on whether each rubber chain is anchored to the spherical domain(s) at no chain end, one chain end, or both chain ends and whether each rubber chain has enough mobility to flow into the lower density region to average out the density fluctuations.

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Distribution of Long and Short Branches in Low-Density Polyethylenes

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ABSTRACT: The distribution of long and short branches in three commercial low-density polyethylenes has been determined by combining gel permeation chromatography, viscometry, and infrared spectra analyses. The results indicate that different manufacturing polymerization conditions can lead to significant departures from ideal branch distribution.

Low-density polyethylene (LDPE) produced in high-pressure reactors is one of the oldest and most important commercial polymers. Its physical properties depend upon the concentration and distribution of both long and short chain branches (LCB and SCB).[1–3] Exact definitions of the structure–property correlations in this regard have not been possible to date. Theoretical and (especially) experimental techniques simply have not been available which permit accurate measurement of LCB, SCB, and their relationship to MWD. The advent of gel permeation chromatography and particularly its universal calibration has afforded the potential of improved analysis.[4–7] The purpose of our effort is to analyze the distribution of LCB and SCB in three commercial low-density polyethylenes by combining gel permeation chromatography with a variety of other techniques. The results are viewed with particular attention to the limitations of current theory.

In the high-pressure polymerization of ethylene, it is generally accepted that LCB arises from intermolecular chain transfer to polymer while SCB is generated by intramolecular H abstraction *via* a cyclic intermediate. Treatments of polymerization under constant conditions (T, P, [M], [PE]) in general predict that

$$\lambda_{\mathrm{LCB}} = b/M \qquad (1)$$

where b = number of LCB per molecule; M = polymer molecular weight; and λ_{LCB}, called the long-chain branching coefficient,[8–10] is a constant independent of extent of reaction or molecular weight. This prediction has been apparently confirmed in some cases.[6,7,11,12] In the variety of commercial high-pressure polymerization reactors employed, however, it seems unlikely that the uniform conditions necessary to validate eq 1 apply. Therefore we doubt the generality of eq 1 and suggest that variations in λ with M can provide useful data for the characterization of LDPE'ss.

The analysis of LCB revolves about the observation that branched chains occupy a smaller volume in solution than linear molecules of the same molecular weight. There are a number of experimental techniques available to measure the dimensions of polymer molecules in solution: intrinsic viscosity, $[\eta]$; translation friction coefficient, Ξ; light scattering, the limit of K_C/R_θ as C approaches zero; and gel permeation chromatography elution volume, V_e. In the cases of Ξ, the dimension derived is the Stokes' radius R_H, and, for the limit of K_C/R_θ as $C \rightarrow$ zero, the radius of gyration, R_G. Interpretation of $[\eta]$ and V_e in terms of molecular size involves a degree of ambiguity, especially for branched polymers. An equivalent hydrodynamic radius, R_e, is defined by $[\eta]$ and may be correlated with V_e.[13] The supposedly simple relationship between R_e and R_G for linear polymers has been the subject of continued study[14,15] and is virtually unknown for branched polymers. Experimental and theoretical studies have indicated a V_e–R_G correlation, but the matter is not resolved.[4,13,16] The basic problem is simply that the mechanism of separation in gel permeation chromatography has not been completely defined

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and new theroetical approaches to gel permeation chromatography are appearing.[17]

In view of the success by a number of workers in establishing the universal calibration, we accept the practical utility of its concept and in this work evaluate R_G from gel permeation chromatography data.

The structure-sensitive size parameters g and h are defined as

$$g \equiv \bar{R}_{G,b}^2/\bar{R}_{G,l}^2 \tag{2}$$

$$h \equiv \bar{R}_{H,b}/\bar{R}_{H,l} \tag{3}$$

where the subscripts b and l indicate branched and linear molecules of the same molecular weight. The values of g and h have been calculated[18-20] for molecules of well-defined branch geometry. For fractions of uniform molecular weight and a uniform number of trifunctional branches, b, per molecule

$$g_3 = 3(\pi/4b)^{1/2} - 5/2b \tag{4}$$

For fractions of uniform molecular weight with a random number of trifunctional branches per molecule

$$\langle g_3 \rangle = [(1 + b_n/7)^{1/2} + 4b_n/9\pi]^{-1/2} \tag{5}$$

where b_n is the average number of branch points per molecule. The values of g derived from eq 4 and 5 agree within a few per cent for moderate values of b and b_n.

