

## Effects of Degradation on Polypropylene Melt Rheology

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### Synopsis

The viscous flow behavior of molten polypropylene has been correlated with the viscosity-average molecular weight under degradative and nondegradative conditions. The effects of unequal extents of degradation on molecular weight distribution are shown to be an important parameter in this correlation.

### Introduction

The rheological behavior of a molten polypropylene resin is governed primarily by its weight-average molecular weight and its molecular weight distribution. However, when the polymer is exposed to processing operations carried out at high temperatures, oxidative conditions, and high shear stresses, significant degradation often results, causing major changes in molecular weight and molecular weight distribution. Thus, Schott and Kaghan<sup>1</sup> found that at 500°F., six passes through a commercial screw extruder decreased the weight-average molecular weight of a polypropylene sample from 270,000 to approximately 80,000, and that the melt viscosity of the polymer decreased markedly, as anticipated. From the foregoing, it may be seen that the understanding and prediction of flow properties at high temperatures requires both a general knowledge of the effects of molecular parameters on rheological behavior and an estimate of the extent of degradation expected under varying conditions. It is, therefore, necessary to correlate the observed rheological properties with the molecular weight and molecular weight distribution which the process die or rheometer capillary actually "sees."

In these studies, rheological properties have been determined at high temperatures for several polypropylene melts. The results have been related to the molecular properties of the degraded resins via measurement of degraded molecular weights and an analysis of the expected differences between molecular weight distributions.

### Experimental

Several experimental polypropylene resins were used in these investigations. These resins are listed in Table I in groups of similar intrinsic vis-

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cosities. All reported values of intrinsic viscosity were obtained from extrapolation of plots of  $\eta_{sp}/c$  and  $\ln \eta_{rel}/c$  versus  $c$ . The best fit for the double extrapolation was obtained by choosing the intrinsic viscosity value which resulted in a value of 0.5 for the sum of the constants in the Huggins' equations. These values for  $k_1$  and  $k_2$ , defined by

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2c \quad (1)$$

$$\ln \eta_{rel}/c = [\eta] - k_2[\eta]^2c \quad (2)$$

were found to be  $0.32 \pm 0.01$  and  $0.18 \pm 0.01$ , respectively, in agreement with published values.<sup>2</sup>

TABLE I  
Polypropylene Resins

Group	Sample	$[\eta]$ of resin (decalin, 135°C.)	Melt flow rate, dg./min.*
A	1	2.90	1.8
	2	3.00	
	3	2.90	
	4	2.88	
	5	2.84	
	6	2.92	
B	1	2.25	5.5
	2	2.25	
C		2.15	11.5
D		1.92	20

\* ASTM D-1238-57T.

Rheological measurements at low temperatures (ca. 465°F.) were performed by use of a hydrostatic rheometer.<sup>3</sup> In this instrument, the polymer is confined between pistons, melted, and brought to operating temperature under a fixed hydrostatic pressure. The required heat-up time is approximately  $1/2$  hr. To make a run, a differential pressure is applied, forcing the polymer through a die of known dimensions. The rate of flow is measured by a fixed distance timing switch, and the shear rate is calculated from the expression  $4Q/\pi R^3$ , where  $Q$  is the volumetric flow rate and  $R$  is the capillary radius. The applied differential pressure is measured by a Helicoid gage, and the shear stress is calculated from the expression  $PR/2L$ , where  $L$  is the capillary length and  $P$  the applied pressure, corrected for piston friction, viscous loss in the chambers, and capillary entrance effects, if necessary. If desired, shear rates may be corrected for non-Newtonian behavior by means of the Rabinowitsch correction.<sup>4</sup> This has not been done in these studies.

