

Effects of Molecular Weight Distribution and Branching on Rheological Properties of Polyolefin Melts*

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Synopsis

The objective of this work was to determine the relationships among molecular and melt parameters of polyolefins. The polyolefins studied are polypropylene, poly-1-butene, poly-1-hexene, poly-1-octene, and poly-1-dodecene; these have regularly spaced short-chain branches. Conclusions from previous work, as well as some new data, on polyethylene are given. As the molecular weight increases, the critical shear rate decreases but the melt viscosity and non-Newtonian ratio increase. As the molecular weight distribution broadens, the critical shear rate decreases, whereas the normal forces and the non-Newtonian ratio increase. Increasing the number of short-chain branches increases the energy of activation and the melt viscosity but decreases the non-Newtonian ratio. As the length of the short-chain branches increases, the non-Newtonian ratio increases, but the melt viscosity, critical shear rate, and energy of activation decrease. Increasing the number of long-chain branches decreases the non-Newtonian ratio, but the normal forces and the melt viscosity increase. Such information allows the polymer chemist to design a polyolefin molecule having the critical melt properties required for a given production technique.

INTRODUCTION

Previous papers in this series related the molecular structure of polyethylene to its rheological parameters.^{1,2} The molecular structure included molecular weight, molecular weight distribution, and short- and long-chain branching irregularly spaced on the polymer backbone. In this paper, the influence of regularly spaced short-chain branches on rheological parameters will be examined; thus, polypropylene, poly-1-butene, poly-1-hexene, poly-1-octene, and poly-1-dodecene were investigated. A unified presentation of the effect of molecular structure of polyolefins on their melt or rheological parameters is also given. Our purpose here is to permit consideration of material modification as well as mechanical modification whenever a processability problem arises.

The rheological parameters which will be discussed are melt viscosity, energy of activation for viscous flow, non-Newtonian ratio, normal forces,

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and critical shear rate. The influence of molecular structure on each of these melt parameters will be considered separately.

EXPERIMENTAL

Molecular Parameters

The molecular weight of a polymer is represented in this paper by the inherent viscosity, $\{\eta\}$, of the polymer in Tetralin at 100°C or 145°C and at a concentration of 0.10g/100 ml, as well as by the melt viscosity given by the melt index or flow. The number-average molecular weight \bar{M}_n and weight-average molecular weight \bar{M}_w are not calculated separately but are used in defining the molecular weight distribution, MWD, which is described by fractionation curves,³⁻⁵ the U ratio, or by the $\{\eta\}_{95}$. The U ratio is \bar{M}_w/\bar{M}_n calculated from the fractionation curves by the method of Wesslau;⁶ $\{\eta\}_{95}$ is the inherent viscosity read from the integral-fractionation curve at 95% of the summation of fraction weight. The larger the $\{\eta\}_{95}$, the broader the MWD for polymers having the same MW; $\{\eta\}_{95}$ is very sensitive to the high-molecular weight end of the fractionation curve.

Short-chain branching (SCB) was varied by the use of different monomers, such as propylene, 1-butene, 1-hexene, 1-octene, and 1-dodecene, polymerized with low-pressure catalysts. This allows the influence of length of regularly spaced short-chain branching to be studied. Long-chain branching (LCB) was discussed in an earlier paper.² The length of these long-chain branches approaches the length of the main backbone of the polymer chain.

Rheological Parameters

Table I summarizes the parameters used in this investigation. The melt viscosity η of polymers is indicated by the melt index (MI), melt flow (MF), and melt strength (MS). Note that melt index and melt flow are reciprocals of η , since they are melt flows. These measurements were made by using the melt indexer and the high-pressure melt indexer described previously.^{1,2} The term "index" is used for measurements under fixed conditions at 190°C, whereas "flow" indicates a change from these conditions. Melt strength is a melt viscosity; however, it is measured at even lower shear stresses than the melt index or melt flow. Essentially, the melt strength is a measure of the ability of the melt to support its own weight.⁷ The melt recovery (MR) is a measure of the swelling of the extrudate as it leaves the die and indicates the magnitude of the normal forces. The non-Newtonian ratio is the ratio of melt flow at high shear stresses to melt flow at low shear stresses. The ratio previously used^{1,2} was the ratio of high-pressure melt flow at 1450 psi. measured in the high-pressure indexer to the melt index measured in the melt indexer at a pressure of 43.2 psi.¹ Any ratio of η at low shear stress to η at high shear stress can be used. The shear stress in the high-pressure melt indexer can be varied continuously over a wide range by a change in the nitrogen pressure. This

