

Effects of Molecular Weight Distribution and Branching on Rheological Parameters of Polyethylene Melts. Part II. Fractions and Blends*

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Synopsis

Studies of the rheological properties of fractions of linear and branched polyethylenes have shown that the melt recovery of linear polyethylene fractions is very small and independent of molecular weight over a wide range. Fractions containing high degrees of long-chain branching, on the other hand, have high melt recoveries. The melt recovery of a fraction can therefore be used as an index of long-chain branching. Alternatively, if no long-chain branching is present, the melt recovery is a unique function of the molecular weight distribution. This effect is illustrated by blends of fractions. The log of the critical shear rate is a linear function of the log melt viscosity of the fraction for both linear and branched polyethylenes. This would indicate that the critical shear rate of polydisperse samples would depend primarily on the weight-average or *Z*-average molecular weight of the polymer. This is confirmed by previous studies on polydisperse samples. It also appears that critical shear rate is highly dependent on the homogeneity of the sample. Blends of the same fractions had quite different critical shear rates, depending on the procedure used to prepare them, even though their molecular weight distributions were identical. The change in viscosity with shear rate is not a unique function of molecular weight or melt viscosity. Fractions of linear polyethylene show a greater change in viscosity with shear rate than branched fractions of similar low shear melt viscosity. This suggests that the effect is related to chain entanglement or coordinated segmental motion.

INTRODUCTION

The studies reported in the previous paper of this series¹ concerned the experimental relationships observed between molecular weight distribution and various rheological parameters. Since the data were obtained on samples of high pressure polyethylene, the possibility remains that some of the effects attributed to molecular weight distribution were actually caused by long-chain branching. The reason for this is that the synthesis conditions which favor the formation of long-chain branches in polyethylene also result in a broader molecular weight distribution.

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In the present study, an attempt has been made to separate the effect of distribution from that of long-chain branching by the use of fractions and blends of fractions. Linear polyethylene of the Phillips type was fractionated, and the fractions were used to determine the rheological parameters for a linear, unbranched ethylene polymer of uniform molecular weight. These results were then compared with data on fractions of branched polyethylenes prepared by various methods.

EXPERIMENTAL

Unless otherwise designated, the experimental procedures and methods used for determining properties were the same as those described in the previous paper.¹ Several additional measurements which were used are the following.

True Melt Recovery (TMR)

This is the melt recovery $100(d - d_0/d_0)$ in which the value of d is the actual diameter of the molten cord as it first emerges from the die. It was determined by measuring the diameter as a function of the length of the cord and extrapolating to zero length. The value was also corrected for the density change which occurs when the molten plastic is cooled to room temperature. In contrast to the MIR as defined in Part I of this series, this value then represents the actual expansion of the melt as it emerges from the die. The precision of the method was $\pm 12\%$ (2σ limits) of the measured value.

Long-Chain Branching (LCB)

Long-chain branching was determined from viscosity and ultracentrifuge data on fractions by the procedure described by Moore, Greear, and Sharp.²

Fractionation

The fractions were prepared by a scale-up of the chromatographic method described by Guillet and co-workers.^{3,4} A 100-g. portion of polyethylene could be separated into sharp fractions containing 5–10 g. by this procedure.

Molecular Weight

Molecular weights of fractions were determined from solution viscosity measurements in tetralin at 100 or 145°C. For linear polymers the relation of Tung⁵ was used. Molecular weights for branched fractions were calculated by the method described by Guillet.⁶

Melt Viscosity

Melt viscosities were calculated from melt index (MI) measurements by Poiseuille's law and without correction for entrance effects by using eq. (1):

$$\eta \text{ (poises)} = 8.25 \times 10^4 / \text{MI} \quad (1)$$

RESULTS AND DISCUSSION

Linear Fractions

The results of rheological studies on fractions of linear polyethylene are shown in Table I. Perhaps the most surprising of the results is that the true melt recovery of these linear fractions is low (about 23%) and independent of molecular weight over a range of four decades (10^4) in melt viscosity.