High temperature rheological measurements were carried out in a specially designed extrusion rheometer.<sup>5</sup> In this apparatus, the polymer is melted and brought to temperature in a band-heated stainless steel

cylindrical barrel. The heat-up time is approximately  $\frac{1}{2}$  hr. A regulated nitrogen pressure is instantaneously applied to a stainless steel follower, which forces the polymer through a capillary die. The use of a recessed die cavity and spacer-die combination allows variations in die length, diameter, and entrance to be readily made. When sufficient polymer has been extruded, the pressure may be immediately released and the sample weighed. Extrusion time is automatically measured by means of an electric timer. The shear rate may be calculated from the extrudate weight, molten density, efflux time, and capillary radius. Shear stresses are determined from the applied pressure and die dimensions, with entrance corrections applied when necessary. The extrusion rheometer is also well suited to measurements of the extrudate swell.

### Results and Discussion

Steady-state flow curves (shear stress versus apparent shear rate) were determined for the resins listed in Table I in order to illustrate differences in behavior observed at low and high temperatures. Figure 1 shows the results obtained on the hydrostatic rheometer at the relatively low temperature of 465°F. Major differences, predictable from the melt flow rates ("melt indices") listed in Table I, may be observed between resins of vary-

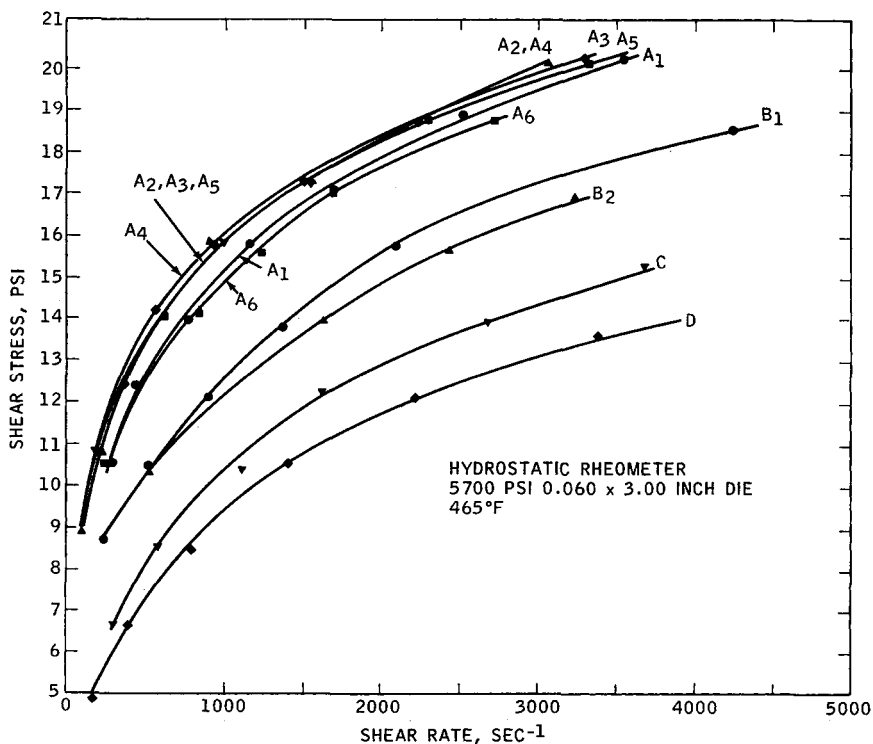


Fig. 1. Steady-state flow curves, polypropylene resins, 465°F.