TABLE I
Summary of Rheological and Molecular Parameters

Parameter	Abbreviation	Unit	Reference
Critical shear rate	CSR	sec ⁻¹	1
Critical shear stress	CSS	dyne/cm ² × 10 ⁻⁶	—
Energy of activation for viscous flow	<i>E_a</i>	kcal/mole	—
High-pressure melt flow	HPMF	g/min	1
Long-chain branching	LCB	—	2
Melt flow	MF	g/10 min	1
Melt index	MI	g/10 min at 190°C	1
Melt recovery	MR	%	1
Melt strength	MS	in.	1, 7
Molecular weight	MW	g/mole	—
Molecular weight distribution	MWD	—	3, 4, 5
Shear rate	SR	sec ⁻¹	—
Shear stress	SS	dyne/cm ² × 10 ⁻⁶	—
Short-chain branching	SCB	—	—
Weight-average MW/number-average MW	<i>U</i>	—	6
Melt viscosity	η	poise	2
Inherent viscosity	{ η }	dl/g	—
{ η } at 95% summation of fraction weight from MWD	{ η } ₉₅	dl/g	3, 4, 5

variation permits the determination of the point at which the extrudate becomes rough. The shear rate at this point has been labeled the critical shear rate. The energy of activation for viscous flow, E_a (in kcal/mole), is defined by the equation

$$E_a = -Rd(\ln MF)/d(1/T)$$

where R is the gas constant and T is the absolute temperature. E_a is at constant shear stress unless otherwise noted. If E_a is high, the melt viscosity of the polymer is sensitive to temperature changes.

RESULTS AND DISCUSSION

Utility of Rheological Parameters

Some indication of the utility of these melt parameters is given in Table II. There are many exceptions to these rules, but this table is given to illustrate how these melt parameters can be used. Melt parameters usually were determined with less than 50 g of material, rather than with the 10–100 lb normally required for an experiment in production-type equipment.

In film extrusion, a low melt index is preferred to achieve toughness and other desirable physical properties of the end product. This low melt index improves the melt strength and handling of the molten web. A high critical shear rate is preferred to achieve high optical quality and extrusion with no interruptions.

TABLE II
Utility of Melt Parameters

Operation	Desired Property
Film extrusion	Low MI High MS, CSR
Extrusion coating	Low E_a High MI, MS, CSR
Injection molding	High MI, HPMI/MI, E_a
Blow molding	Low MI, E_a High MS

Similar requirements are desirable for extrusion coating, except that a high melt index is needed to achieve low melt viscosity during the coating operation. High temperatures are also used to achieve low melt viscosities and good adhesion to the substrate. A low E_a is desirable so that variation in coating thickness due to temperature variation across the long die will not occur.

In injection molding, the critical shear rate can be ignored, since the molded object will take the surface finish of the mold. The higher the melt index and non-Newtonian ratio, the shorter the time required to fill the mold and the lower the cost per unit. Also, a high non-Newtonian ratio allows lowering of the melt index to achieve better physical properties of the end product. A high E_a is preferable, since the melt viscosity can be reduced by using a higher temperature. The temperature used must be below the degradation temperature, however.

In blow molding, the shear rate is usually low and there is a mold surface to give the desired finish. The melt must support its own weight; thus, a low melt index, which improves the melt strength as well as properties of the end product, is desirable. Since temperature changes can cause irregular wall thickness, a low E_a is preferred.

Depending on the equipment used as well as on the operator, one of these factors may override all the others, causing a complete reversal in some of the rules. Other critical requirements in operation or end product have been ignored, but this discussion indicates how these laboratory-determined melt parameters can be used.

