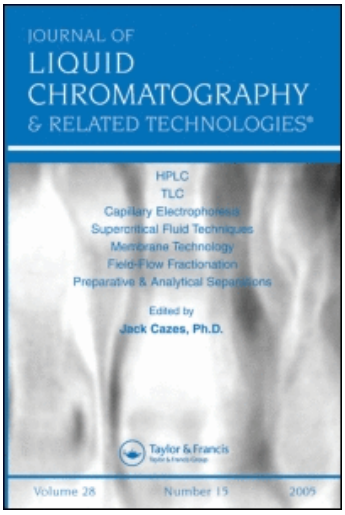

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Long Chain Branching in Polyethylene

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Abstract

Long chain branching frequency in polyethylene has been measured. Molecular weights determined directly by low angle laser light scattering of eluting species in gel permeation chromatography were compared with those estimated by universal calibration. Erroneous values for long chain branching frequency are produced if care is not taken to disrupt polyethylene aggregates in the GPC solvent.

Ethyl and hexyl side chains do not register as long branches in this analysis but sixteen carbon sidechains are counted.

In low density polyethylene the long chain branching frequency is generally highest at low molecular weights. This is because these polymers are produced in a non-isothermal free radical polymerization. Chain transfer to dead polymer, which produces long branches, occurs most frequently under the reaction conditions that also yield low molecular weight polyethylene.

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Introduction

Gel permeation chromatography (GPC) estimates of long chain branching in polymers start with the structure parameter g' which relates the intrinsic viscosities of branched and linear polymers with the same composition and molecular weight:

$$g' = \frac{[\eta]_b}{[\eta]_\ell} \tag{1}$$

where the $[\eta]_b$ is the intrinsic viscosity of the branched polymer and $[\eta]_\ell$ is that of the linear counterpart, in the GPC solvent. It is necessary to invoke a relationship between g' and g, which is the ratio of the mean radii of gyration $\langle R_G^2 \rangle$ of the same polymers:

$$g = \frac{\langle R_G^2 \rangle_b}{\langle R_G^2 \rangle_\ell} \tag{2}$$

The value of g has been calculated for a number of branched structures such as star-shaped, randomly-branched and comb-type molecules (1,2). Calculation of g' for use in equation (1) is much more difficult than that of g because the degree of draining of the macromolecules is not known exactly and because the degree of expansion of linear and branched molecules in a given solvent may be different (1,3). Various relations have been proposed of the form:

$$g' = g^k \tag{3}$$

where k has been suggested to have magnitudes between 0.5 and 1.5 (4,5).

At equal GPC elution volume and infinite dilution (6) the molecular weights of branched and linear species are related by

$$[\eta]_b M_b = [\eta]^* M^* \tag{4}$$

where the subscript b and superscript * refer to the branched and linear species that elute at the same retention time. In general, $M_b \geq M^*$. Now,

$$[\eta]_b = g'[\eta]_\ell = g'KM_\ell^a = g'KM_b^a \quad (5)$$

since M_ℓ is specified as equal to M_b in the definition of g' (in eq. (1)). In equation (5), K and a are the Mark-Houwink constants for monodisperse versions of the linear polymer in the GPC solvent:

$$[\eta] = KM^a \quad (6)$$

Also,

$$[\eta]^* M^* = K(M^*)^{a+1} \quad (7)$$

Therefore, equation (4) can be written:

$$g'KM_b^{a+1} = K(M^*)^{a+1}$$

and

$$g' = \left(\frac{M^*}{M_b}\right)^{a+1} = g^k \quad (8)$$

M^*, M and g' can be obtained directly. At any given elution volume M_b is measured by low angle laser light scattering (LALLS), while M^* is calculated from the universal calibration curve for linear polymers. The long chain branching frequency is measured implicitly by g'. To estimate the actual number of long branches per molecule it is necessary to assume a value for k and a model for the architecture of the branched species. Following Axelson and Knapp (7) we have assumed the Zimm-Stockmayer relation for a randomly branched macromolecule with trifunctional branch points (2):

$$g = \frac{6}{n_w} \cdot \frac{1}{2}\left[\frac{2 + n_w}{n_w}\right]^{1/2} \ln\left[\frac{(2 + n_w)^{1/2} + n_w^{1/2}}{(2 + n_w)^{1/2} - n_w^{1/2}} - 1\right] \quad (9)$$

Most of our calculations were made with k = 0.5, but other values were also used, as described below.

Data handling procedures used in this study were basically those suggested earlier by Axelson and Knapp (7). However, improvements in analytical and computational methods have produced long chain branching data that are quite different from the cited authors, and, indeed, from all previous analyses, so far as we know.