For unfractionated material with random distribution of molecular weights and branches

$$\langle g_3 \rangle_w = \frac{6}{b_w}\left\{\frac{1}{2}\left(\frac{2 + b_w}{b_w}\right)^{1/2} \ln\left[\frac{(2 + b_w)^{1/2} + b_w^{1/2}}{(2 + b_w)^{1/2} - b_w^{1/2}}\right] - 1\right\} \tag{6}$$

where b_w is the weight-average number of branches per molecule. The values of $\langle g \rangle_w$ have been computed by Drott and Mendelson for a range of b_w[7]. The differences between calculation from eq 5 or 6 are considerable. For example, for $b_n = 10$, (5) gives $\langle g \rangle_3 = 0.5799$, while for $b_w = 10$, (6) gives $\langle g \rangle_w = 0.4151$. The approach of Kurata and Fakatsu yields

$$h^{-1} = {}^1/_2\Gamma({}^7/_4)(b + {}^1/_2)^{1/4} + {}^3/_4\Gamma({}^5/_4)(b + {}^1/_2)^{-1/4} \tag{7}$$

where Γ denotes a gamma function. The relationships between g and h for a variety of molecular geometries have also been developed by Kurata and Fukatsu.

In practice, one must determine g and calculate b. By far the least ambiguous way would be measuring R_G *via* light scattering. This method has indeed been employed.[21] However, the R_G's of linear and especially branched polyethylenes up to molecular weights of about 10^5 are near $\lambda/20$ (Hg lamp) which normally defines the limit of accurate measurement. This, combined with other experimental difficulties associated with light scattering at high temperatures, limits the quality and quantity of data which can be obtained this way.

The alternate way which is widely accepted in practice, albeit less satisfactory theroetically, is to employ

$$f = [\eta]_b/[\eta]_l \tag{8}$$

with[22]

$$f(g) = g^{1/2} \tag{9}$$

and

$$f(h) = h^3 \tag{10}$$

While eq 9 has been shown to hold for certain branching geometries, there is some uncertainty in extending this relation to branched polymers in general. For example, based on measured viscosity depressions of branched poly(vinyl acetates), the number of branches indicated by eq 9 with eq 5 is much larger than the number of branches indicated by polymerization kinetics and other measures of size. On the other hand, the estimates by eq 10 with eq 7 are lower than predicted. The branching levels indicated by eq 9 and 6 provide fair agreement.[10,21,23] The unanswered question of whether any single approach is valid to branched molecules of arbitrary geometry is the least satisfying aspect of branched polymer analysis, representing the major obstacle to unambiguous results.

Perhaps the relative success of eq 6 on "fractionated" material should be expected. Since any polymerization is likely to produce a fraction of linear material along with the branched,[8] and since the value of A_2 varies with branching,[21] it is doubtful that any existing fractionation method (solubility or size) can provide samples which meet the criteria of eq 4, 5, and 7. With these limitations in mind, we will place our major emphasis on the results calculated by eq 9 and 6.

Experimental Section

In general, the approach to the problem is the same as taken by Drott and Mendelson[7] with some additions and modifications.

Materials. A linear polyethylene, LPE-I, was chosen for a reference material. Three branched polyethylenes, BPE-I, BPE-II, and BPE-III, were the objects of the investigation. All of the branched polymers arise from continuous commercial processes. BPE-II comes from an autoclave reactor, while the other two are produced in tubular reactors. All three polymers have similar densities (0.92–0.93), similar melt indices (0.2–0.3), and similar overall methyl group contents, 2.4–2.8CH_3/100CH_2 (infrared analysis).