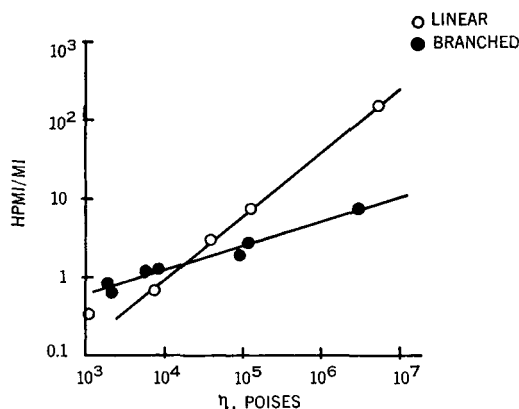


Fig. 1. Non-Newtonian behavior of polyethylene fractions.

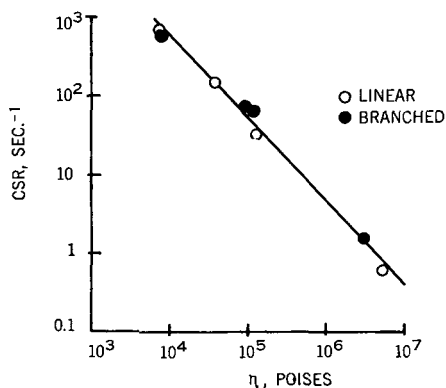


Fig. 2. Critical shear rate for polyethylene fractions.

As expected from theory, the higher the molecular weight of the fraction, the greater is the change in melt viscosity with increasing shear rate. This is shown in Figure 1, where the ratio HPMI/MI is plotted as a function of melt viscosity, and in the regular decrease in the exponent n as the molecular weight is increased. The critical shear rate decreases rapidly with increasing melt viscosity, as shown graphically in Figure 2.

TABLE I
Melt Flow Properties of Linear Polyethylene Fractions, $T = 190^\circ\text{C}$.

Fraction	MI, g./10 min.	η , poises $\times 10^{-4}$	TMR, %	CSR, sec. ⁻¹	CSS, dynes/cm. ² $\times 10^{-6}$	HPMI/MI	Power law parameters ^a		
							n_2	K_2 , poises $\times 10^{-4}$	M
D-1	0.015	546	23	0.60	1.90	157	0.356	64.7	205,000
D-2	0.63	13.1	24	32.0	2.59	7.28	0.483	16.2	82,000
D-3	2.12	3.89	27	158	3.66	2.90	0.541	8.20	57,500
D-4	10.45	0.79	22	656	3.71	0.64	0.675	2.25	37,000
D-5	73.3	0.11	23	>40,600	>12.5	0.32	0.760	0.386	23,000

^a Calculated from HPMI/MI ratio.

TABLE II
Melt Flow Properties of Branched Polyethylene Fractions, $T = 190^\circ\text{C}$.

Fraction	MI, g./10 min.	η , poises $\times 10^{-4}$	TMR, %	CSR, sec. ⁻¹	CSS, dynes/cm. ² $\times 10^{-6}$	HPMI/MI	Power law parameters ^a			Long- chain branches/ molecule
							n_2	K_2 , poises $\times 10^{-4}$	M	
E-1	0.028	300	73	1.5	1.98	7.73	0.480	72.5	200,000	7.2
E-2	0.695	11.9	24	63.3	2.50	3.37	0.531	15.1	74,000	2.6
E-3	0.915	9.02	—	71.2	2.76	1.93	0.572	10.1	65,000	2.3
E-4	10.0	0.825	14	651	2.59	1.24	0.610	2.86	40,000	1.5
E-5	14.7	0.561	24	>31,000	>12.5	1.20	0.612	2.24	39,000	1.4
E-6	37.6	0.219	25	>40,800	>12.5	0.62	0.679	0.93	36,000	1.4
E-7	45.1	0.183	19	>64,200	>12.5	0.80	0.651	0.94	31,000	1.2

^a Calculated from HPMI/MI ratio.