The results of this investigation provide new insights into the mechanism of the high pressure, free radical polymerization of ethylene.

Experimental

Polyethylene solutions were prepared in trichlorobenzene. All solutions contained 0.1% (w/w) 4,4-thiobis (3-methyl-6-tert-butylphenol) antioxidant. GPC measurements were made at 145°C with a Waters 150 C liquid chromatograph equipped with 500 A°, 10^4 A° and 10^5 A° (nominal porosity) Ultrastyragel columns. A solvent flow rate of 0.5 mL/min was found to give good resolution. In some experiments du Pont Zorbax porous silica columns SE-60, SE-1000 and SE-4000, were used. Both sets of columns gave equivalent results and the molecular weight parameters that were calculated agreed very closely with those of earlier analyses of reference polyethylenes (8).

Polymer concentration in the eluant was monitored with a Waters differential refractive index detector. Molecular weights of the eluting polyethylenes were measured in-line with a Chromatix KMX-6 low angle laser light scattering photometer (LALLS) using light scattered at 6-7° to the incident beam. This photometer incorporates a He-Ne laser source (λ = 6328 A°). The specific refractive index increment (dn/dc) of the various polyethylenes in trichlorobenzene were measured at 145°C with a Chromatix laser differential refractometer. Molecular weights (M_i) of polyethylene species that appeared at elution $(ve)_i^{volume}$ were calculated

$$\frac{K'c_i}{R_{\theta_i}} = \frac{1}{M_i} + 2A_2c_i \qquad (10)$$

where K' is the appropriate optical constant (related to $(dn/dc)^2$), R_θ is

the excess Rayleigh scattering determined from the LALLS detector response and A_2 is the second virial coefficient of the whole polymer. A_2 was measured from static light scattering analyses of the whole polymer sample. In equation (10) the concentration, c_i, of the eluting species was obtained from the differential refractive index detector response by:

$$c_i = \frac{mX_i}{V_i \Sigma X_i} \tag{11}$$

where m is the mass of polymer injected, X_i is the detector response and V_i is the increment of solution volume between data points.

Universal calibration for linear species was based on hydrodynamic volumes of anionic polystyrenes (9,10). The Mark-Houwink relation for polystyrene in trichlorobenzene was based on $K = 1.75 \times 10^{-3}$ cm^3g^{-1}, $a = 0.67$ (11). For linear polyethylene, the values of Ram and Miltz (12) ($K = 5.96 \times 10^{-2}$ cm^3g^{-1}, $a = 0.7$) were used.

An analytical solution to equation (9) is not available. An iterative computer program was written to calculate n_w at each value of M_b from equations (8) and (9).

We have previously shown that dissolution of polyethylene in trichlorobenzene at 145° will usually not produce aggregate-free solutions (13). Solutions free of aggregates can be produced, however, by storing the mixtures at 160°C for appropriate times before making molecular weight measurements at 145°C. The effects of aggregation on measurements of long chain branching were examined in this study by analyses of polymer solutions prepared with and without the 160°C treatment. Storage at 160°C for about one hour was sufficient to provide aggregate-free solutions of the polyethylenes studied in this work. Storage at this temperature for longer periods up to several days had no effect on molecular weight or branching results.

NBS 1476 Polyethylene

Figure 1 shows the relation between number of long branches per 1000 carbons and molecular weight for National Bureau of Standards Standard

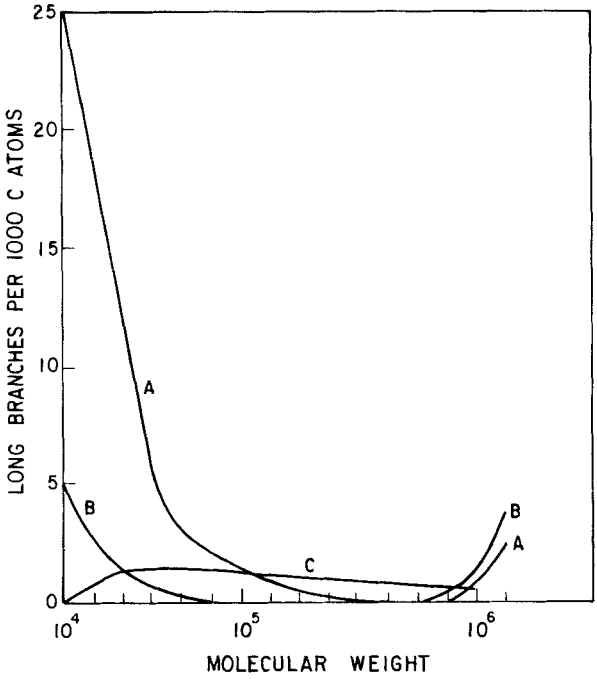

Figure 1

Long branch frequency-molecular weight relation for NBS 1476 polyethylene. Estimate made with k (eq. (3)) = 0.5. A: polymer dissolved and analyzed in trichlorobenzene at 145°C; B: polymer dissolved at 160°C and analyzed at 145°C; C: data of reference (7), measured in alpha-chloronaphthalene at 145°C and recalculated by us from original data.

