an  $\bar{M}_w/\bar{M}_n$  of 1.2. Our GPC analysis resulted in  $\bar{M}_w = 2.1 \times 10^6$  and indicated an  $\bar{M}_w/\bar{M}_n$  index of 1.5. A value larger than 1.2 has been independently observed.<sup>14</sup> Ionol (2,6-di-*tert*-butyl-*p*-cresol) was used as an antioxidant. It was supplied by Shell Chemical Co. The tetrahydrofuran used was analytical grade. Toluene of high purity was used.

### GPC Procedure

A Waters Associates GPC Model 200 equipped with an automatic injection system was used for determination of molecular weights and distributions. The experimental conditions were as follows: solvent, tetrahydrofuran; temperature, 25°C; columns, 10<sup>7</sup>, 3×10<sup>5</sup>, 3×10<sup>4</sup>, and 3×10<sup>3</sup> Å; sample concentration, 1 mg/ml; flow rate, 1 ml/m. Calibration of the columns was performed using narrow-distribution polystyrene standards obtained from Pressure Chemical Co., Pittsburgh, Pennsylvania, and Waters Associates, Milford, Massachusetts. The column set employed gives good resolution for even higher molecular weight polymers. A polystyrene with a molecular weight  $\bar{M}_w$  of 7.1 × 10<sup>6</sup>, Duke Standards, California, has been well resolved on this column set. To account for axial peak spreading, the Tung's dispersion equation<sup>15</sup> was applied as given by Pierce and Armonas.<sup>16</sup> For details, see reference 11.

### Rheological Measurements

Experiments were conducted using an Instron capillary rheometer, Model TT-CM (Instron Equipment Corp., Canton, Massachusetts) with a 0.375-in.-diameter capillary reservoir. The tungsten carbide capillary used had an  $L/D$  ratio of 66.7. It was 2 in. long with an entrance angle of 90°. The rheometer temperature was regulated by a proportional control device and had four thermocouple positions along the barrel. Temperature variations along the barrel could be kept within 1°C. The lower section of the rheometer barrel is shown in Figure 1.

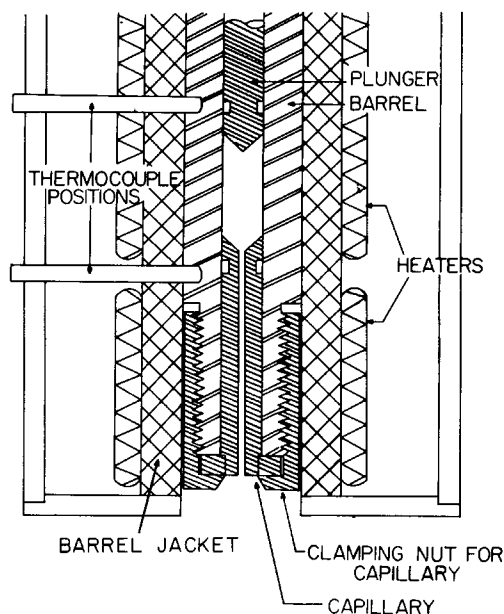


Fig. 1. Lower section of Instron rheometer barrel.

In order to minimize the effect of oxidative and thermal degradation of the polymer during the loading of the rheometer barrel, a pretreatment of the flocculent polymer powder was necessary. The polymer was thus loaded in portions into the cold barrel (below 70°C). After each loading, the sample was compacted by manual tamping. Finally, further pressure was applied by the rheometer crosshead and plunger to compress the polymer into a hard plug, which was then extruded out after removing the clamping nut for the capillary. Before each experiment, such a plug was slipped into the heated reservoir and the polymer was then kept at the desired temperature for 10 min before extruding. In some cases, the preformed plugs were kept in a vacuum chamber at 80°C for 15 to 20 days before extrusion to reduce the amount of dissolved and absorbed oxygen. Periodically, the vacuum chamber was purged with pure nitrogen gas to atmospheric pressure before vacuum again was established.

In every extrusion, the experiment was stopped when 50% of the original polymer volume was extruded. The extrusions were carried out at a constant shear stress ( $\sim 5 \times 10^6$  dynes/cm<sup>2</sup>), which corresponded to a large difference in shear rates (45 to 224000 sec<sup>-1</sup>). Residence times thus varied from about 1 min to 3.5 hr, excluding the standard preheating period (10 min).