About 20 g of each of the four polyethylenes was fractionated (*ca.* 20 fractions each) using preparative gel permeation chromatography by DeBell and Richardson, Inc. The solvent was 1,2,4-trichlorobenzene (TCB) at 135°, and one or two columns were employed. The fractions generally exhibited good elution profiles with $\bar{M}_w/\bar{M}_n$ calculated between 1.2 and 1.4 with no corrections for spreading.

Eight samples of NMWD polystyrene (Pressure Chemical Co.) were employed for calibration purposes. Their molecular weights and intrinsic viscosities are given in Table I.

Measurements. Each fraction was subjected to analytical gel permeation chromatography (Waters Associates, Model 100) using

Table I
Polystyrene Calibration Data

Sample	$\bar{M}_w$	$[\eta]_{TCB,135°}$, dl/g	V_e, cm^3
PS-1	4,800	0.05	176.7
PS-2	10,300	0.08	163.0
PS-3	19,800	0.12	157.0
PS-4	51,000	0.28	143.8
PS-5	160,000	0.54	129.2
PS-6	411,000	1.23	118.5
PS-7	860,000	1.80	111.8
PS-8	1,800,000	2.83	107.0

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TABLE II
LPE-I MOLECULAR WEIGHT DISTRIBUTION

Fraction	$W_i \times 10^{-2}$	$C(M_i)$	$[\eta]_{\mathrm{DEC},135°}$	$[\eta]_{\mathrm{TCB},135°}$	$\overline{M}_v(\mathrm{DEC})^b$	$\overline{M}_v(\mathrm{TCB})^c$	V_e, cm^3
1	0.08	0.999	11.0	9.30	1.17×10^6	1.23×10^6	105.5
2	0.29	0.998	9.13	8.70	9.00×10^5	9.70×10^5	107.0
3	0.61	0.993	8.63	8.00	8.31×10^5	8.76×10^5	108.8
4	1.13	0.984		6.60		5.69×10^5	111.0
5	1.81	0.970		4.91		4.40×10^5	112.0
6	2.64	0.947		4.50		3.88×10^5	113.0
7	3.65	0.916	4.50	3.80	3.28×10^5	3.05×10^5	114.2
8	4.60	0.875		2.81		1.99×10^5	118.2
9	5.56	0.824		*a*			
10	6.32	0.764	2.35	2.10	1.29×10^5	1.33×10^5	123.0
11	7.20	0.697		1.96		1.20×10^5	127.0
12	7.89	0.621		1.65		9.37×10^4	128.5
13	8.70	0.538	1.53	1.33	6.96×10^4	6.90×10^4	132.5
14	9.23	0.449		1.09		5.21×10^4	134.0
15	9.02	0.358		0.96		4.35×10^4	136.6
16	8.53	0.270	0.83	0.76	2.90×10^4	3.11×10^4	141.5
17	7.46	0.197		0.60		2.37×10^4	146.0
18	6.01	0.120		0.47		1.58×10^4	149.5
19	4.30	0.071		0.36		1.08×10^4	156.0
20	2.62	0.036		0.28		7.59×10^3	159.2
21	1.53	0.016					165.0
22	0.81	0.004					174.2

[a] Not available. [b] $[\eta]_{\mathrm{DEC},\,135°} = 6.2 \times 10^{-4} M^{0.70}$. [c] $[\eta]_{\mathrm{TCB},\,135°} = 5.1 \times 10^{-4} M^{0.706}$.

a four-column series with nominal pore sizes, 1.5×10^5–7×10^4, 1.5×10^4–5×10^3, 5×10^3–2×10^3, and 2×10^3–7×10^2 Å. The unit was operated at 135° using TCB (0.1% Santonox R antioxidant) as the solvent. The flow rate was maintained at 1.0 ± 0.1 ml/min, with a 1.0-ml syphon used to improve elution count accuracy. In view of the large number of samples, mixed fractions of widely different molecular weights were injected. A 2-min injection of ~2-mg/ml (~0.1 mg/ml each fraction) solutions was adopted as standard procedure with a conventional 2-ml injection loop. The whole (unfractionated) polyethylene and polystyrene fractions were also examined.

