On the Effects of Very Low Levels of Long Chain Branching on Rheological Behavior in Polyethylene

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Synopsis

A comparison is made of the effects of very low levels of long chain branching (less than 0.1 branch per 1000 CH_2) on the rheological behavior of polyethylene for samples, in which the branching has been introduced by means of peroxide decomposition or thermal-mechanical degradation. Both the activation energy and viscosity at low rates are shown to increase considerably more rapidly with branching level for samples containing branching formed from peroxide decomposition than for samples containing branching formed as a result of thermal or mechanical degradation. A model, which is based on parameters obtained for highly branched low density polyethylene and experimental molecular structure measurements, is shown to adequately account for the flow curves of samples containing branching introduced by thermal or mechanical degradation. Poor agreement of the model with experimental flow curves for peroxide branched samples is obtained, presumably because of the inability of the low density polyethylene parameters to adequately describe the flow properties of these samples, which are thought to contain tetrafunctional branch points. The good agreement between theoretical models, predicting relationships between activation energy and branching level, and experimental data is taken as lending further credence to the idea that the large variations seen in the rheological behavior with branching concentration at low branching levels are due to changes in the relative proportion of discrete branched and linear species with branching level. In accord with experimental results, a maximum in low rate viscosity with branching level is predicted. The maximum is predicted at approximately 0.25 branches/1000 CH_2.

INTRODUCTION

Long chain branching has been demonstrated to have significant effects on the rheological behavior,[1,2] morphology, physical properties,[3] and environmental stress cracking[3] of polyethylene. Until recently,[1,4] no method of systematically characterizing polyethylenes with very low long chain branching (LCB) levels has been suggested. One model,[1] giving a relationship between melt viscosity and branching level, was based on the assumption that variations in rheological behavior with branching level reflects the variations in the proportion of discrete branched and linear molecular species.

Another method of characterization has been reported,[4] which involves the measurement of flow activation energy for samples of "known" branching level. In this case, the activation energy was shown to monotonically increase with LCB level, for LCB levels assumed from known peroxide levels and the assumption that each peroxide molecule leads to one tetrafunctional branch or two branches as per the NMR and infrared conventions.

It is the purpose of this paper to compare the experimental and predicted relationships between activation energy, viscous behavior, and branching

level for branching which has been introduced by peroxide decomposition, thermal-mechanical degradation, or free radical polymerization (LDPE).

EXPERIMENTAL

The polyethylene samples involved in this study are given in Table I, together with pertinent data. Samples P_1–P_5 were all prepared from the unstabilized HDPE powder sample, P_0, by the addition of varying amounts of dicumyl peroxide. The resulting sample was compression molded for 15 min at 190°C between aluminum foil. All samples were then stabilized before rheological measurements were made. The #LCB/1000 CH_2 was calculated by assuming[4] one tetrafunctional crosslink or two LCBs will be produced by each peroxide molecule. Samples H_1–H_7 are various experimental and commercial samples, which have been subjected to various thermal and mechanical histories, such that it is assumed that any LCB present has been formed as a result of these mechanisms. Samples L_1–L_4 are commercial high-pressure polyethylenes, which are known to contain relatively high LCB levels, while L_5 is the NBS 1476 standard LDPE.

Activation energy was measured using the Rheometrics mechanical spectrometer to obtain the dynamic shear modulus at temperatures ranging from 150 to 190°C. A single specimen was used for the various temperatures, since it was demonstrated that comparable results could be obtained on samples corrected (for degradation) to the use of multiple specimens at the various temperatures. Only the range from 10^0 to 10^1 rad/s was covered in order to minimize time in the instrument. The time between runs at successive temperatures was about 5 min and the total test time approximately 40 min. The dynamic shear modulus was used in this study, because only a simple shift along the frequency axis[5] should be required, in order to superimpose the data at the different temperatures. The shift factors, a_T, were obtained from

$$a_T = \frac{\omega(\text{reference})}{\omega(T)} \qquad (1a)$$

where $\omega(\text{reference})$ and $\omega(T)$ are the ω at which a given G' is observed at the different temperatures. An apparent activation energy was calculated from a regression analysis of the temperature shift factors using an Arrhenius-type relationship,[5] $a_T = \exp[(E/R)(1/T - 1/T_R)]$, where E is the activation energy, R the gas constant, and T_R the reference temperature. The data were corrected for any slight degradation as indicated in the Appendix. The viscosity as a function of rate was a combination of dynamic complex viscosity, η^*, which has been generally found to be close to the steady shear viscosity for $\dot{\gamma} = \omega$ at low rates, and steady shear data from an Instron capillary rheometer. The low rate data were generated in the dynamic mode, because, in the steady shear cone and plate configuration, the time for sample relaxation was prohibitively long (>6 hs).