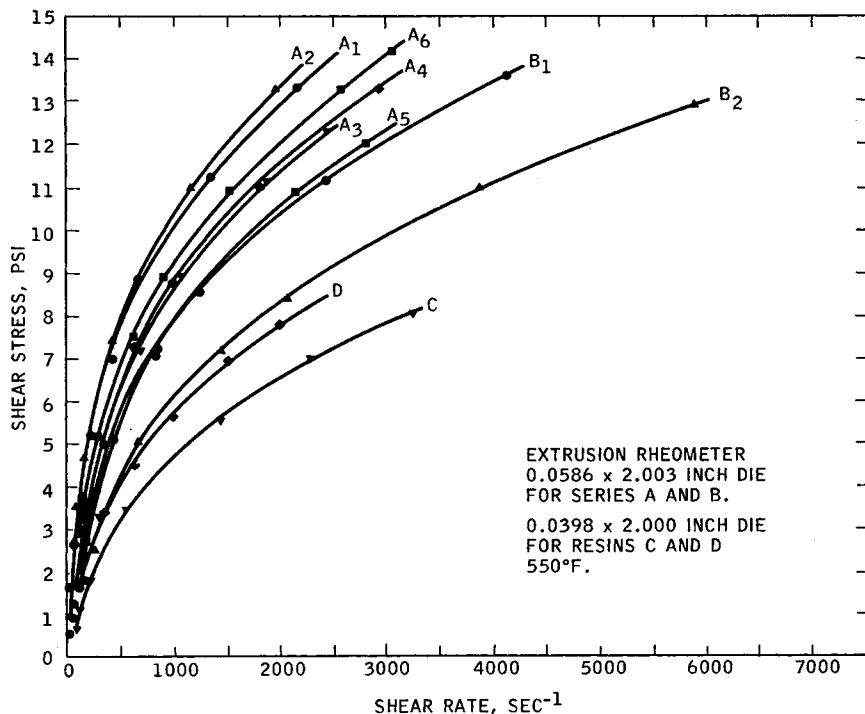


Fig. 2. Steady-state flow curves, polypropylene resins, 550°F.

ing viscosity-average molecular weight. However, within a group, e.g., group A, variations in flow behavior may be readily noted between samples of almost identical intrinsic viscosity and melt flow rate. These differences, while appreciable, are confined to bands which are well separated from those observed for resins of different melt flow rates and intrinsic viscosities. The variations observed within a group, however, illustrate the important fact that low shear stress measurements such as the melt index may not necessarily provide revealing information about flow behavior at high shear stresses.

Figure 2 shows flow curves obtained on the extrusion rheometer for the same resins at 550°F. At this rather high temperature, variations between resins of identical original molecular weight become very great. For example, it may be seen that at 10 psi shear stress, the observed shear rates for resins B1 and B2 differ by over 1000  $\text{sec}^{-1}$ . At 465°F., the shear rates observed for these resins are identical at the 10 psi shear stress level. It may further be observed that, due to the large changes in the relative positions of the flow curves, the flow properties of resins of widely different original molecular weights may actually become similar at the higher temperatures. Thus, resin B1 (original  $[\eta] = 2.25$ , original melt flow rate = 5.5) exhibits a flow curve at 550°F. very similar to that of resin A5 (original  $[\eta] = 2.84$ , original melt flow rate = 1.8). Finally, the changes

may be so pronounced that in some cases major inversions in flow behavior are observed. Figure 2 shows that resin C, whose original melt flow rate is only about one half that of D, actually flows considerably more readily than resin D at 550°F.

Results obtained at 600°F. are shown in Figure 3. The differences observed between resins of identical original melt index and molecular weight are particularly pronounced at this temperature. The relative positions of several of the flow curves are again changed. It is particularly striking that resin D (initial melt flow rate = 20) exhibits higher apparent