After cooling the rheometer, the capillary was removed and the residual plug in the reservoir was withdrawn as a single solid piece. Certain of these plugs were sectioned into discs or lathed into concentric layers for GPC examination. A solvent coring technique was used for the examination of the molecular weight profile across the extrudate. A detailed description of this procedure was given in a previous paper.<sup>8</sup>

In some of the experiments, antioxidant (Ionol) was added to the polymer. Ionol in two concentrations (0.036 g and 0.090 g) was dissolved in 25 ml pure

TABLE I  
Molecular Weights at Different Axial Positions in the Instron Rheometer Reservoir  
After 50% Extrusion at 190°C

Section no. <sup>a</sup>	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
1	0.889	1.63	1.84
2	0.874	1.62	1.85
3	0.926	1.63	1.77
4	0.900	1.65	1.83
5	0.935	1.69	1.80
6	0.975	1.67	1.71
7	0.922	1.68	1.81
8	0.810	1.53	1.88
9	0.893	1.66	1.85
10	0.888	1.66	1.86

<sup>a</sup> Section 1 is closest to the tip of the plug, and section 10, closest to the plunger. Each disc was cut 2–3 mm thick.

toluene. This solution was then added to a solution of 18 g polystyrene in 250 ml toluene. The excess solvent was evaporated in air, and the resulting somewhat rubbery solid was then cut into small pieces and kept in a vacuum oven for about ten days at 80°C. Before preparing the plugs, the polymer was kept an additional couple of days under vacuum at 110°C. The pre-formed solid plug was finally kept under vacuum at 80°C for at least 14 days in order to remove toluene as efficiently as possible.

## RESULTS AND DISCUSSION

### Molecular Weight Profiles Across the Rheometer Reservoir

The high molecular weight polystyrene,  $\bar{M}_w = 2,100,000$ , was partially extruded at 190°C as described in the experimental section. The residual plug was then removed and analyzed to determine whether any change in molecular weight had occurred along the axis during extrusion. The molecular weights for different sections are listed in Table I. Section 1 is the disc taken closest to the tip of the plug, and section 10 is the disc closest to the plunger.

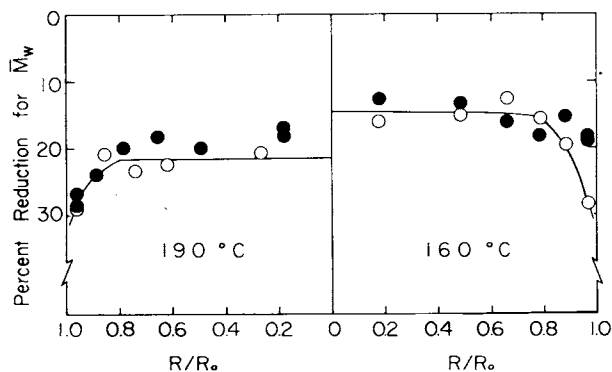


Fig. 2. Radial molecular weight profile across barrel of capillary reservoir at 160° and 190°C: (0) after 50% extrusion; (○) without extrusion. Changes shown as per cent reduction for  $\bar{M}_w$ .

The first section was taken at the base of the conical tip, and each disc was cut 2–3 mm thick. Except for section 8, the variation in  $\bar{M}_n$  and  $\bar{M}_w$  is well within the precision of the GPC technique. The lower molecular weight observed for section 8 might be explained by the presence of small amounts of entrapped air, which greatly promotes polymer degradation. An analysis of the molecular weight of concentric layers of the residual plug was also made. The results from extrusions at 160° and 190°C are shown in Figure 2 (open circles). At 160°C, the molecular weights of the outer layers had decreased appreciably more than the interior of the plug. About 80% of the cross section showed a decrease of about 15%, but at the surface layer a decrease of about 30% was observed. In an earlier investigation,<sup>9</sup> the molecular weight profile was found to be close to parabolic, exhibiting a somewhat lower drop in molecular weight than was found in this study. At 190°C, the degradation was still more pronounced, but with a similar cross-sectional profile. The extent of degradation at 160°C is minimal although the extrusion lasted for 3.5 hr. The exposure time at 190°C was only 15–20 min, but the process caused a somewhat larger degradation than at 160°C. This is probably due to the increase in thermo-oxidative degradation. As the shear stresses at the wall of the rheometer reservoir are low, a mechanical degradation cannot explain the lower molecular weights observed at the plug surface. To analyze the effect of polymer flow on this profile, we thus let the plug go through the same temperature history, but without any extrusion. The filled circles in Figure 2 represent these data. At 190°C, the radial distribution of molecular weights in the static case was more or less identical to that obtained from the dynamic test. The smaller molecules observed at the reservoir wall, therefore, could