The molecular weight distribution data were obtained using a Waters Model 150C GPC at 135°C with trichlorobenzene as solvent. Calibration was effected using a modification of the universal calibration procedure. Long chain branching determinations for L_1–L_4 were made using the Ram–Miltz

TABLE I
Molecular Characteristics and Activation Energy of the Polymers Used

Sample ID	Corrected for LCB[1]				E_a (kcal/mol)	#LCB/1000C[a]				Viscosity at $\omega = 10^{-2}$ rad/s (P)
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$		(1)	(2)	(3)	(4)	
P_0 (0% peroxide)	24.7	161	625	6.6	5.5	0	0	0	0	2.1×10^5
P_1 (0.01% peroxide)	27.7	177	631	6.4	6.2	0.0103	0.017	0.048		1.6×10^6
P_2 (0.02% peroxide)	26.2	177	633	6.9	6.3	0.0207	0.02	0.092		4.2×10^6
P_3 (0.03% peroxide)	27.9	187	672	6.7	7.2	0.0311	0.047	0.096		8.1×10^6
P_4 (0.04% peroxide)	23.6	185	688	7.9	7.5	0.0415	0.062	0.132		1.2×10^7
P_5 (0.05% peroxide)	24.1	185	649	7.7	7.5	0.052	0.062	0.122		
HDPE										
H_1	12.1	129	818	10.6	7.0			0.043		6.5×10^5
H_2	17.7	137	801	7.7	7.0			0.046		8.6×10^5
H_3	26.8	163	852	6.1	6.0			0.016		3.7×10^5
H_4	17.7	139	822	7.8	7.8			0.061		1.18×10^6
H_5	12.7	161	891	12.8	7.1			0.052		1.96×10^6
H_6	10.9	161	1070	14.8	5.5			0		1.8×10^5
LDPE										
L_1	21.3	167	630	7.8	12.0				1.16	1.60×10^6
L_2	17.6	147	560	8.4	12.0				0.90	1.35×10^6
L_3	15.0	198	1680	13.2	12.1				2.40	7.0×10^3
L_4	20.5	184	1000	9.0	12.3				1.60	2.1×10^5

[a] For tetrafunctional branching, two branches per branch point are assumed according to the NMR or infrared conventions: (1) Branching calculated based on the assumption that one tetrafunctional crosslink or two branches will be produced from each peroxide molecule, according to the conventions commonly used in NMR or infrared analysis. (2) Branching calculated based on measured activation energy and eqs. (11), (14), and (15). (3) Branching level calculated by the method in text of comparison of predicted low shear viscosity to experimentally determined data. (4) Branching calculated by the Ram–Miltz[6] technique.
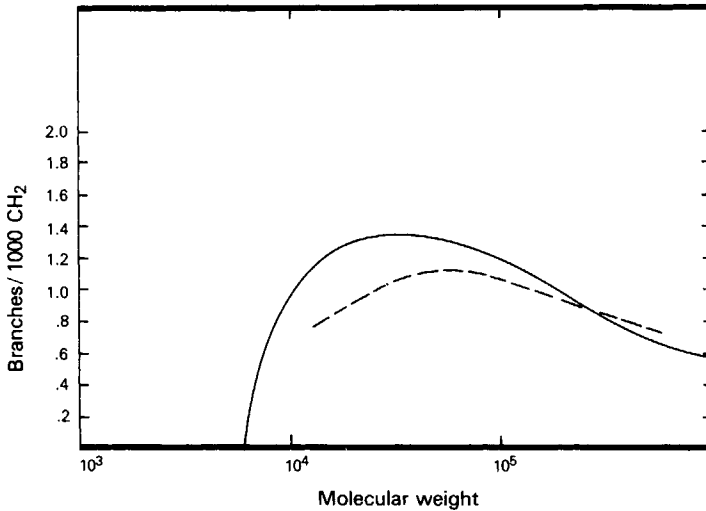
Fig. 1 Comparison of branching as a function of molecular weight for the NBS 1476 standard: (-) our analysis; (- - -) based on the analysis of fractions by Wagner and McCrackin.[8]

technique.[6] The ratio of the branched to linear viscosity was assumed to be related to $g^{0.75}$ as found appropriate by Hamielec et al.[7] Good agreement with Wagner and McCrackin[8] on branching as a function of molecular weight for the NBS 1476 LDPE standard as obtained using $g^{0.75}$ as shown in Figure 1.