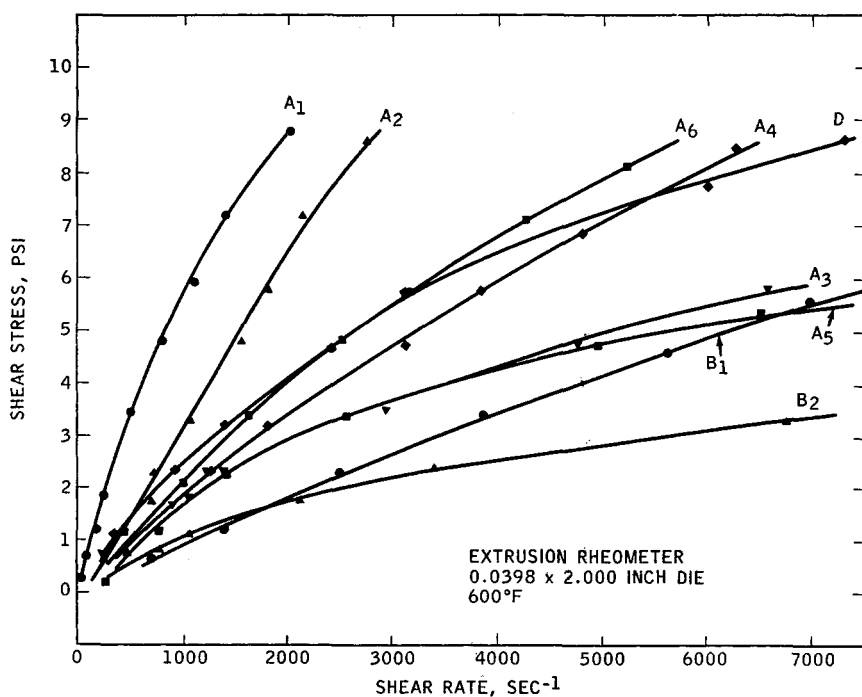


Fig. 3. Steady-state flow curves, polypropylene resins, 600°F.

viscosities at 600°F. than resins A3 and A5, whose original melt indices are approximately 1.8.

The experimental results described above illustrate the profound effects which degradative conditions may exert on the viscous flow properties of polypropylene resins. An attempt has been made, therefore, to correlate the observed rheological behavior with the degraded molecular properties of the resins studied. In view of the strong dependence of polypropylene melt rheology on weight-average molecular weight, initial efforts were made to correlate viscous flow properties with intrinsic viscosity. It has been assumed that, for the resins studied, these correlations should yield similar information to that which would be obtained using weight averages determined by light scattering or other techniques.

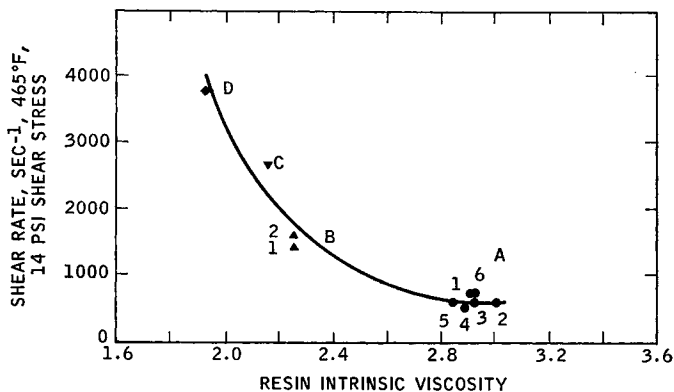


Fig. 4. Shear rate vs. resin intrinsic viscosity, 465°F.

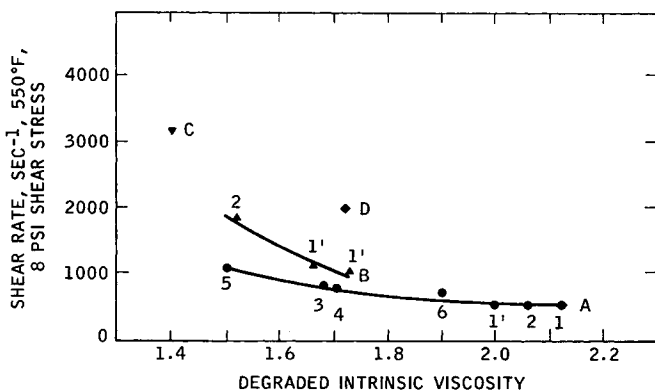


Fig. 5. Shear rate vs. degraded intrinsic viscosity, 550°F.