Melt Viscosity

The effect of molecular structure on the melt viscosity at low shear rates was studied. In Figure 1, the melt index (MI) and $\{\eta\}$ of various whole polyolefins are compared. The data show that the molecular weight, MWD, and both long-chain branching and short-chain branching affect the results. To remove the MWD effect, one of the low-density polyethylenes and one of the high-density polyethylenes were fractionated on a large enough scale⁵ to determine the melt index and $\{\eta\}$ of the fractions. These results, plus the curve for another low-density polyethylene prepared by a different technique are shown in Figure 2. Note the range of nine decades

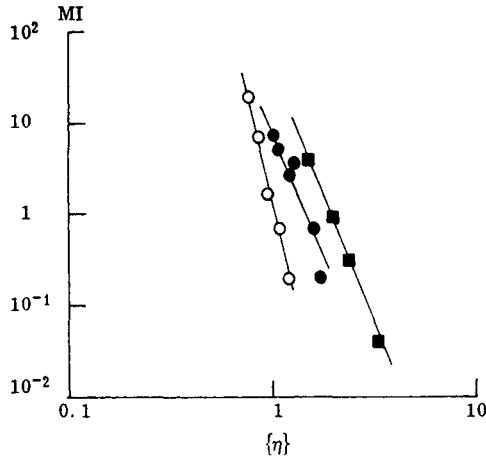


Fig. 1. Relationship between melt index and solution viscosity of whole polyolefins: (○) low-density polyethylenes; (●) high-density polyethylenes; (■) polypropylenes.

of melt index found for the fractions from one polyethylene. Special experimental techniques were developed to measure the MI of these fractions. Thus, removing the MWD variable still shows differences between these polyethylenes. When the $\{\eta\}$ is converted to molecular weight, the high-density curve is closer to the low-density (0.921) polyethylene curve. It does not, however, affect the differences between the two low-density polyethylenes. Studies of the lower molecular weight fractions of these two polyethylenes, by using the ultracentrifuge and solution viscosity in three different solvents,⁸ indicated that polyethylene having a density of 0.912 g/ml has 1.49 LCB/100 C atoms, and polyethylene having a density

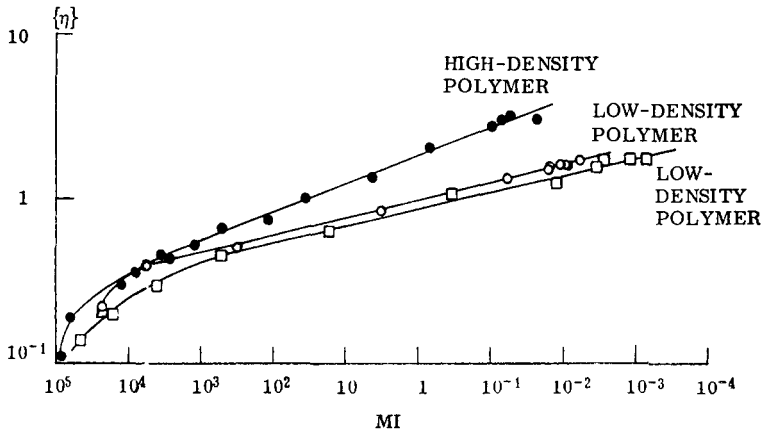


Fig. 2. Relationship between melt index and solution viscosity of polyethylene fractions: (●) density = 0.972 g/ml, 0.2 $\text{CH}_3/100\text{C}$; (○) density = 0.921 g/ml, 1.9 $\text{CH}_3/100\text{C}$; (□) density = 0.912 g/ml, 2.3 $\text{CH}_3/100\text{C}$.

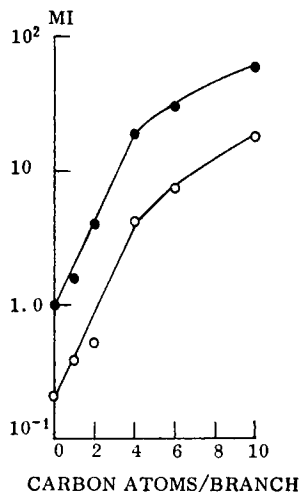


Fig. 3. Effect of length of short-chain branching on melt index: (\bullet) $\{\eta\} = 1.0$ dl/g; (\circ) $\{\eta\} = 2.0$ dl/g.

of 0.921 g/ml has 0.58 LCB/100 C atoms in the first 20% of the fractions. The remainder of the material for both polymers has a lower amount of long-chain branching. Thus, one can conclude that long-chain branching reduces the melt index of a polymer, presumably by chain entanglement. This conclusion is based on only one fraction, however. The short-chain branching difference is indicated by both the density of the annealed material and the $\text{CH}_3/100$ C determined from the infrared spectra on the whole polymers. Thus, increasing the number of short-chain branches decreases the melt index of a polymer. This conclusion is based on all the fractions of both of the low-density polyethylenes.