PREDICTIONS OF VISCOSITY AS A FUNCTION OF SHEAR RATE

The viscosity as a function of shear rate was predicted as follows. The viscosity for a given sample was assumed[1] to be related by

$$\eta(\dot{\gamma}) = (\eta_L(\dot{\gamma}))^{W_L} (\eta_B(\dot{\gamma}))^{W_B} \tag{1}$$

where η_B and η_L are the viscosities of the branched and linear distributions making up the sample under consideration, and W_B and W_L the respective weight fractions. The respective distributions were calculated[1] from

$$\overline{h}_{Li} = \frac{\overline{h}_i P_i}{W_L} \qquad \overline{h}_{Bi} = \frac{\overline{h}_i(1 - P_i)}{(1 - W_L)} \tag{2}$$

where $\overline{h}_i$ is the normalized weight fraction of component i in the sample and P_i the probable fraction of component i that is linear. As will be shown later, P_i can be calculated from simple statistical considerations. Predictions of the viscosity as a function of molecular structure were made from

$$\eta(\dot{\gamma}) = K((gM)_w{}^*)^A$$

where

$$(gM)_w{}^* = \sum_{i=1}^{c-1} \overline{h}_i(gM)_i + (gM)_c \sum_{i=c}^{\infty} \overline{h}_i \tag{3}$$

and

$$(gM)_c = M_0(\dot{\gamma})^d$$

For linear polyethylene ($g \equiv 1$) log(K), A, M_0, and d were determined to be -12.50, 3.36, $850,000$, and -0.29, respectively. As reported previously[1] for $g^{0.5}$, log(K), A, M_0, and d were determined here for branched LDPE to be -48.79, 11.44, $127,000$, and -0.16, respectively for $g_{0.75}$. Predictions from MWD measurements for a given intrinsic viscosity given from the Ram–Miltz[6] technique gave the g_i. P_i was calculated for use in eq. (2) from the statistical relationships given in the next section. Predictions of the viscosity as a function of shear rate from eqs. (1)–(3) were compared to experimental low shear rate (0.01 s^{-1}) viscosity measurements.

By varying the intrinsic viscosity used to give varying branching levels, agreement between the predicted and experimental viscosity at $\dot{\gamma} = 10^{-2}$ was obtained by means of an interval halving technique. The number of branch points per 1000 CH$_2$ units was calculated from

$$\frac{\text{number of LCB}}{1000\ \text{CH}_2} = 14,000\ \Sigma\ \bar{h}_i m_i / M_i \tag{4}$$

where m_i is the average number of LCB/molecule for species i.

STATISTICS FOR BRANCHING MECHANISMS

In accounting for the variation in viscosity and activation energy with branching level, the weight fractions of branched and linear species will be necessary. As will be shown from the following arguments, the dependency of these weight fractions at a given branching level should depend on branching mechanism and functionality. For branching that arises as a result of mechanical or thermal degration, the following scheme for LCB formation is generally agreed upon.[9]
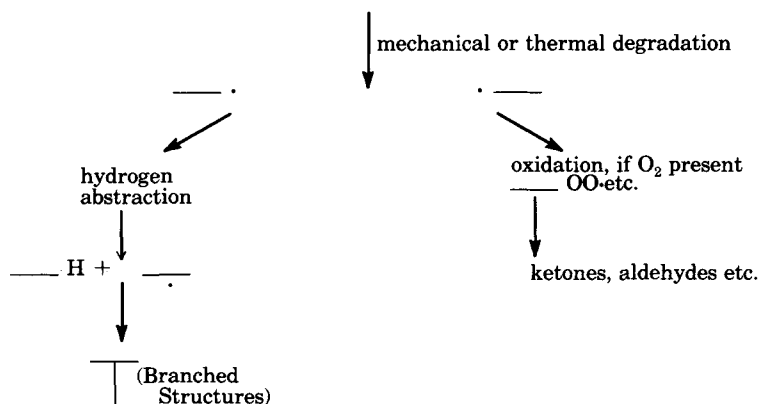
In order to calculate W_L, we must evaluate P_i, the probable fraction of species i that is linear. From the Ram–Miltz technique, g_i can be obtained. Additionally, from a rearrangement of the Zimm–Stockmayer[10] relationship for trifunctional branching, a good approximation to n is

$$n = 3.5\ [2g^{-2} + 1\ -\ \sqrt{4g^{-2} + 5}] \tag{5}$$

where n is the number of branch points/molecule.