The $[\eta]$ of each fraction and whole polymer of polyethylene as well as each polystyrene was determined in TCB at 135°, using Cannon–Ubbelhode semimicro viscometers. The $[\eta]$ for some LPE fractions was also determined in decalin at 135°. The following $[\eta]$–M relations were found to be in good agreement.[24,25]

$$\text{LPE } [\eta]_{\mathrm{TCB},135°} = 5.1 \times 10^{-4} M^{0.706} \qquad (11)$$

$$\text{LPE } [\eta]_{\mathrm{DEC},135°} = 6.2 \times 10^{-4} M^{0.70} \qquad (12)$$

The methyl group contents of several fractions were determined by infrared spectroscopy. The method used is the determination of the absorbance ratio of the 1378-cm^{-1} (CH_3) band to the 1368- and 1306-cm^{-1} (CH_2) bands. The $A(1378)/A(1368)$ and $A(1378)/A(1306)$ ratios are compared to values from a series of polyethylenes containing known amounts of branching. The average value for the two determinations is employed.

The values of $\overline{M}_w$ for several LPE fractions were determined by light scattering at 135° in distilled 1-chloronaphthalene. A SOFICA instrument was employed, and calculations were performed using the constants found by Chiang.[25] Clarification of the solutions prior to measurements was achieved by filtration through 0.2-μ sintered silver filters (Selas Flotronics). Solvent dissymmetry was 1.05 or less.

Computations. The data from intrinsic viscosity and peak elution volumes for the polystyrene standards and LPE fractions were used to construct a universal gel permeation chromatography calibration, shown in Figure 1. The two sets of data are virtually superimposed, validating eq 11 as an accurate relationship for LPE. Further confirmation is obtained from the light-scattering data discussed later. The cumulative weight fractions were calculated using the Schultz method

$$C(M_i) = (W_i/2) + \sum_{j=1}^{i-1} W_j \qquad (13)$$

and the resulting molecular weight distribution is presented in Table II.

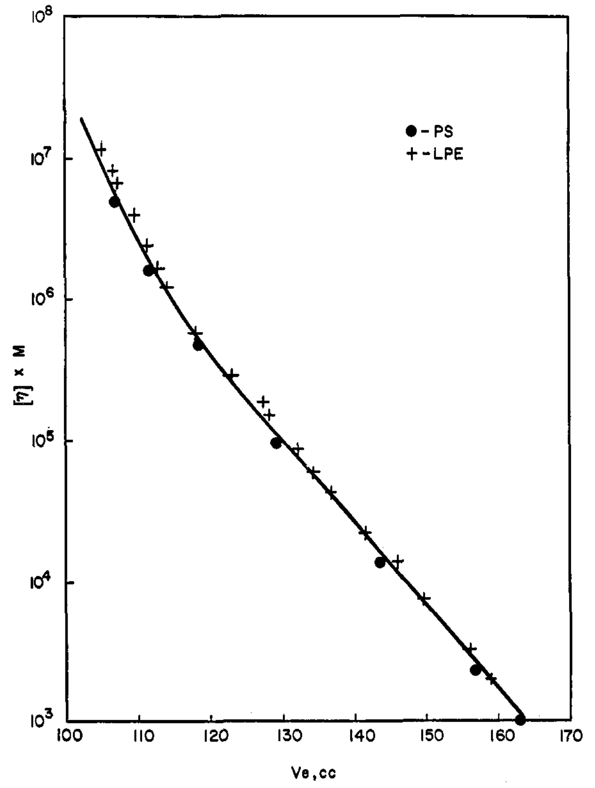

Figure 1. Universal calibration data.