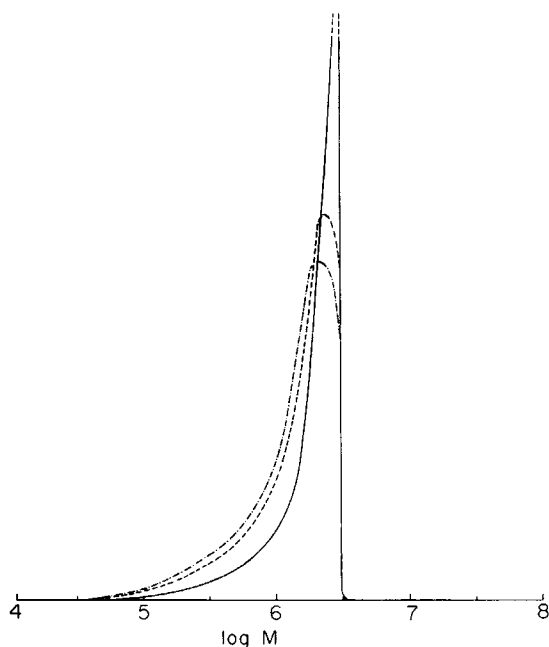


Fig. 3. Changes in MWD of polystyrene in capillary reservoir. Extrusion at 160°C: (—) original sample; (- -) plug interior after 50% extrusion; (· · · ·) plug surface after 50% extrusion.

not be the result of either flow or the shear stress profiles. A reasonable conclusion in this case is that the residual presence of air in trace amounts causes a preferential polymer degradation near the wall. Of course, air is always present at the surface of both the plug and the reservoir wall, and, when the plug is loaded, air may be entrapped between the two surfaces. The air may also diffuse a short distance into the melt. Thus, in this study a decrease in molecular weight was observed after keeping the polystyrene in the Instron rheometer for 3.5 hr. This is contradictory to what was reported in a previous paper.<sup>11</sup> The discrepancies are probably due to the difference in materials used. The high molecular weight sample ( $\bar{M}_w = 2 \times 10^6$ ) employed in this study has a much higher melt viscosity compared to the one used in reference 11 ( $\bar{M}_w = 0.67 \times 10^6$ ) and is therefore more difficult to compress. This results in a larger amount of occluded air, which causes an increase in degradation.

At 160°C, there is a difference between the molecular weights of the outer layer in the static test and the dynamic test, although the radial molecular weight profiles across the rheometer reservoir have a similar trend. The less pronounced profile in the static case may be the result of diffusion of air. The MWD at different radial positions in the residual reservoir plug for the extrusion at 160°C is shown in Figure 3. Similar results were obtained at 190°C. The original MWD is compared with the MWD's of the interior and outermost material in the plug obtained after 50% extrusion.

### Extrudate Analysis

To find out whether the extruded strands were significantly oxidized as the polymer melt was extruded into air, the polymer was extruded into liquid nitrogen. Figure 4 shows the molecular weights of the extruded strand as a function of time. The extrusion was performed at 160°C. The data point to the far left in the figure represents the extreme tip of the extrudate (at the capillary entrance), which was in contact with air during the preheating period. This material degraded as a result of the exposure of the hot polymer melt to air. The corresponding MWD is shown in Figure 5. It is compared