We therefore will consider n as given by the Ram–Miltz procedure; for N molecules we have a total of nN branch points. Since n is obtained from the Ram–Miltz technique at a given hydrodynamic volume, $[\eta]_B M_B = [\eta]_L M_L$ or $M_B = [\eta]_L/[\eta]_B\, M_L$. However, for low branching levels $[\eta]/[\eta]_B$ is close to unity and $M_B \simeq M_L$. In distributing the nN branch points for a given molecular weight species, the probability of a given molecule of molecular weight M remaining linear will be proportional to ratio of the mass of all molecules minus the chosen molecule to the mass of the molecules. Letting the average branch molecular weight be bM, the initial molecular mass is $NM - nNbM$ and the mass after the addition of m branches $NM - nNbM + mbM$. The probability P of this molecule remaining linear after the distribution of nN branch points is

$$P = \left(\frac{NM - nNbM - M}{NM - nNbM}\right) \cdot \left(\frac{NM - nNbM + bM - M}{(NM - nNbM + bM)}\right) \cdots \cdots$$
$$\left(\frac{NM - nNbM + mbM - M}{NM - nNbM + mbM}\right) \cdots \left(\frac{NM - M}{NM}\right) \tag{6}$$

In the limit of large N, eq. (6) becomes

$$P = [1 - bn]^{1/b} \tag{7}$$

In order to evaluate b, we shall consider that no molecule contains more than two branch points, for low branching levels. Further, we will assume that, on average, a molecule with one branch has a branch molecular weight $M/3$ and with two branches a branch molecular weight of $M/5$. Therefore, the average branch molecular weight is

$$\langle M_B \rangle = \alpha M/3 + (1 - \alpha)\, M/5 \tag{8}$$

where α is the distribution function between single and double branching. α can be obtained from

$$n = 1(1 - P)\alpha + 2(1 - \alpha)(1 - P)$$
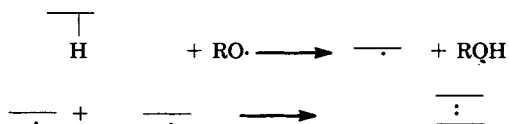
or

$$\alpha = 2 - \frac{n}{(1 - P)} \tag{9}$$

Finally

$$b = \frac{1}{3}\left(2 - \frac{n}{(1 - P)}\right) + \frac{1}{5}\left(\frac{n}{(1 - P)} - 1\right) \tag{10}$$

From Equations (7) and (10) we have an implicit relationship between P and n. Numerical calculation shows that P for trifunctional branching can be closely approximated by

$$P = \exp(-1.18\, n) \tag{11}$$

For the case of a radical initiator, such as using a peroxide, as the following depicts:

$$\text{H} \quad + RO\cdot \longrightarrow \quad \overline{}\cdot \quad + RQH$$

$$\overline{}\cdot \; + \; \overline{}\cdot \quad \longrightarrow \quad \overline{\overline{}}$$

There are two major differences between this branching scheme and that is due to thermal or mechanical degradation. First, LCBs are generally added two at a time. Second, for each union of macroradicals, the number of molecules is reduced by one.

For the tetrafunctional case a good approximation of the Zimm–Stockmayer relationship for tetrafunctional branching is

$$n = 6\left[\left(\frac{-1 + \sqrt{1 + 10.2 \ (2.55 + g^{-2})}}{5.1}\right)^2 - 1\right] \tag{12}$$

where n is the number of branch points or tetrafunctional branches per molecule. b can be shown to be

$$b = \frac{1}{2}\left(2 - \frac{n}{1 - P}\right) + \frac{2}{7}\left(\frac{n}{(1 - P)} - 1\right) \tag{13}$$

Similar to the trifunctional case and combining eqs. (7) and (12), P for tetrafunctional branching can be approximated by

$$P = \exp(-1.34n) \tag{14}$$

RESULTS AND DISCUSSION

Comparison of Predictions of the Statistical Branching Model for Peroxide-Introduced Branching with Experimental Activation Energy Data

It has been experimentally found[11] that the activation energy for a blend of branched and linear species of polyethylene is a linear function of weight fraction of each species such that

$$E = W_L E_L + W_B E_B \tag{15}$$

where E_L and E_B are the activation energies characteristic of linear and branched materials, respectively. Consequently, from eqs. (11), (14), (15), and (16), we should be able to obtain a theoretical relationship between activation energy and branching level for a given sample. E_L and E_B have been determined to be 5.5 and 12 kcal/mol (for LDPE), respectively, as indicated in Table I. However, even the highly branched LDPE samples used here contain ~15% linear polyethylene for molecular weights less than ~6000. Therefore, using eq. (15), we get $E_B = 13.1$ kcal/mol for pure

branched polyethylene. It should be noted that the degree of branching for the LDPE samples had no apparent systematic effect on E_a.