In a previous publication,¹ the melt strength of polyethylene was shown to increase as the MWD broadens, indicating that broadening the MWD increases the melt viscosity, particularly at low shear rates. In this case it was the high-molecular weight end of the distribution that was changed. The MWD can be varied in many ways, some of which might not show this increasing of melt viscosity with broadening of the MWD. Another point is that this is melt viscosity at low shear rate. The melt viscosity at high shear rate decreases as the MWD broadens, as will be shown later.

In Figure 3 the influence of increasing the length of short-chain branching on the melt index is indicated. These results were achieved by measuring the melt index versus $\{\eta\}$ for samples representing three different molecular weights of the same polyolefin, such as poly-1-butene. Thus, these data points are interpolated between the measured values to give the melt index for an $\{\eta\}$ of 1 and 2. All the polyolefins studied have similar slopes on their $\{\eta\}$ fractionation curves, but this does not necessarily mean that their MWD are the same. In fact, from $\{\eta\}$ -MW relationships available⁹⁻¹³ the molecular weight for $\{\eta\} = 1.0$ is as follows: high-density

polyethylene,¹⁰ 45,000; polypropylene,¹¹ 89,000; polybutene,¹² 320,000; poly(C₁₂-C₁₈) olefin,¹³ 1,070,000. Thus in spite of the increase in molecular weight and the probable broadening of MWD of these materials as the short-chain branch length increases, the melt index increases, indicating that the length of short-chain branches is overriding these other two effects. This type of short-chain branching is found on alternate C atoms, and there are a great many more branches than are found in low-density polyethylene. Most likely, the molecular explanation of this effect is that these short-chain branches cause the molecule to be more compact and do not entangle as readily as the long-chain branches and those short-chain branches irregularly spaced on the low-density polyethylene backbone.

In summary, melt flow can be decreased by shortening the length of regularly spaced short-chain branches and by increasing the molecular weight, the number of irregularly spaced short-chain branches, and the number of long-chain branches. The melt strength or low-shear melt viscosity can be increased by broadening the MWD.

Energy of Activation for Viscous Flow

The variation of several melt parameters as the molecular weight of polypropylene increases is given in Table III. The E_a increases, but the shear rate decreases as the molecular weight increases, although usually not enough to explain the change in E_a observed. In studies with polyethylene, the E_a appeared relatively insensitive to molecular weight changes. For polypropylene, there is some indication that, as the molecular weight increases, the E_a increases. In Table IV properties of polypropylenes having similar molecular weights, as indicated by their $\{\eta\}$ and melt flow, but different MWD are given. As the U increases, there is some increase in E_a but less than that observed with the molecular weight series.

In Figure 4, the influence of the length of short-chain branches on E_a is given. Note that absence of short-chain branches gave a low E_a . There is a large increase in E_a when the methyl group is added in a regular fashion to the backbone. This is also true when the short-chain branches are added in an irregular fashion, as with low-density polyethylene, where the E_a is in the range of 8-11 kcal/mole. Thus, on a molecular basis a larger

TABLE III
Influence of Molecular Weight on Rheological Properties of Polypropylene

U	$\{\eta\}$, dl/g	MF (230°C), g/10 min	MS, in.	CSR, sec ⁻¹	CSS, dyne/cm ² × 10 ⁻⁶	E_a , kcal/mole
4.6	1.48	9.58	2.9	7600	4.2	9.9
5.3	1.95	2.32	9.4	1200	3.5	10.6
4.3	2.33	0.84	13.2	1100	4.0	11.6
5.3	3.28	0.18	>100	100	3.1	17.8

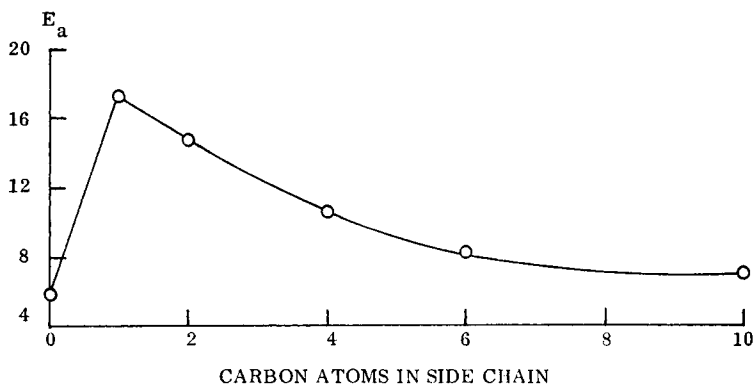


Fig. 4. Energy of activation of flow of poly-1-olefins.