Branched Fractions

Rheological data on branched fractions obtained from a typical high pressure polyethylene (designated polymer A in previous publications^{3,6}) are shown in Table II along with branching data calculated from the data of Moore, Greear, and Sharp.² Here also the melt recovery is low and independent of molecular weight except for the highest fraction, which has a very high melt recovery. Since the linear fraction of similar melt viscosity has a melt recovery of only about 23%, it seems reasonable to attribute the melt recovery in this case to the large number of long-chain branches per molecule (7.2). Further confirmation of this theory is given in Table III, which shows data obtained on fractions of linear polyethylene which had been irradiated with γ -rays prior to fractionation. The radiation dose used was sufficient to cause only partial crosslinking, and it is reasonable to suppose that soluble polymers of this type would contain structures nearly equivalent to the long-chain branches found in conventional polyethylene. Again, the melt recovery of the fractions containing long-chain branches is very high indeed. On the basis of infrared determination of endgroups, the number of long-chain branches is estimated at about 20–40 per molecule for these fractions.

TABLE III
Effect of Long-Chain Branching on Polyethylene Fractions

Sample	γ^a	$[\eta]$	MI, g./ 10 min.	MIR, %	HPMI/ MI	n_2	M
Linear fraction	0	1.09	12.6	32.0	0.76	0.655	31,000
Branched fractions	1.6	1.08	0.052	80.5	1.4	0.598	170,000
Branched fractions	~ 1.6	1.22	1.29	73.2	—	—	350,000

^a γ is the long-chain-branching frequency in terms of endgroups per 1000 carbon atoms determined in this case by infrared determination of endgroups.

The data in Table II also indicate that, for a given low shear melt viscosity, a branched molecule changes viscosity to a lesser degree with increasing shear rate than a linear molecule, as might be expected from the fact that the coordination between segments in a branched molecule must be higher than in a linear molecule. This is shown graphically in Figure 1. When the HPMI/MI ratio is plotted as a function of M , the results indicate that, for a given molecular weight, there is still a considerable difference between the behavior of linear and branched fractions (Fig. 3).

On the other hand, the critical shear rate for fractions of both linear and branched polyethylenes seems to be a function only of the molecular weight of the fraction, as shown in Figure 4. Data from both linear and branched fractions fall on the same line and the experimental relationship appears to be linear over a wide range of molecular weights. This linear relation is also shown when the critical shear rate for linear and branched fractions is

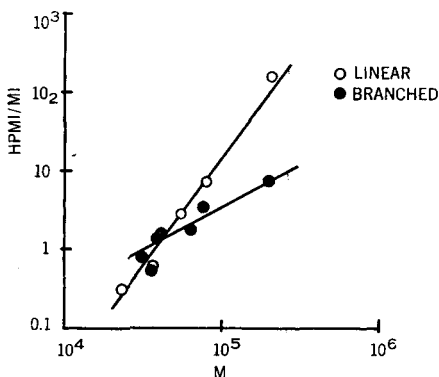


Fig. 3. Non-Newtonian behavior of polyethylene fractions.

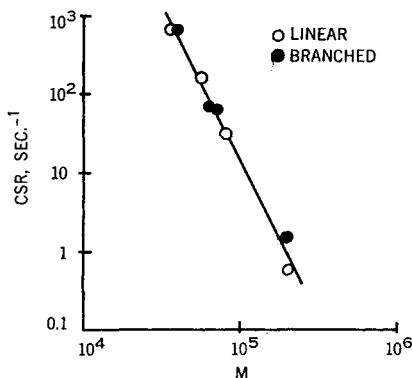


Fig. 4. Critical shear rate for polyethylene fractions.

plotted as a function of melt viscosity (Fig. 2). The data in Figure 2 can be fitted to eq. (2):

$$\log \text{CSR} = 7.09 - 1.07 \log \eta$$

One may conclude from this that the critical shear rate is a unique function of the melt viscosity and independent of chain branching. With suitable calibration this parameter could be used as an independent measurement of molecular weight. A similar relation has been proposed by Spencer and Dillon,⁷ except in their relation the critical shear stress is used in place of the critical shear rate.

Effects of Distribution

The data reported so far indicate that there are relatively simple relations between the rheological parameters for fractions and their molecular weights. The problem remains to establish the effects of distribution of molecular weight and branching on these properties. The effects of molecular weight distribution can be shown by the data on blends of linear poly-

TABLE IV
 Blends of Linear Polyethylene Fractions

Low molecular weight component		MI of high molecular weight component	Δ^a	MI, g./10 min.	TMR, HPMI/		Power law parameters ^b	
Amt., %	MI				%	MI	n_2	K_2 , poises $\times 10^{-4}$
—	—	—	0	10.45	22	0.54	0.694	2.12
46.0	73	2.10	1.5	7.23	54	1.03	0.627	3.30
43.4	312	0.77	2.6	4.59	53	1.93	0.572	5.02
50.7	1000	0.097	4.0	3.12	56	2.95	0.540	6.69

^a $\Delta = \log \text{MI (low mol. wt. component)} - \log \text{MI (high mol. wt. component)}$.