For polydisperse samples the weight fraction of linear species can be calculated from

$$W_L = \Sigma \bar{h}_i P_i \qquad (16)$$

where $\bar{h}_i$ is the weight fraction of species i. For a given sample MWD the P_i can be calculated from eq. (14) and the Ram–Miltz branching analysis, and different branching levels can be generated by choosing different sample intrinsic viscosities to be used in the Ram–Miltz procedure. Consequently, from eq. (15), a theoretical relationship between E_a for the polydisperse sample and branching level is obtained. The MWD used in these evaluations was that of sample P_0, since the results were found to be relatively insensitive to the sample choice.

The theoretical relationship, along with both experimental data (as given in Table I), and the previously reported relationship by Hughes[4] are compared in Figure 2. The line of Hughes has been shifted to reflect different values of E_a for no branching. This difference may only reflect differences in the branching levels in the starting sample with no peroxide treatment, which is tacitly assumed to be linear. In any case, the comparison between our data and the shifted data of Hughes reveals essentially the same trend of E_a with branching level. Additionally, the theoretical treatment for the peroxide-induced LCB formation, which is based on the statistics of eq. (14), is in relatively good agreement with the experimental trends of our data and experimental data of Hughes.[4] However, the experimental data do not appear to reflect the curvature predicted by theory, but considering the extremely low branching levels and the scatter in the data, the agreement is considered good.
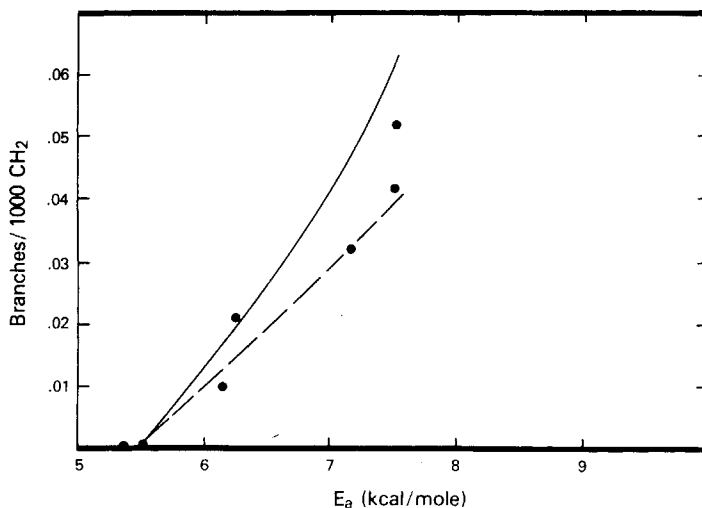

Fig. 2 Relationship between branching (one tetrafunctional branch is considered two branches to correspond to the convention of NMR and infrared analysis) and activation energy: (●) data for samples P_0–P_5; (-) a theoretical relationship based on eq. 14; (- - -) the trend established by Rideal and Padget.[9]

It is also interesting to note that the experimental relationships in Figure 2 suggest that the E_a equivalent to that found for low density polyethylene should be reached at much lower branching levels (ca. 0.15 LCB/1000 CH_2) than those present in the LDPE samples. It therefore appears that the activation energy is "saturated" for the high branch levels in LDPE. This conclusion is consistent with the idea that E_a varies at the lower branching levels because of varying proportions of branched and linear species with branching level.

Comparison of Experimental Activation Energy with Model Predictions for Branching By Thermal-Mechanical Degradation

The samples H_1-H_6 are commercial and experimental resins, which have experienced varying thermal-mechanical histories. It is beyond the scope of this paper to correlate these histories with the levels of LCB, but rather our concern will be with the estimation of LCB and activation energy from experimental measurements, and the subsequent comparison to the expected relationship based on eq. (11).

The LCB levels were estimated from a relationship reported previously,[1] which predicted the viscosity as a function of shear rate for branched materials. In the present case, hypothetical LCB levels were systematically introduced on the computer until a best match of the predictions with the rheological data was obtained. A comparison of the calculated branching level with activation energy is given in Figure 3. Also included is the theoretical relationship between activation energy and branching level based
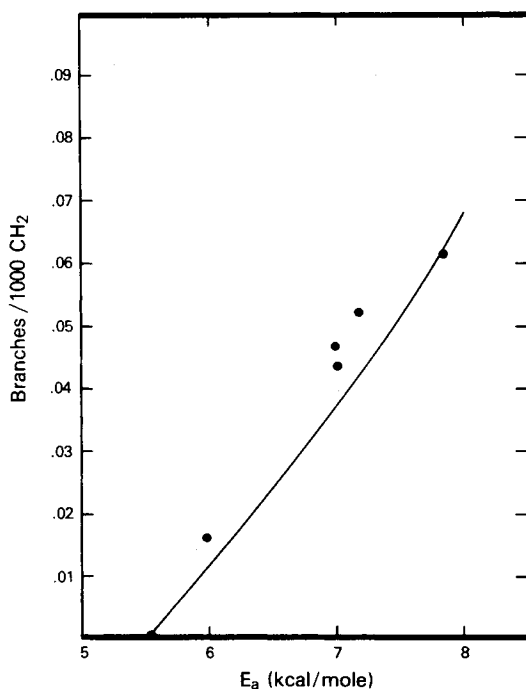