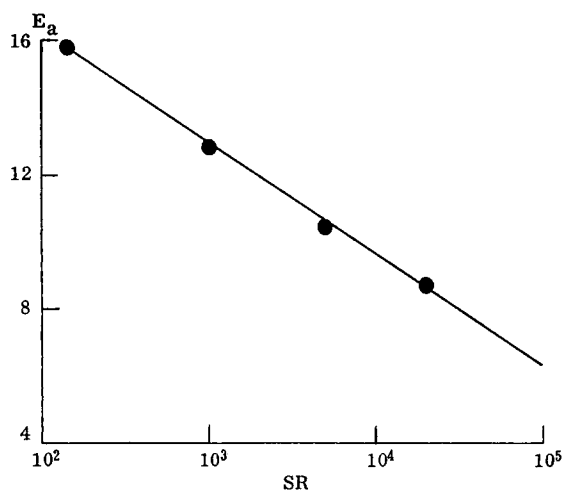


Fig. 5. Effect of shear rate on energy of activation of polypropylene.

hole is required for the movement of a low-density polyethylene or a polypropylene molecule than for a linear polyethylene molecule. Thus, short-chain branching increases E_a but as the length of these short-chain branches increases the E_a is reduced, presumably because of a more compact molecule or less entanglement.

TABLE IV
Influence of Molecular Weight Distribution on Rheological Properties of Polypropylene

U	$\{\eta\}$, dl/g	MF, (230°C), g/10 min	MS, in.	CSR, sec ⁻¹	CSS, dyne/cm ² $\times 10^{-6}$	E_a , kcal/mole
4.6	1.48	9.58	2.9	7600	4.2	9.9
12.1	1.68	5.86	4.4	4300	2.8	11.3
15.8	1.59	7.60	3.7	5800	3.0	14.7
25.6	1.74	5.35	4.7	2700	2.9	13.0

In Figure 5 is shown the effect on the E_a of polypropylene of increasing the shear rate (SR). These E_a values were at constant shear rate as measured on the Instron rheometer. A tenfold increase in shear rate reduces the E_a by about 3.4 kcal/mole. Thus, at high shear rates, the melt viscosity is not as sensitive to temperature as at low shear rates.

In summary, E_a may be increased by increasing the number of short-chain branches, by decreasing their length, and by decreasing the shear rate.

Non-Newtonian Ratio

The melt viscosity versus shear stress (SS) is plotted in Figure 6 for two polyethylenes having different MWD. The polyethylene having the broadest MWD, the one having $\{\eta\}_{95} = 2.14$, has the greatest sensitivity to shear stress or shear rate. Thus, its non-Newtonian ratio, which is the ratio of melt viscosity at low shear to that at high shear, is greater than that for the polymer having a narrower MWD. Note that increasing the MWD causes the melt flow to decrease at low shear, whereas such a change causes the melt flow to increase at high shear.

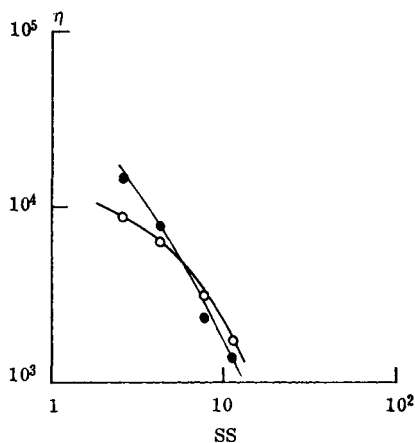


Fig. 6. Effect of shear stress on melt viscosity of two polyethylenes: (○) $\{\eta\}_{95} = 1.91$ dl/g; (●) $\{\eta\}_{95} = 2.14$ dl/g.

A previous investigation² showed that irregularly spaced short-chain branching decreases the non-Newtonian ratio and that, as molecular weight is increased, this ratio increases. This previous study also indicated that, as the MWD increases, the non-Newtonian ratio increases. Increasing the number of long-chain branches per molecule decreases the non-Newtonian ratio; presumably the entanglement causes less sensitivity to shear rate.