Figure 4 shows the effect of resin intrinsic viscosity on the shear rate observed at 465°F. and the relatively high shear stress of 14 psi. At this temperature, polymer degradation is mild, and it may be seen that the use of original resin intrinsic viscosity allows an adequate correlation to be obtained, particularly between groups of widely differing molecular weight. The observed correlation illustrates the marked dependence of polypropylene viscous flow behavior on molecular weight, particularly at intrinsic viscosities below 2.5. The fact that a single correlation is adequate to describe the high shear stress flow behavior over a relatively wide range of molecular weights indicates that, over the range studied, molecular weight is the primary variable, and that the initial molecular weight distributions are probably quite similar. (This is to be expected, since the resins were made by the same process.) Dissimilar distributions would be expected to yield deviations from a single correlation, since several investigations<sup>6-8</sup> have shown that for polypropylene and other thermoplastics, major differences between molecular weight distributions would be expected to result in large variations in fluidity at high shear stresses.

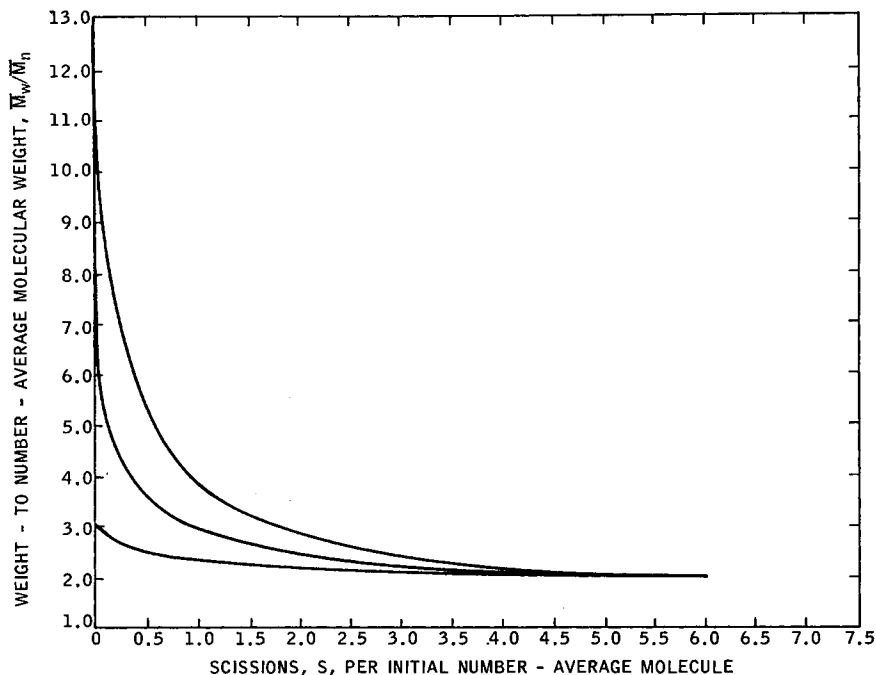


Fig. 6. Effect of degradation on molecular weight distribution.

Deviations from the correlation shown in Figure 4 may be attributed primarily to small amounts of degradation, experimental error, and second-order molecular weight distribution differences.

Inspection of Figures 2 and 3 readily reveals that a simple correlation between high shear viscous flow behavior and original resin intrinsic viscosity is unobtainable at the higher temperatures. In order to account for the effects of polymer degradation and to search out possible molecular weight distribution effects, the high temperature viscous flow behavior was correlated with intrinsic viscosities determined on the degraded rheometer extrudates. It should be pointed out that the use of an extrusion rheometer, in which all extrudates are readily accessible, facilitated the high temperature correlations.

Figure 5 shows the shear rates observed at 550°F. and a shear stress of 8 psi plotted as a function of degraded intrinsic viscosity for all of the resins investigated. It may be seen that good correlations exist for resins of originally similar molecular weight, thereby proving conclusively that differences in extent of degradation are primarily responsible for the variations in flow behavior observed between these resins at elevated temperatures. Several duplicate runs, made under slightly varied degradation conditions (A1' versus A1 and B1' versus B1), were used to validate further the results obtained.