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Table III

BPE-I Molecular Weight Distribution[a]

Fraction	$W_i \times 10^{-2}$	$C(M_i)$	$[\eta]_{TCB}$, dl/g	V_e, cm^3	$\overline{M}_i$(GPC)	CH$_3$/100CH$_2$
1	2.6	0.989	3.07	111.0	8.90×10^5	
2	3.5	0.960	2.82	113.5	5.32×10^5	
3	3.6	0.923	2.50	114.0	5.20×10^5	2.38
4	4.5	0.882	2.15	118.0	2.85×10^5	
5	5.6	0.832	1.78	121.0	2.30×10^5	
6	6.0	0.774	1.56	122.0	2.22×10^5	
7	6.3	0.710	1.33	125.0	1.71×10^5	
8	6.8	0.645	1.15	129.0	1.18×10^5	2.39
9	7.5	0.574	1.02	131.2	9.35×10^4	
10	7.0	0.501	0.89	133.2	8.55×10^4	
11	8.5	0.424	0.75	137.2	5.75×10^4	
12	6.9	0.347	0.62	141.5	3.88×10^4	3.45
13	8.1	0.272	0.51	145.8	2.60×10^4	
14	7.7	0.194	0.42	147.9	2.38×10^4	
15	6.2	0.124	0.31	153.0	1.57×10^4	
16	4.8	0.069	0.26	158.0	9.62×10^3	
17	2.7	0.032	0.21	162.0	6.74×10^3	
18	1.5	0.011		165.9		4.8
19	0.4	0.002		169.2		

[a] From fractions $\overline{M}_w = 1.51 \times 10^5$, $\overline{M}_n = 3.83 \times 10^4$; $[\eta]_w = 1.08$ (not counting no. 18 and 19); whole polymer $[\eta] = 1.04$.

Table IV

BPE-II Molecular Weight Distribution[a]

Fraction	$W_i \times 10^{-2}$	$C(M_i)$	$[\eta]_{TCB}$ dl/g	V_e, cm^3	M_i(GPC)	CH$_3$/100CH$_2$
1	0.59	0.997	3.26	105.0	$\sim 3 \times 10^6$ [b]	
2	0.80	0.990	3.85	103.0	$\sim 5 \times 10^6$ [b]	
3	1.18	0.980	3.20	104.0	$\sim 3 \times 10^6$ [b]	2.55
4	1.74	0.966	2.90	109.5	1.24×10^6	
5	2.45	0.945	2.70	110.8	9.64×10^5	
6	3.43	0.915	*c*	*c*	*c*	
7	4.66	0.875	2.14	114.0	5.62×10^5	
8	5.88	0.822	1.79	118.1	3.35×10^5	2.45
9	6.81	0.759	*c*	*c*	*c*	
10	7.43	0.687	1.40	124.1	1.79×10^5	
11	7.69	0.612	1.19	126.9	1.50×10^5	
12	8.17	0.532	1.10	130.3	8.85×10^4	2.25
13	8.39	0.450	*c*	*c*	*c*	
14	8.13	0.367	0.71	139.5	4.54×10^4	
15	7.84	0.287	0.59	142.8	3.39×10^4	
16	6.94	0.213	0.53	145.0	2.84×10^4	
17	5.97	0.148	*c*	*c*	*c*	
18	4.72	0.095	0.35	155.9	9.42×10^3	3.6
19	3.57	0.054	0.29	159.0	7.24×10^3	
20	2.54	0.023	*c*	*c*	*c*	
21	0.76	0.007		167.3		
22	0.29	0.001		172.0		

[a] From fractions $\overline{M}_w = 2.57 \times 10^5$, $\overline{M}_n = 2.99 \times 10^4$, $[\bar{\eta}]_w = 1.16$; from whole polymer $[\eta] = 1.16$. [b] Estimated. [c] Not available.

Table V

BPE-III Molecular Weight Distribution[a]