In Figure 7 the influence of increasing the length of the SCB is shown. These data were corrected for all polymers to $MI = 10$. The high shear stress melt viscosity was measured in a melt indexer with a 10-kg weight rather than the normal 2.16-kg weight and is designated as MF_{10} . Thus,

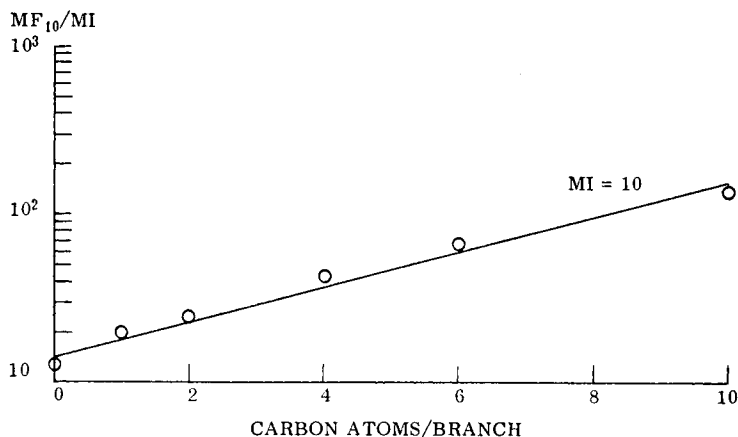


Fig. 7. Non-Newtonian ratio as a function of short-chain branching.

the non-Newtonian ratio increases as the length of the short-chain branches increases. The data in Table V illustrate that, as the temperature increases, the non-Newtonian ratio decreases. The non-Newtonian ratio in Figure 7 and Table V is not the non-Newtonian ratio used in previous work.^{1,2}

TABLE V
Effect of Temperature on Non-Newtonian Ratio of a Polyethylene^a

Temperature, °C	η_{100}/η_{100}
150	12.7
190	8.1
230	4.7

^a MI = 1.62 g/10 min; density = 0.920 g/ml.

In summary, the non-Newtonian ratio can be increased by increasing molecular weight, the U value, and the length of the short-chain branches. It can also be increased by decreasing the short-chain branching, the long-chain branching, and temperature.

Normal Forces and Critical Shear Rate

Normal forces may be defined as those forces which are normal to the plane of shear. Such forces are inherent in the definition of a viscoelastic fluid. These normal forces cause melt recovery and appear to be connected to the critical shear rate. As the MWD broadens, the melt recovery (MR) increases and the critical shear rate decreases.¹ Thus, in the previous study there appeared to be an inverse relationship between the melt recovery and the critical shear rate. In Figure 8 are shown the extrudates from three polyethylenes to illustrate the critical shear rate. With the polyethylene having very narrow MWD, the critical shear rate occurs only

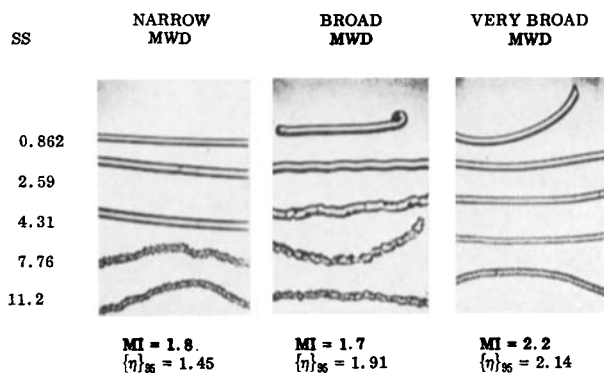


Fig. 8. Effect of molecular weight distribution on critical shear rate of polyethylenes.

over a new narrow shear rate range and is very drastic when it occurs. However, for the broader MWD, the critical shear rate occurs over a broader shear rate range, and the exact critical shear rate is sometimes difficult to pinpoint. In the polyethylene having $\{\eta\}_{95} = 2.14$, for instance, even the first extrudate has a mat surface; the first three extrudates for the polyethylene having $\{\eta\}_{95} = 1.45$ and the first two extrudates for the polymer having $\{\eta\}_{95} = 1.91$ all have high-gloss surfaces. The critical shear stress (CSS) varies from 0.9 to 7.8 for these three polymers. This range is outside the narrow range of 2 to 4 expected for most polymers. We have observed an even broader range for critical shear stress (<0.4 to 10.3) for other polyethylenes whose molecular structures are greatly different. Bagley emphasized that there is probably more than one point of origin for extrusion defects, e.g., die entry, die land, and/or die exit.¹⁴ Our critical shear rate, as recorded, merely indicates the point at which roughness of the extrudate surface was detected. No effort was made to pinpoint the location of this melt fracture. In Table IV data for polypropylene indicate that, as the MWD broadens the critical shear rate decreases, as it does with polyethylenes.¹ The rule apparently is that, as the MWD broadens, the critical shear rate decreases. The critical shear stress for these polypropylenes are within or near the expected range.