^b Calculated from HPMI/MI ratio.

ethylene fractions summarized in Table IV. It is apparent that the melt recoveries of the blends are greater than that of the fraction. These blends were prepared with the use of approximately equal portions of high and low molecular weight polymer, the proportions being calculated by the viscosity law, eq. (3), to give a melt index of 2.0:

$$\log \eta = \sum_i \omega_i \log \eta_i / \sum_i \omega_i \quad (3)$$

There appears to be a systematic deviation from this law, since the blends did not have the desired melt index. This could possibly be due to shear effects.

 TABLE V
 Effect of Long-Chain Branching on Melt Flow Properties

Low molecular weight component		High molecular weight component		MI, g./10 min.	MIR, HPMI/		Power law parameters ^a	
Amt., %	MI	MI	LCB/mole-cule		%	MI	n_2	K_2 , poises $\times 10^{-4}$
54.9	236	0.006	2.5	1.03	27	2.88	0.542	12.1
51.0	236	0.014	2.8	1.47	36	1.88	0.574	9.6
57.7	236	0.003	3.4	1.24	48	1.92	0.571	10.6
54.9	236	0.006	5.5	1.61	74	1.62	0.586	9.0

^a Calculated from HPMI/MI ratio.

The effects of long-chain branching are illustrated by the data in Table V. In this experiment a fraction of low molecular weight, high pressure polyethylene was blended with high molecular weight fractions with known degrees of long-chain branching. These blends were also designed to have the same melt viscosity, as calculated by using the logarithmic viscosity law. The melt indices of the blends were closer to the predicted values than those of the blends of linear polyethylene. The data again indicate

the remarkable sensitivity of the melt recovery measurement to changes in the structure of the polyethylene. The melt recovery increases in a uniform manner with an increase in the number of long-chain branches per molecule in the high molecular weight end of the distribution. The change in viscosity with shear rate as measured by the HPMI/MI ratio or the index n of the power law also decreases with increasing long-chain branching in the upper fractions.

The critical shear rates for all blends were lower than expected and no particular trend could be established with changes in branching. It was later established that the critical shear rate is exceedingly sensitive to the "macrostructure" of the polymer, as evidenced by the data in Table VI. These data show the very large effect of homogenization on the critical shear rate of the polymer. The MIR and HPMI/MI values were independent of blending procedures. The effect on the rheological parameters of dissolving and reprecipitating a polymer sample is shown in Table VII. Again, the critical shear rate is substantially reduced by this procedure, but the values of MIR and HPMI/MI are unchanged within the precision of the experimental techniques. It is not known exactly what changes in macrostructure account for this very large change in CSR, but this is presently the subject of further investigation.

TABLE VI
Influence of Blending on Critical Shear Rate

Blending method ^a	MI, g./10 min.	MIR, %	HPMI/MI	CSR, sec. ⁻¹
Banbury	0.70	48	0.96	6800
Brabender	0.73	49	0.96	5800
Solution	0.61	49	0.98	7

^a Polyethylene of 0.03 MI blended with 31% of a polyethylene of 2400 MI.

TABLE VII
Effect of Dissolving Polymer on Melt Properties

Treatment	MI, g./10 min.	MIR, %	HPMI/MI	CSR, sec. ⁻¹
—	1.65	35	2.8	537
Dissolved, precipitated	1.70	35	3.3	275

CONCLUSION

It is concluded from this study that long-chain branching in polyethylene increases the melt recovery and decreases the divergence from the Newtonian viscosity law (change in viscosity with shear rate) for molecules of equivalent melt viscosity.

The critical shear rate may be largely a function of the macrostructure and unrelated to the structural details of the polymer molecules in the melt.

It does, however, appear to be strongly influenced by the degree of homogeneity of the melt on a macroscale.