The multiple correlations observed at high temperatures for resins of differing original molecular weight result in a situation in which several

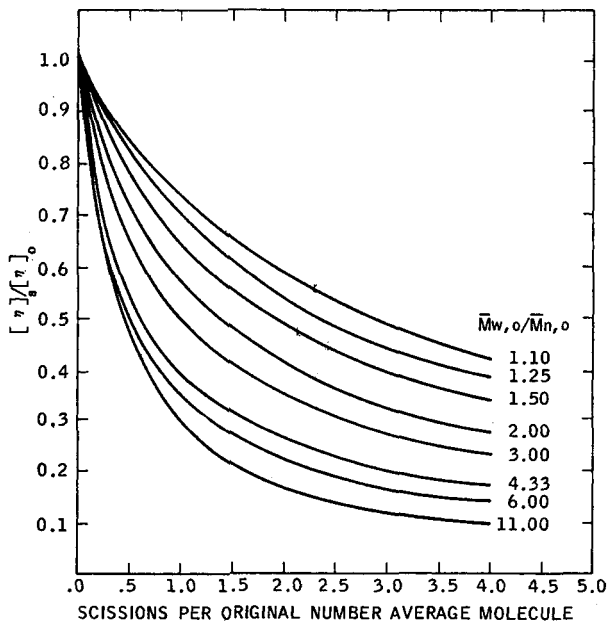


Fig. 7. Effect of degradation on intrinsic viscosity ratio for  $\alpha = 0.8$ .

values of high shear stress fluidity are possible at a single value of degraded intrinsic viscosity. Such rheological differences can best be interpreted as being due to differences in molecular weight distribution which are related to the degree of degradation that the polymer suffers at higher temperatures. It will be shown below how the data presented in Figure 5 may be explained by an analysis of the effects of random scission on intrinsic viscosity and molecular weight distribution.

Using a Monte Carlo sampling technique, Kotliar<sup>9</sup> has evaluated the distributions of molecular sizes and the molecular weight averages resulting from random chain scissions for broad Schulz-Zimm distributions.<sup>10</sup> Figure 6 illustrates the effect of the extent of random degradation on the resulting distribution width, as measured by  $\bar{M}_w/\bar{M}_n$ , for broad Schulz-Zimm distributions of varying initial breadth. In this treatment, the extent of degradation may be defined as the number of scissions per initial number-average molecule. In all cases, increases in amount of chain scission result in decreases in  $\bar{M}_w/\bar{M}_n$  ratio, in which the ratio approaches the value of two (the most probable distribution) as a limit. The Monte Carlo treatment also permits the evaluation of the ratio of degraded to initial intrinsic viscosity with a probable error of about 10%.<sup>9</sup> Thus, Figure 7 shows the effect of extent of degradation on this ratio for varying initial distribution widths and for a Mark-Houwink exponent of 0.8 (polypropylene in decalin). When the calculations are presented in the manner shown in Figure 7, the  $[\eta]_s/[\eta]_0$  ratio is independent of the initial intrinsic viscosity. It is interesting to observe that the initial slopes of the



TABLE II  
Effect of Degradation on Viscous Flow Properties of  
Molten Polypropylene

Resin	Shear rate (550°F., 8 psi shear stress), sec. <sup>-1</sup>	Resin intrinsic viscosity [ $\eta$ ] <sub>0</sub>	Degraded intrinsic viscosity [ $\eta$ ] <sub>s</sub>	[ $\eta$ ] <sub>s</sub> /[ $\eta$ ] <sub>0</sub>
A1	550	2.90	2.12	0.73
2	500	3.00	2.06	0.69
3	850	2.90	1.68	0.58
4	790	2.88	1.70	0.59
5	1030	2.84	1.50	0.53
6	700	2.92	1.90	0.65
B1	1030	2.25	1.73	0.77
2	1820	2.25	1.52	0.68
C	3180	2.15	1.40	0.65
D	2000	1.92	1.72	0.90