Fig. 3   Comparison of the theoretical relationship (-) based on eq. 11 and experimental data for samples H_1-H_6.

on eq. (11). As in the case with the peroxide-treated samples, relatively good agreement between the theoretical relationship and experimental determinations is seen, considering the extremely low levels of LCB that are believed to be present. The agreement between the theoretical relationship for activation energy and branching and that determined using experimental E_a data and branching data, based on a highly branched LDPE model, suggests a high degree of self-consistency in the approach used here.

It should be pointed out that the statistical model as reflected in eq. (11) has been used in both the theoretical relationship between E_a and LCB/1000 CH_2 and the independent estimation[1] of LCB concentration from the combination of rheology and molecular weight distribution results. Consequently, the agreement between the theoretical relationship and that based on experimental data does not necessarily prove that the model for the thermal-mechanical introduction with trifunctional branching is the correct one for this group of samples. However, it does suggest that given the assumption of this model, the relationship between LCB as determined using GPC and melt viscosity data and activation energy is consistent with that obtained from the simple statistical model given for thermal-mechanical introduction of LCB.

Dependence of Rheological Behavior on Long Chain Branching Content

The predicted dependence of viscosity on LCB content for polyethylenes, which branch according to the thermal-mechanical mechanism, has previously been reported.[1] Figure 4 compares the predicted viscosity as a function of rate with experimental data for samples H_3 and H_4. As can be seen, the experimental crossover in the data for the two samples containing different branching levels is predicted based on the molecular structure and the models, as given in eqs. (1)–(3). This agreement is gratifying in that
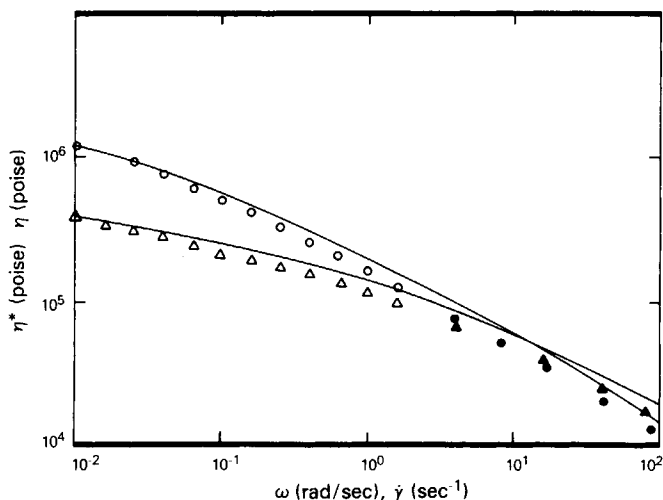

Fig. 4 Viscosity as a function of rate for samples H_3 (○,●) and H_4 (△,▲): (-) predicted responses based on eqs. (1)–(3) (●,▲) steady shearing; (○,△) dynamic data.

the parameters used in the model were those obtained from highly branched LDPE samples, and no flexibility in the model or adjustable parameters were allowed. This agreement also tends to reinforce the assumption of similar branch types (trifunctional) for both the LDPE and thermal-mechanical branched samples.

For the case of samples P_0–P_5 the comparison in Figure 5 is not so good. This is not surprising, since the rheological model as given in eqs. (1)–(3) was based on LDPE samples, which are generally assumed to contain trifunctional branching. The results in Figure 5 suggest that branching obtained by means of peroxide degradation, assumed to be tetrafunctional, produces considerably more dramatic differences in low rate viscosity behavior than trifunctional branching obtained by thermal or mechanical degradation.