Reference Material 1476. This is a melt index (14) 1.2, 0.931 g cm^{-3} density polymer that is reported to be a low conversion tubular reactor product (15). Curve A in Figure 1 records long chain branching for samples dissolved and measured at 145°C. Curve B is for the same material after the polyethylene solution was given a 160°C treatment to destroy polymer aggregates. The branching frequency at low molecular weights is seen to have decreased, while that at high molecular weights has increased slightly.

These changes can be explained as follows. The erroneously high values for long chain branching at low molecular weights in aggregate-containing solutions reflects the behavior of smaller agglomerates that appear effectively in the GPC as bigger entities with branches. This will occur if only a portion of a molecule is incorporated into an aggregate with the dangling remainder functioning essentially as a long branch. Large aggregates are presumably composed of large individual macromolecules. These aggregates will appear in the LALLS trace as "spikes" that behave like dust particles. These agglomerates will be rejected in the molecular weight computations (8,16). When the solution is treated to dissolve these aggregates the "spikes" are no longer present and the large branched species produce signals that are registered by the LALLS detector. The frequency of long chain branching at high molecular weights is seen to increase if aggregate-free solutions of NBS 1476 are analyzed.

Curve C records the long chain branching frequencies reported by Axelson and Knapp (7). The discrepancies between their results and ours are, we believe, due to differences in experimental procedures. The cited authors used relatively high concentrations of polyethylene dissolved in alpha-chloronaphthalene, which is a poor solvent for this polymer. No special dissolution time or procedure was measured. All these factors usually lead to aggregation and uncertainties in molecular weight measurements (8). Furthermore, for molecular weights > 8×10^5 the calibration procedure used by Axelson and Knapp (7) may not give reliable results.

As mentioned earlier, the value of k for use in equation (8) is uncertain. Figure 2 shows branching frequency calculated with various K's between 0.5 and 1.5, which is the usual range suggested for polyethylenes (17). The choice of this exponent affects the magnitude of the branching frequency calculated, but the form of the branching-molecular weight relation is not altered.

Since the relation observed differs from that reported by earlier workers it may be appropriate here to defend the accuracy of the present

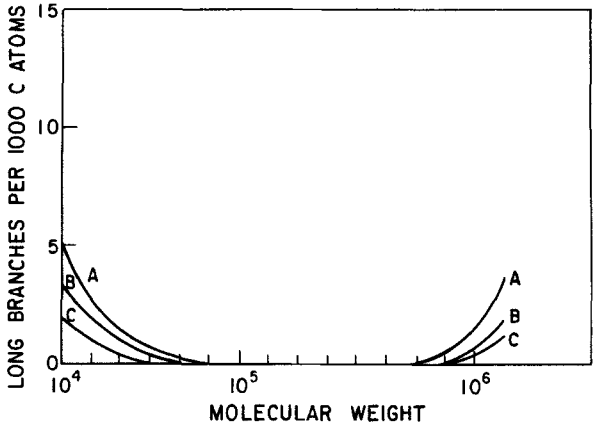

Figure 2

Long chain branch frequency of NBS 1476 polyethylene as a function of molecular weight. Estimates using k (eq. (3)) = 0.5 (A), 0.75 (B) and 1.5 (C).

results by pointing out that our measurements of the molecular weight parameters of this sample agree very well with those from other recent careful studies (8). This agreement holds both for LALLS and universal calibration methods of measurement. The branching frequency is calculated as described above from a combination of these two procedures, each of which is in good agreement with earlier measurements on this polymer.

How Long is a Long Branch?

Short chain branching in polyethylene is believed to have no significant effect on solution or melt rheological behavior, whereas long chain branching is considered to be important in this connection (18). Long branches can be defined generally as having about the same dimensions as the main chain (19). It is obvious, however, that branches much shorter than this length will affect the radius of gyration of solvent-swollen polymer coils. The minimum branch length for long chain behavior has been indeter-

minate, to date. For this reason, the question is not usually addressed in recent reviews of the subject (18,20).