curves are essentially equal for broad distributions. It also may be seen from Figures 6 and 7 that the width of a distribution, as measured by the  $\bar{M}_w/\bar{M}_n$  ratio, changes very rapidly with the degree of degradation, and that the broader the initial distribution, the greater the change. This means that when two polymers of a given distribution type have different initial distribution widths, but identical initial and degraded intrinsic viscosities, the difference in distribution width is decreased by degradation. However, when polymers suffer different extents of degradation, as indicated by different [ $\eta$ ]<sub>s</sub>/[ $\eta$ ]<sub>0</sub> ratios, the differences between the degraded distributions may be greater than those observed initially. Such induced distribution variations may be used to explain the flow differences observed at constant intrinsic viscosity.

Table II presents the flow data determined at 550°F. as a function of the ratio of degraded to original intrinsic viscosity. It may be seen that the resins of the A series (highest original viscosity-average molecular weight) exhibit the greatest amount of degradation (lowest [ $\eta$ ]<sub>s</sub>/[ $\eta$ ]<sub>0</sub> ratio) at a given final intrinsic viscosity, e.g., [ $\eta$ ] = 1.7. Resin D, the resin of lowest original molecular weight, degrades least. Resins B1 and B2, and resin C, samples of intermediate molecular weight, exhibit intermediate amounts of degradation. If the original resins have similar molecular weight distributions, which is supported by the results of Figure 4, then it may be concluded that at a given intrinsic viscosity after degradation, resin D would possess a broader distribution than resins B and C, which would, in turn, have broader distributions than corresponding group A resins. Again, these conclusions result from the fact that resins exhibiting a high value of [ $\eta$ ]<sub>s</sub>/[ $\eta$ ]<sub>0</sub> have undergone relatively fewer scissions per number-average molecule (Fig. 7) than those having a lower ratio. It then follows that the resins which have undergone fewer scissions have a higher ratio of  $\bar{M}_w/\bar{M}_n$  after degradation (Fig. 6).

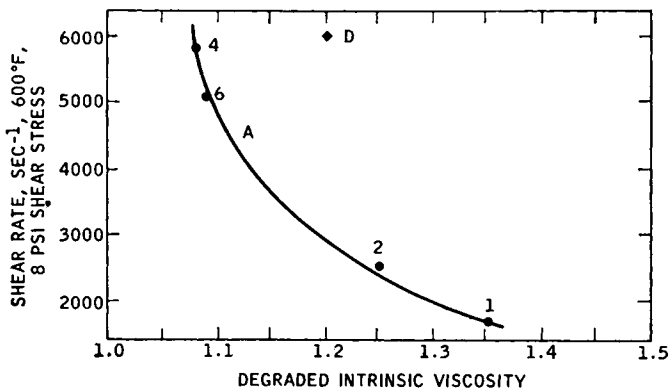


Fig. 8. Shear rate vs. degraded intrinsic viscosity, 600°F.

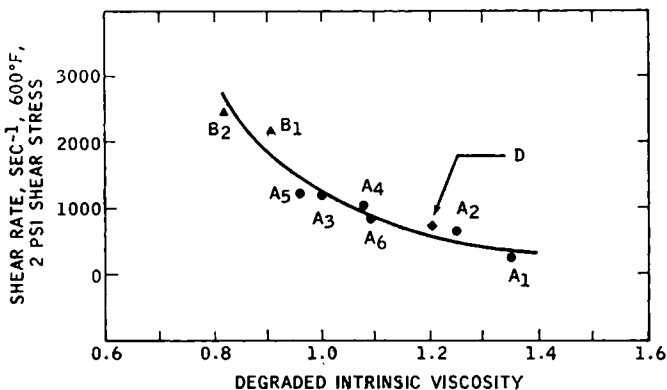


Fig. 9. Shear rate vs. degraded intrinsic viscosity, 600°F., low shear stress.