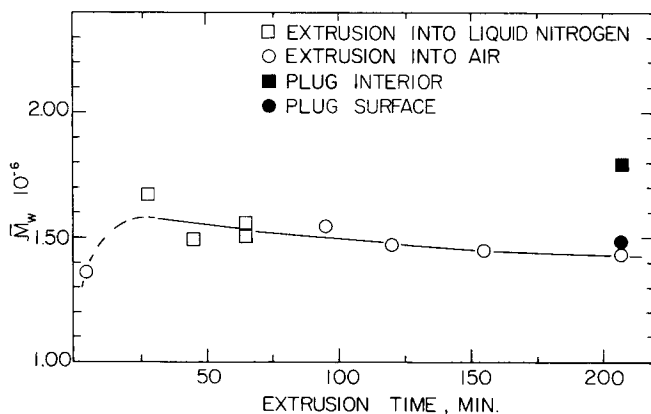


Fig. 4. Weight-average molecular weight of extrudate as a function of extrusion time. Extrusion at 160°C.

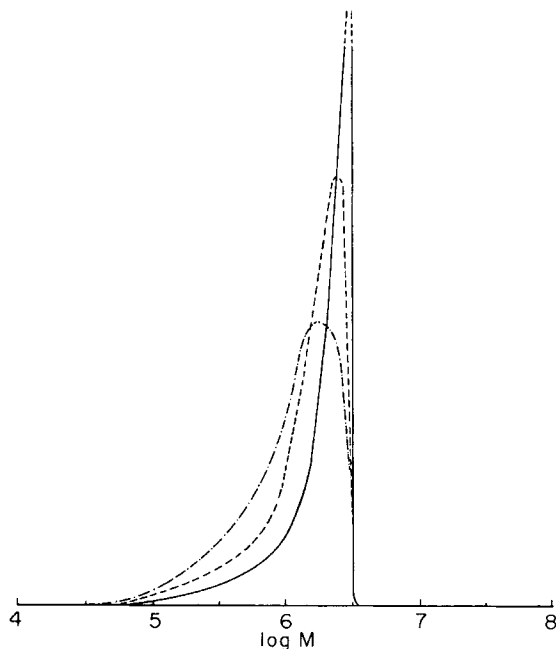


Fig. 5. Changes in MWD of polystyrene in extrudate. Extrusion at 160°C: (—) original sample; (---) extrudate taken after 28 min (extruded into liquid nitrogen); (-·-·-) very first extrudate (exposed to air).

with the MWD's of the original polymer and an extrudate taken after 28 min. As can be seen from the figure, thermo-oxidative degradation at the capillary entrance region causes a substantial broadening of the distribution during the preheating period. The open squares in Figure 4 represent measured molecular weights of extrudates being extruded into liquid nitrogen. These values should be compared with the data for strands extruded into air. There is no significant difference between the molecular weights of these extrudates, which shows that the extruded strands cool so rapidly that the effect of air on the extrudate is negligible, but this is only at 160°C where degradation due to O<sub>2</sub> in rheometer and outside will be minimal. A slight decrease in  $M_w$  with extrusion time was observed (see Fig. 4). This is an effect of the degradation of the bulk polymer during this time. The molecular weights of the outer and interior material of the residual plug are also included in Figure 4. Filled symbols represent capillary reservoir data (after 50% extrusion), and open symbols represent extrudate data. The interior has a much higher molecular weight than the resulting extrudate. As most of the material in the plug has a molecular weight like the interior, an average molecular weight for the whole plug is close to that of the interior. This indicates that the polymer degrades substantially when it passes the capillary. It is reasonable to believe that this degradation originates from the action of the high shear stresses at the capillary wall ( $\sim 6 \times 10^6$  dynes/cm<sup>2</sup>). Figure 6 gives an idea of what is happening when polymer passes through the capillary. The broadest MWD is the distribution of an extrudate taken after 75 min of extrusion at 160°C. The dashed curve is the MWD of the polymer just at the entrance of