Both the experimental data and predictions show spectacular increases in low rate viscosity with increases in branching at low branching levels. Predictions of low shear rate viscosity as a function of branching is given in Figure 6. A very distinct maximum is predicted; this predicted maximum comes about because of the opposing effects of branching on the weight percent of the higher viscosity branched component and the reduction of the mean squared radius of gyration with branching level. At low branching levels, increases in branching level mainly increase the proportion of the more viscous branched component, while at higher levels the reduction in the mean squared radius of gyration is the dominant effect, such that low shear rate viscosity steadily decreases with branching level. The LDPE, L-3, point in Figure 6 appears to adequately agree with the predictions. Based on the experimental data of Constantin,[12] a maximum in η_0 is predicted at a ratio of branched to linear intrinsic viscosities of 0.77 for a molecular weight of 120,000. For a MWD similar to that calculated in Figure 6, this would correspond to ~0.24 LCB/1000 CH$_2$, which is in good agreement with the predictions in Figure 6 for $\overline{M}_w = 130,000$. Also agreement
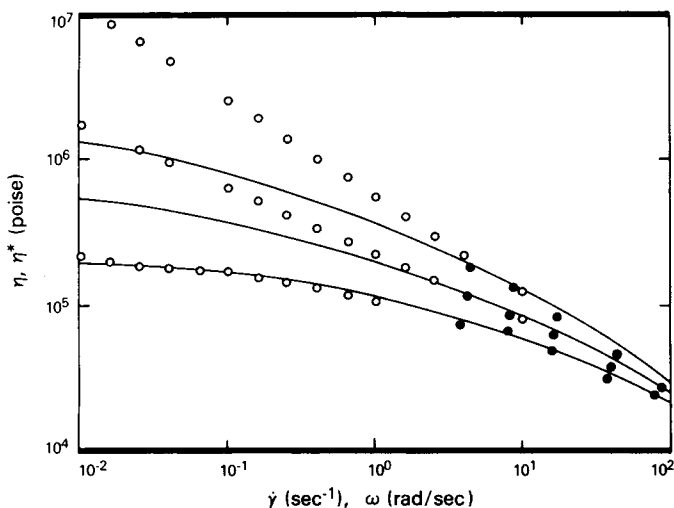

Fig. 5 Flow curves for samples P_0, P_1, and P_4: (-) predicted curves based on eqs. (1)–(3); (●) steady shearing; (○) dynamic data.
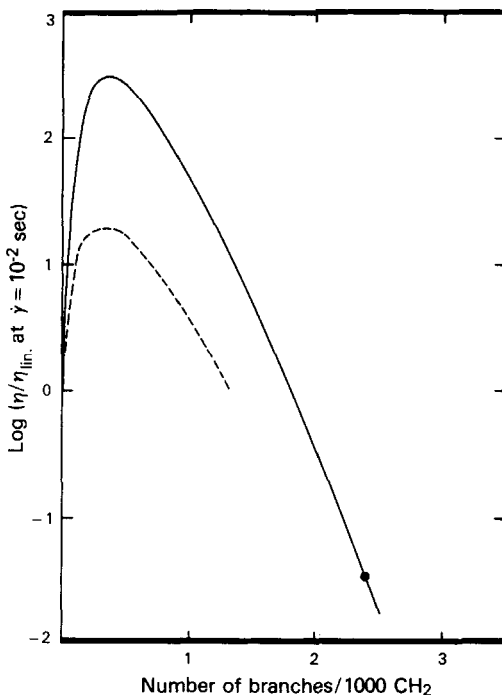
Fig. 6 Predictions of normalized low shear rate viscosity ($\dot{\gamma} = 10^{-2}$ s^{-1}) as a function of branch level and molecular weight. The molecular weights are $\overline{M}_w = 200{,}000$ (——) and 130,000 (- - -) with $\overline{M}_w/\overline{M}_n = 7$. η/η_{lin} is the ratio of the branched to linear viscosity at constant molecular weight distribution. The data point at higher branching levels is the sample L$_3$.

between the experimental data of Constantin and our predictions is seen in the movement of the peak to higher branching as molecular weight increases.

The results of molecular weight determinations for P$_0$–P$_5$ group of samples as given in Table I do not show much variation in apparent MWD with LCB content. This demonstrates conclusively that the very small branching levels thought to be present in HDPE, which can give rise to spectacular differences in rheological behavior, cannot readily be detected by means of molecular weight determinations. Upon filtering these samples through 0.5 μm filters, increasing insolubles with peroxide levels were noted, suggesting the apparent MWD does not represent the same sample characterized by rheological measurements.

Predictions of Branching Content from Rheological Behavior

The present study demonstrates that variations in both the viscosity[1] at low shear rates and the activation energy at low branching levels are consistent with the idea that not every molecule can contain a long chain branch, and that the resultant rheological behavior is based on the relative proportions of branched and linear species. Moreover, the relative proportions of branched and linear species, and consequently the rheological behavior, at a given branching level will depend on the branching mechanism; LCB formation as a result of peroxide degradation will affect both the proportion of branched species and the rheological behavior more than

equivalent branching levels as a result of thermal or mechanical degradation. The above observations lead to the conclusion that a fixed relationship between LCB content and rheological behavior is valid only as long as the branching mechanism is fixed. Consequently, estimations of LCB content from rheological and MWD measurements are only advisable when the branching mechanism is known.