It has been shown that short-chain branching has little if any effect on the critical shear rate;² also, as the molecular weight increases the critical shear rate decreases. Figure 9 shows that lengthening the short-chain branches decreases the critical shear rate. Most of the scatter is due to the difficulty in correcting to the same melt flow. However, the decrease in critical shear rate as the length of the short-chain branches increases is clearly established.

A previous study showed that irregularly spaced short-chain branching has no effect on MR or critical shear rate. MR does not appear to be a function of molecular weight, whereas the critical shear rate decreases as the molecular weight increases. The study also showed that, as the amount

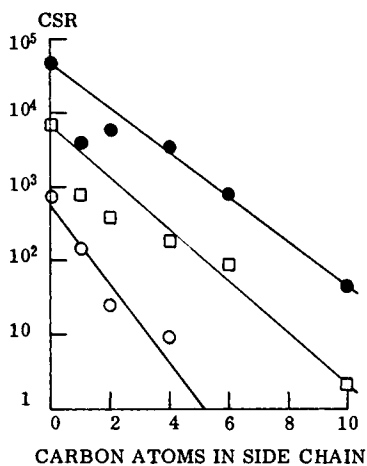


Fig. 9. Critical shear rate as a function of side-chain length: (●) MI = 10; (□) MI = 1; (○) MI = 0.1.

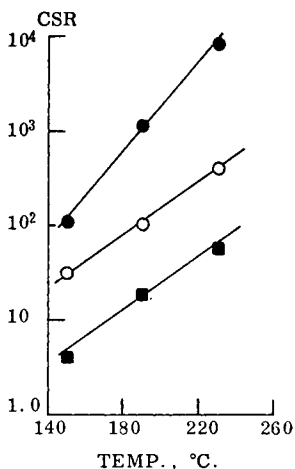


Fig. 10. Effect of temperature on critical shear rate of polyethylenes: (●) MI = 7.0; (○) MI = 1.6; (■) MI = 0.4.

of long-chain branching increases, the melt recovery increases. All of this information was determined on fractions that had been dissolved and precipitated.³⁻⁵ Schreiber and co-workers pointed out that, with such fractions, the melt recovery measurement may be a nonequilibrium measurement.^{15,16} They found that melt recovery increased as the molecular weight decreased, although they agreed that the extrudate swelling was very low compared to swelling of the whole polymer. Their explanation for the apparent increase in melt recovery at lower molecular weight was reentanglement occurs more quickly in the less viscous melts. The theory was confirmed by their finding an increase in melt recovery of a higher

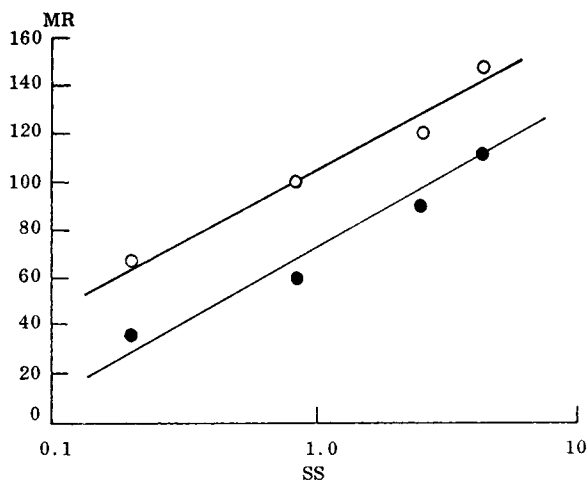


Fig. 11. Effect of shear stress on melt recovery of polyethylene: (○) MI = 1.7, density = 0.917 g/ml; (●) MI = 1.59, density = 0.923 g/ml.

molecular weight fraction with longer residence time in the melt. This effect has not been studied with our fractions. The only discrepancy between these two studies is the increase in melt recovery with decrease in molecular weight found by Schreiber and co-workers, which might be due to the variations in MWD for the fractions. Our fractions had U values⁵ between 1.0 and 1.2, whereas the fractions of Schreiber and co-workers had U values¹⁵ of about 2.