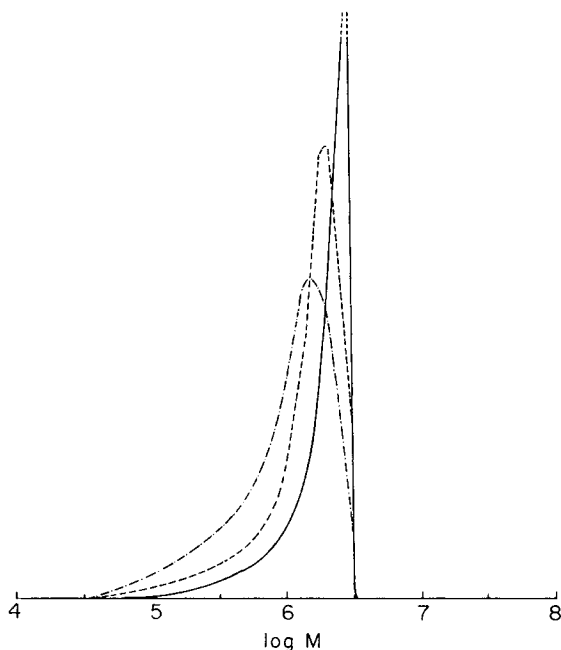


Fig. 6. Changes in MWD of polystyrene in extrudate. Extrusion at 160°C: (—) original sample; (---) polymer taken at capillary entrance after 100 min of extrusion; (.....) extrudate taken after 75 min.

the capillary. This sample was taken after about 100 min of extrusion. (The extrusion was stopped). It is obvious that the passage through the capillary gives rise to significant polymer degradation. This underlines the results presented in Figure 4. The weight-average molecular weight of the extrudate, as a function of extrusion temperature, is shown in Figure 7. The open squares show the cases where the majority of the air in the plugs was removed and exchanged with nitrogen prior to testing. The circles in Figure 7 mean that no special precaution was taken to avoid air in the sample. The extrudates from the nitrogen-treated plugs were considerably less degraded than the ordinary extrudates. In this case, the amount of degradation slowly increased with temperature and had its origin mainly in the reaction taking place in the reservoir during polymer preheating. When the plugs were pre-

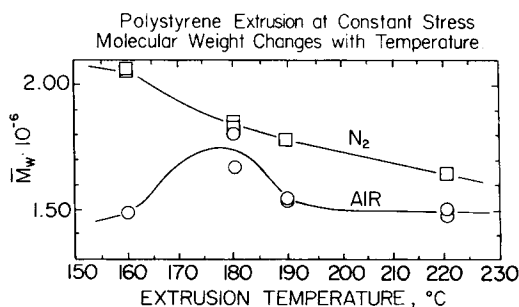


Fig. 7. Extrudate molecular weight as a function of temperature. Experiments performed at approximately the same shear stress.

pared in the conventional way, a decrease in molecular weight with an increasing temperature was also observed, except for the lowest temperatures. At 160°C, the decrease in molecular weight was much larger than expected from a usual thermal degradation. It therefore seems reasonable to believe that a mechanical degradation is predominant at the lowest test temperatures. As this reaction is not observed in the case of the nitrogen-treated plug, the difference may be explained by the presence of oxygen, which prohibits mechanically-generated radicals from recombining. Radicals formed when high stresses are applied could, of course, also react with other molecules and form branches. Extensive branching reactions (gel formation) as a result of high static pressures has only been observed above  $10^4$  atmospheres.<sup>17</sup> The pressures in this study were approximately ten times lower. The presence of oxygen appears to favor chain termination, and the absence of oxygen should be more favorable for branching reactions. If extensive branching occurred, it should show up in the high molecular weight region of the MWD for the extrudate. No such changes were observed. This, of course, does not totally exclude the possibility of such reactions as they could

TABLE II  
Molecular Weights at Different Radial Positions in the Extrudate  
After 50% Extrusion at 160°C

Section no. <sup>a</sup>	Approx. strand diameter, %	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
1	10	0.686	1.38	2.02
2	15	0.660	1.29	1.96
3	15	0.681	1.40	2.05
4	60	0.679	1.40	2.06

<sup>a</sup> Section 1 is the outer layer of the strand.

be below the limit of GPC detection. The minimum degradation of the extrudate, when no air exclusion precautions were taken, occurred at about 180°C. This is in agreement with an earlier investigation.<sup>9</sup> It should be kept in mind that the relatively small changes in degradation with temperature are to some extent the result of different extrusion times. At 160°C, the extrusion lasted around 3.5 hr, at 190°C, a few minutes, and at the higher temperatures, in the order of seconds. Thus, at higher temperatures, the degradation was more extensive during the preheating than during the extrusion. The reason for the choice of different extrusion times was governed by the aim to keep the shear stress at a high constant level at all extrusion temperatures. The shear stresses were kept fairly constant ( $\sim 6 \times 10^6$  dynes/cm<sup>2</sup>), except for the highest temperature where a lower shear stress was reached. Except for the extrudate processes at 160°C, no change in molecular weight due to mechanical degradation in the capillary was observed. The radial distribution of molecular weights in the extrudate at 160°C is shown in Table II. There is a very slight tendency toward lower molecular weights in the outer layers. However, the difference is not significant, although the molecular weight profile in the capillary reservoir may also affect the corresponding profile in the extrudate.