Several investigations<sup>6-8</sup> have shown that, at high shear stresses, the viscous flow tendency of a thermoplastic at a given weight-average molecular weight increases with increasing distribution width. The increase in fluidity is generally the result of an increase in pseudoplasticity or pressure sensitivity of flow. It would, therefore, be expected that at a given degraded intrinsic viscosity, resin D should exhibit the highest fluidity, and A resins the lowest. Resins B and C should be intermediate. This is clearly borne out by the results of Figure 5. It should be realized that the correlation lines drawn for A and B now cover a range of distribution widths, e.g., A5 is considerably narrower than A1. This variation has the effect of causing a marked flattening of the lines drawn.

It is important to bear in mind in these discussions that the terminology "broad" and "narrow" can be appropriately applied only to distributions having the same analytical form but differing in  $\bar{M}_w/\bar{M}_n$  ratio. With Schulz-Zimm type distributions undergoing random degradation, the analytical form remains essentially unaltered, and hence this type of distribution lends itself to the above treatment.

The results described above are further confirmed by measurements carried out at a temperature of 600°F. Figure 8 shows the shear rate-degraded intrinsic viscosity correlation obtained at a shear stress of 8 psi. Many of the resins are too fluid at this temperature for the shear rate at this shear stress to be accurately determined (see Fig. 3). It may be observed that resin D, which undergoes the least degradation at both 600 and 550°F., exhibits marked flow advantages over the more degraded A resins. The dependency of these results on molecular weight distribution is well illustrated by Figure 9, in which the shear rate at a somewhat lower shear stress (2 psi) is plotted as a function of degraded intrinsic viscosity. It may be seen that flow differences between resins of varying degraded molecular weight distribution are minimized or completely removed at the lower shear stress. This result is in agreement with published studies<sup>7,8</sup> which indicate that differences in molecular weight distribution have their primary effect on pseudoplasticity, and that distribution-induced flow differences decrease as zero shear stress is approached. It should be noted that the general form of the shear stress-shear rate relationship for non-Newtonian melts is as yet poorly defined and that a dependency of zero shear viscosity on molecular weight distribution may be possible and of some significance.

The work described in this paper shows that it is possible to interpret high temperature viscous flow behavior if it is realized that the original weight-average molecular weight of a polymer may be altered considerably by degradation, with variations in molecular weight distribution being superimposed upon the change in molecular weight. It is recognized that the extent of degradation observed in the rheological instruments used in this study may not approximate that observed in commercial processing and other operations. This should, however, impose no serious limitations on the general conclusions reached. In addition, nonrandom degradation processes, such as those induced by very high shear stresses, have not been considered here. Finally, it should be pointed out that further work, including more extensive characterization of the initial polymer distributions, is necessary for a complete evaluation of the effect of degradative conditions on the viscoelastic behavior of polymers.

### Summary and Conclusions

Rheological studies of polypropylene melts have been conducted at high temperatures over a range of molecular weights. It has been found that major changes in viscous flow behavior may be induced at these temperatures, primarily as a result of polymer degradation. Although it is possible to correlate part of the viscous flow data as a function of degraded molecular weight, large differences in fluidity may still be observed at constant molecular weight. These differences may best be explained as being the result of differences in molecular weight distributions. It is shown that the results obtained are in good agreement with those predicted from an

analysis of the effects of random chain scission on molecular weight distribution and intrinsic viscosity.

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### Résumé

On a mis en corrélation l'écoulement visqueux du polypropylène fondu avec le poids moléculaire moyen viscosimétrique dans des conditions dégradantes et non-dégradantes. On montre que l'influence d'une progression différente de la dégradation sur la distribution du poids moléculaire est un paramètre important dans cette corrélation.

### Zusammenfassung

Das Verhalten von geschmolzenem Polypropylen bei viskosem Fliessen wurde zum Viskositätsmittelwert des Molekulargewichtes unter Abbau- und Nichtabbaubedingungen in Beziehung gebracht. Der Einfluss des ungleichen Ausmasses des Abbaus auf die Molekulargewichtsverteilung erweist sich als wichtiger Parameter bei dieser Korrelation.

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