One further point needs to be made with regard to low levels of branching of star model polymers. If one accepts the preceding explanation of the variation of rheological behavior with branching level for low branching levels, then star model compounds should not react similar to the randomly branched materials, because, in the case of the star molecules, each molecule contains a fixed number of branches, where only the branch length (not the proportional branched species) varies with branching level. This is consistent with the observation[13] that low shear rate viscosity increases with increasing branch length (decreasing branching level and increasing molecular weight), which is in sharp contrast to what has been observed for random branching. Consequently, model compounds such as star molecules are not correct models for commercial randomly branched materials.

CONCLUSIONS

Branching, which is introduced by means of peroxide decomposition is shown to affect rheological behavior to a considerably greater extent than equivalent branching contents for samples, in which the branching has been introduced by thermal or mechanical degradation. Simple statistical models giving the relationship between branching content and activation energy agree well, considering the very low branching levels (<0.1 branch/1000 CH_2) in these samples, with experimental data for both samples containing branching arising from either peroxide decomposition or sample degradation.

The results of these investigations are consistent with and lend credence to the idea that the often spectacular variations in rheological properties at very low branching levels is primarily due to changes with branch concentration of the relative proportions of branched and linear species. The agreement of the theoretical model of activation energy as a function of branching level and that produced using experimental activation energy measurements and branching as calculated from a rheological model, based on LDPE, suggests that branching level can be estimated for high density polyethylene from measurements of activation energy, if the branching mechanism is known. Additionally, the results presented here suggest that the assumption of a fixed relationship between molecular structure at very low branching levels and measured rheological behavior is only valid as long as the branching mechanism is fixed.

For the low levels of branching present in the samples formed by peroxide decomposition, the molecular weight distribution does not appear dramatically changed with branching level. Consequently, it would appear that, while molecular weight distribution is unable to reliably reflect changes in branching at very low levels, the rheological behavior at low deformation rates is a very sensitive indicator.

The preceding conclusions suggest that the study of model compounds, such as star molecules, is not relevant to the understanding of low levels

of randomly introduced branching. For very low levels of branching in star molecules, the molecular weight must be very high, but no linear species are present. In contrast, randomly branched polymers at very low branching levels must generally contain a sizeable linear fraction of molecules.

APPENDIX: CORRECTION TO ACTIVATION ENERGY FOR DEGRADATION

A typical problem involved in the estimation of E_a is degradation; a rerun of the modulus after the tests at the various temperatures does not reproduce itself exactly. Tests as a function of time and temperature on the modulus show that, between 170 and 190°C, the slope of G' vs. time, $\dot{G}$, is approximately a constant. This observation implies G' vs. ω is shifted in a parallel fashion with temperature at the temperatures of interest. Generally, the activation energy is related to the angular frequency shift (A_T) of the modulus curves by

$$A_{T - T_R} = \exp[E_a/R(1/T_R - 1/T)] = \omega(T)/\omega(T_R) \tag{17}$$

where T_R is the reference temperature. Similarly,

$$A_{T_n - T_0} = \Delta t \dot{\omega} \sum_{i=1}^{n} A_{T_n - T_i} + A_{T_n - T_0}^{\circ} \tag{18}$$

where Δt is the change in time, $\dot{\omega}$ the frequency shift with time (assumed constant), the ° superscript on A_T is the shift factor in the absence of degradation, and T_0 is the reference temperature (150°C).

For our case, in which $A_{T_5 - T_0}$ represents the shift of the rerun lowest temperature (150°C), we can estimate the undegraded shift factor at any temperature T_n from

$$A_{T_n - T_0}^{\circ} = A_{T_n - T_0} - \frac{(A_{T_5 - T_0} - 1)}{\sum_{i=1}^{5} A_{T_5 - T_i}} \sum_{i=0}^{n} A_{T_n - T_i} \tag{19}$$

Now for HDPE the E_a is ca. 6.5 kcal/mol, so that the ratio of R_n of the summations in eq. (19) can be evaluated, independent of the sample. We get for R_n

$$R_4 (T_4 = 190°C) = 1.24$$

$$R_3 (T_3 = 180°C) = 0.98 \tag{20}$$

$$R_2 (T_2 = 170°C) = 0.60$$

Equation (19) becomes

$$A_{T_n - T_0}^{\circ} = A_{T_n - T_0} - (A_{T_5 - T_0} - 1)R_n \tag{21}$$

Equations (20) and (21) allow us to correct the experimental shift factor, $A_{T_n - T_0} - 1$, to give the shift factor, had no degradation between present, ($A_{T_n - T_0}$), where A_{T_5} is the shift factor at 150°C at the test start to test end.

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