### The Effect of Antioxidant

Experiments were also conducted using polystyrene containing an antioxidant. In the first experiment, 0.5% Ionol was added to the polystyrene as described in the experimental section. The results from an extrusion at 190°C for this system is shown in Figure 8. As can be seen, only a very slight decrease in molecular weight was observed in the capillary reservoir after 50% extrusion, and the molecular weight was almost constant across the diameter. The relative, stable molecular weight indicates that the amount of antioxidant was sufficient to prevent the thermo-oxidative degradation resulting from occluded air. To obtain a more significant degradation of the polystyrene, a smaller amount of antioxidant was added (0.2%). Although the temperature was only 160°C, the extrusion time was much longer than at 190°C. In this case, a substantial degradation was observed in the capillary reservoir after 50% extrusion (Fig. 8). Still, however, the molecular weight across the reservoir diameter was constant. In comparison, the molecular weight profiles for the polystyrene without any additives are also shown in Figure 8. The open circles are the same data as shown in Figure 2 (open circles). In the case when only a small amount of antioxidant was added, a uniform degradation across the diameter of the capillary reservoir was observed. Since there is degradation, one would expect—assuming a well dispersed antioxidant—a molecular weight profile similar to that obtained for the unstabilized polymer. To prevent a selective degradation, as shown in Figure 2 (right-hand side), a higher concentration of antioxidant may be required closer to the walls. It therefore seems reasonable to believe that the antioxidant migrates toward the walls of the capillary reservoir, where it is active in preventing an excessive polymer degradation. This is also in agreement with the concept of migration for low molecular weight species in a high molecular weight matrix.<sup>5,6</sup> It should be kept in mind that the extrusion process lasted for approximately 3.5 hr, which is long enough to allow migration. The difference in molecular weight between the polystyrene in the extrudate and in the reservoir plug was insignificant for the system containing antioxidant.

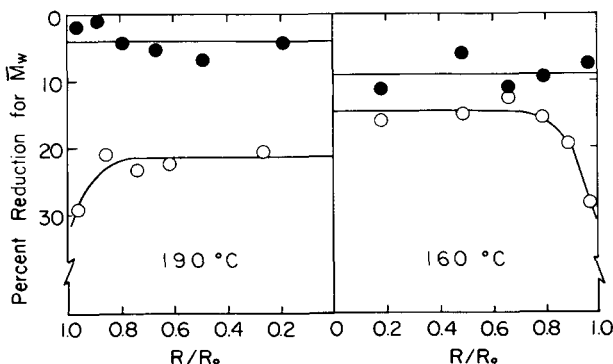


Fig. 8. Radial molecular weight profile across barrel of capillary reservoir at 160° and 190°C: (○) after 50% extrusion; (●) polystyrene samples containing Ionol analyzed after 50% extrusion. Samples extruded at 160° and 190°C contained 0.2% and 0.5% Ionol, respectively.

This supports the conclusion that the mechanical forces results in degradation only in the presence of oxygen.

### CONCLUSIONS

No conclusive evidence of polymer fractionation during extrusion of a polystyrene melt through a capillary was found. However, in the presence of oxygen, a mechanically induced polymer degradation did occur in the capillary during extrusion at 160°C at high shear stresses ( $\sim 6 \times 10^6$  dynes/cm<sup>2</sup>).

It was also found that a selective degradation occurred in the capillary reservoir and that oxygen played a key role in this process. The polystyrene near the walls of the capillary reservoir reacted more extensively than the material closer to the reservoir axis. The results with polystyrene containing Ionol suggested that migration of the antioxidant toward the walls of the capillary reservoir may occur.

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