The critical shear rate for both linear and branched fractions appears to be a unique function of the low-shear melt viscosity (η) or molecular weight (M). Over a relatively broad range of shear rates, the relationship is of the form:

$$\begin{aligned}\log \dot{\gamma}_{cr} &= A - B \log M \\ &= A' - B' \log \eta\end{aligned}$$

Although we have not determined the proper average molecular weight to use with this relation when the samples are polydisperse, the observed sensitivity of the CSR to small changes in the upper end of the distribution¹ would indicate that the weight-average or Z -average molecular weight should be used.

The change in viscosity with shear rate, as measured by the ratio of high-shear to low-shear viscosity or by the parameter n of the power law, is not a unique function of molecular weight or viscosity. It is strongly dependent on the degree of branching as well, being much reduced by the presence of long-chain branches. This suggests that the effect is related to chain entanglement or coordinated segmental motion.

For molecules containing little or no long-chain branching, the melt recovery appears to be a function only of the breadth of the molecular weight distribution. When the number of branches per molecule exceeds about three, the melt recovery increases rapidly. The melt recovery of polydisperse samples with similar breadths of distribution increases with an increase in the amount of long-chain branching in the high molecular weight end of the distribution.

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Résumé

L'étude des propriétés rhéologiques de fractions de polyéthylène linéaires et ramifiées a montré que le recouvrement du polymère fondu des fractions de polyéthylène linéaires est très petit et pratiquement indépendant du poids moléculaire dans un large domaine. Les fractions qui contiennent de fortes concentrations de ramifications longues ont d'autre part des recouvrements très élevés. Le recouvrement d'une fraction peut par conséquent être considéré comme un indice de ramification à longue chaîne, autrement

dit, s'il n'y a pas de ramification à longue chaîne présente, le recouvrement est une fonction unique de la distribution du poids moléculaire. Cet effet peut être illustré en mélangeant les fractions. Le logarithme de la vitesse de cisaillement critique est une fonction linéaire du logarithme de la viscosité des fractions aussi bien pour les polyéthylènes branchés que linéaires. Ceci montre que la vitesse de cisaillement critique des échantillons polydispersés devrait dépendre en premier lieu de la moyenne en poids ou moyenne 'Z' du poids moléculaire du polymère. Ceci a été confirmé lors d'autres études sur les échantillons polydispersés. Il apparaît également que la vitesse de cisaillement critique dépend de l'homogénéité des échantillons. Des mélanges de ces mêmes fractions ont des vitesses de cisaillement critique, fractions du processus de préparation, même si la distribution de poids moléculaire est identique.

Zusammenfassung

Eine Untersuchung der rheologischen Eigenschaften von Fraktionen von linearem und verzweigtem Polyäthylen zeigte, dass die elastische Erholung von Schmelzen linearer Polyäthylenfraktionen sehr gering und in einem weiten Bereich vom Molekulargewicht unabhängig ist. Andererseits besitzen Fraktionen mit einem hohen Grad an Langkettenverzweigung eine hochgradige Erholung der Schmelze. Die Erholung einer Schmelze kann daher als ein Index der Langkettenverzweigung verwendet werden. Oder, wenn kein Langkettenverzweigung vorliegt, ist die elastische Erholung der Schmelze nur ein Funktion der Molekulargewichtsverteilung. Dieser Effekt wird an Mischungen von Fraktionen illustriert. Der Logarithmus der kritischen Schergeschwindigkeit ist ein lineare Funktion des Logarithmus der Schmelzviskosität der Fraktion für lineares und verzweigtes Polyäthylen. Dies deutet an, dass die kritische Schergeschwindigkeit von polydispersen Proben in erster Linie vom Gewichtsmittel oder Z-Mittel des Molekulargewichts des Polymeren abhängt. Dies wurde durch frühere Untersuchungen polydisperser Proben bestätigt. Die kritische Schergeschwindigkeit scheint auch in hohen Masse von der Homogenität der Probe abhängig zu sein. Mischungen derselben Fraktionen halten in Abhängigkeit von den Herstellungsmethoden ganz verschiedene Schergeschwindigkeiten, obwohl ihre Molekulargewichtsverteilungen identisch waren.

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