Copolymers of ethylene and 1-olefins that are now available can be used to define long branch length more closely. In this study, linear polyethylene and ethylene copolymers with butene-1, octene-1 and octadecene-1 were examined. Butene and octene comonomers are common bases for current linear low density polyethylenes. Linear polyethylene and ethylene copolymers with butene and octene register as having zero long chain branching with the GPC-LALLS method used here. The octadecene copolymer was counted as long branched, however. Thus, we can conclude that a long branch, as measured by GPC-LALLS, has a minimum length > 6 and < 16 carbons. Details of these measurements follow.

Molecular weight parameters of the 1-olefin copolymers are recorded in Table I. Average molecular weights estimated from universal calibration are compared with those measured with the LALLS detector. $\bar{M}_w$ values agree closely for the butene-1 and octene-1 copolymers that have the same molecular weight-hydrodynamic radius as linear polyethylene. $\bar{M}_n$ and $\bar{M}_z$ are higher for the LALLS data because this detector is more sensitive than the differential refractometer to high molecular weight species and less sensitive to lower molecular weight polymers.

Figure 3 shows the long chain branch frequency estimated for the ethylene-octadecene-1 copolymer. The long branch density is found to decrease with increasing molecular weight. It is known from other measurements that lower molecular weight copolymers are richer in the 1-olefin (22) and these results are consistent with those of fractionation experiments.

Discussion

The dependence of long branch frequency on molecular weight of NBS sample 1476 is not typical of the majority of low density polyethylenes that we have examined. A more general relation is one in which branch frequency decreases monotonically from low to high molecular weights. This is not

Table I

Molecular Weight Parameters of 1-Olefin/Ethylene Copolymers

1-Olefin	Density	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	SD (N)[a]	SD (W)[a]	SKEW (N)[b]	SKEW (W)[b]
butene-1	0.918							
universal calibration		32,300	132,000	486,500	57,000	216,000	9	12
LALLS		59,500	134,000	669,500	67,000	268,000	15	220
octene-1	0.920							
universal calibration		37,000	132,000	327,000	59,200	160,000	6	3
LALLS		52,600	132,000	530,000	64,500	229,000	11	193
octadecene-1	0.940							
universal calibration		7,100	133,500	1,350,000	30,000	403,000	47	21
LALLS		43,000	158,000	951,000	70,500	354,000	17	125

(a) SD = standard deviation of number (N) and weight (W) distributions (21).

(b) SKEW = skewness of number (N) and weight (W) distributions (21).

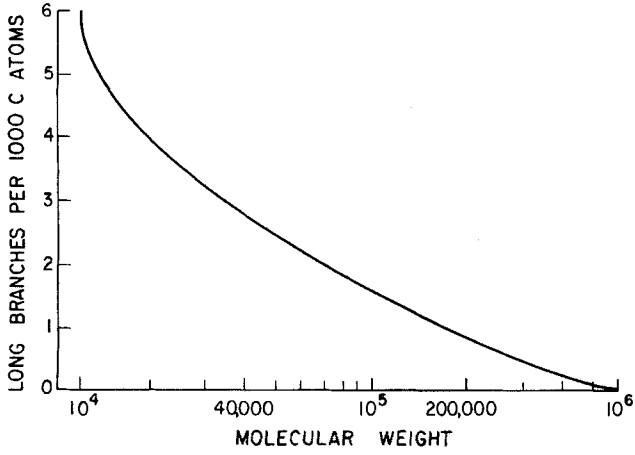

Figure 3

Long chain branching frequency versus molecular weight for ethylene-octadecene-1 copolymer.

expected. Long branches are formed in free radical polymerizations by chain transfer to polymer (19). Since larger dead polymers offer bigger targets it is assumed that encounters with growing macroradicals and long chain branching will be greater at higher molecular weights. This reasoning is plausible for isothermal polymerizations. Low density polyethylene polymerization reactions span a wide range of temperatures, however, and the molecular weight of the polymers produced decreases with increasing temperature. Chain transfer reactions are also enhanced at higher temperatures. The activation energy for chain transfer to polymer is greater than for the polymerization reaction (23). Thus chain transfer to polymer and long branch formation are most frequent under conditions where lower molecular weight polyethylenes are being formed.

The measurements reported here suggest that macroradicals undergo chain transfer reactions primarily with dead polymer that was formed in the same microregion of the flow-through reactor. This is not very surprising, since most polyethylene reactors are not designed to provide back-mixing.

Our conclusions differ from those of previous workers, who found either that long chain branching in low density polyethylene increased with molecular weight or was independent of molecular weight (18,20). The present data are believed to be more realistic, because they are derived with newer and more sensitive analytical methods.

There has also been some question as to whether the presence of short branches should be discounted in the estimation of long branch frequency (24,25). The present data show that short chain branching can be ignored, if a short branch is defined as one with six or less carbons.

Acknowledgment

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