In Figure 10, the effect of increasing temperature on the critical shear rate is indicated. Thus, as the temperature is increased, the critical shear rate is also increased. In Table VI the effect of increasing temperature on the melt recovery is shown. Note that only at the higher shear stresses does a significant trend appear. This increase in MR at the higher shear stress as the temperature increases is surprising, since melt recovery and

TABLE VI
Effect of Temperature on Melt Recovery of Polyethylene^a

SS, dyne/cm ² × 10 ⁻⁶	Temperature, °C	Melt recovery, %
0.862	150	62
0.862	190	64
0.862	230	60
2.59	150	87
2.59	190	94
2.59	230	89
4.31	150	88
4.31	190	101
4.31	230	113

^a MI = 1.59 g/10 min; density = 0.923 g/ml.

critical shear rate have shown an inverse relationship to each other thus far. Here, however, both increase as the temperature increases. Some studies¹⁷ on polypropylene indicate that the swelling ratio decreases as the temperature increases. This effect, however, was at constant shear rate rather than at constant shear stress. Other investigators¹⁸ found the melt recovery of polypropylene to be independent of temperature and capillary dimensions, agreeing without low shear stress data.

Table VI and Figure 11 show that the melt recovery increases as the shear stress increases. This is in agreement with the results of other investigators.^{15,18,19} The critical shear rate is only one point on such a plot. Thus, the melt recovery and the critical shear rate must be considered separately, although inverse correlations between them appear for some polyethylenes.¹

Thus, critical shear rate can be increased by decreasing the molecular weight, the U value, and the length of the short-chain branches while increasing the temperature. The melt recovery can be increased by increasing the temperature at high shear stress, U , and long-chain branching.

CONCLUSION

Table VII summarizes the conclusions derived from this and previous investigations.^{1,2} As the molecular weight increases, the MF and critical shear rate decrease but the non-Newtonian ratio and E_a increase. There is some question about the E_a increase, since it was found only to a slight extent for polypropylene and not at all for polyethylene. As the MWD broadens, the melt flow at low shear and the critical shear rate decrease, whereas the melt flow at high shear, the melt recovery, and the non-Newtonian ratio increase. Increasing the number of short-chain branches increases E_a , but decreases the melt flow and the non-Newtonian ratio. Increasing the length of the short-chain branches increases the MF and the non-Newtonian ratio but decreases the critical shear rate and E_a . In-

TABLE VII
Effect of Molecular Parameters on Rheological Parameters*

Rheological parameter	Molecular parameters						Temp. incr.	SS incr.
	MW incr.	U incr.	Branching increase					
			SCB		LCB			
			Number	Length				
MF	-	-LS +HS	-	+	-	+	+	
MR	0	+	0		+	+HS	+	
CSR	-	-	0	-		+		
HPMF/MF	+	+	-	+	-	-		
E_a	+(?)		+	-			-	

* Code: +, increase in rheological parameter; -, decrease in rheological parameter; 0, little or no effect on rheological parameter; LS, low shear; HS, high shear.

creasing the long-chain branching decreases the melt flow and the non-Newtonian ratio and increases the melt recovery. Increasing the temperature increases the melt flow, the melt recovery at high shear stress, and the critical shear rate but decreases the non-Newtonian ratio. When the shear stress increases, the melt flow and melt recovery increase and the E_a decreases.

Among both the molecular parameters and the melt parameters, there are many interactions which can change these relationships. Here, however, an attempt has been made to separate these molecular parameters into independent critical variables which control the melt parameters. This information brings us one step closer to designing a polyolefin molecule having the critical melt parameters required for the processing technique used to shape it into its final form. Thus, if the need was for the lowest melt flow to give good physical properties but the highest critical shear rate to give good surface finish, the polyolefin would be designed to have the narrowest MWD possible with the highest molecular weight and the greatest number of short-chain branches, and the resin would be processed at the highest temperature possible. Thus, variation in the molecular structure of the polymer should be considered whenever processing difficulties are encountered.

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