Fraction	$W_i \times 10^{-2}$	$C(M_i)$	$[\eta_i]_{TCB}$, dl/g	V_e, cm^3	$\overline{M}_i$(GPC)[d]	CH$_3$/100CH$_2$
1	0.32	0.998	3.08		$\sim 4 \times 10^6$ [b]	
2	1.10	0.991	2.76	105.5	$\sim 3 \times 10^6$ [b]	
3	1.68	0.977	2.68	106.2	$\sim 2.5 \times 10^6$ [b]	2.10
4	3.91	0.949	*c*			
5	4.96	0.905	2.20	111.2	1.09×10^6	
6	6.15	0.849	2.00	114.6	5.77×10^5	
7	6.33	0.787	1.85	117.8	3.51×10^5	1.85
8	6.76	0.722	*c*			
9	7.14	0.652	1.35	123.0	2.22×10^5	
10	7.43	0.579	1.18	127.0	1.47×10^5	
11	7.83	0.503	1.09	131.0	9.18×10^4	
12	8.00	0.424	*c*			
13	7.27	0.350	0.70	137.0	5.66×10^4	2.55
14	6.75	0.270	0.60	141.0	3.71×10^4	
15	6.17	0.213	*c*			
16	4.14	0.161	0.43	152.0	1.30×10^4	
17	5.34	0.114	0.37	156.3	8.64×10^3	6.30
18	4.86	0.064	*c*			
19	2.34	0.053	0.20	163.0	6.81×10^3	
20	1.23	0.012	0.18	167.0	4.00×10^3	
21	0.58	0.003				

[a] From fractions $\overline{M}_w = 3.48 \times 10^5$, $\overline{M}_n = 3.15 \times 10^4$, $[\bar{\eta}]_w = 1.18$; from whole polymer $[\eta] = 1.24$. [b] Estimated. [c] Not available. [d] GPC = gel permeation chromatography.

Table VI

BPE-I Branch Distribution

Fraction	$[\eta]_b/[\eta]_l$	$b_{g^{1/2}}$[a]	b_{h^3}[b]	b_w[c]	b_{short}[d]
1	0.465	145	20	32.2	1446
2	0.479	102	18.7	28.9	875
3	0.481	96	18.6	28.4	856
4	0.514	75	16.1	23.1	461
5	0.530	64	15.0	20.9	370
6	0.532	62	14.8	20.5	356
7	0.559	51	13.1	17.3	274
8	0.570	45	12.3	15.9	285
9	0.583	41	11.5	14.5	163
10	0.600	36	10.0	13.2	147
11	0.626	28	9.0	11.1	113
12	0.654	22	7.7	9.3	84
13	0.671	19	7.2	8.4	49
14	0.694	16	6.2	7.1	38
15	0.720	13	5.4	6.1	22
16	0.788	7.3	3.2	3.7	16
17	0.807	6.2	2.7	3.2	13

[a] Calculated from eq 9 and 5. [b] Calculated from eq 10 and 7. [c] Calculated from eq 9 and 6. [d] $b_{short} = b_{total} - b_w$. b_{total} obtained by interpolation between measured values.

The peak elution volumes of each branched polyethylene were fitted to the universal calibration of Figure 1, determining the $[\eta]\overline{M}$ product. Division by the measured $[\eta]$ (see Tables III, IV, and V) results in determining $\overline{M}$ for each fraction. The data can then be used to determine viscosity ratios. Plots of $[\eta]$ *vs.* M for each BPE are constructed and $[\eta]_b/[\eta]_l$ is calculated from the best curve through each set of BPE data. Using eq 9 and 10 with eq 5, 6, and 7, three relative measures of the branching are shown in Tables VI, VII, and VIII. Most emphasis will be placed on the values of b derived from eq 6.

With the molecular weights for each fraction determined, the infrared data may be converted to total branches per molecule and corrected for chain ends. The SCB may then be determined by subtracting LCB from the total (LCB by eq 6). These values are also shown in Tables VI, VII, and VIII. SCB values for each fraction were obtained by interpolation.

The validity of such an analytical approach hinges on the accuracy of the universal calibration. Light-scattering determinations of the $\overline{M}_w$ of several fractions are given in Table IX, where they are compared to $\overline{M}$ determined by eq 11 for the LPE and the universal calibration for the BPE's. In general, the agreement is quite good. At this point we wish to note that none of the data are "smoothed" in any way in Table IX. The Zimm plots were observed to have some downward curvature for the smallest (30 and 37°) scattering angles. Where the data from these angles were

TABLE VII
BPE-II BRANCH DISTRIBUTION

Fraction	$[\eta]_b/[\eta]_l$	$b_{g^{1/2}}$[a]	b_{h^3}[b]	b_w[c]	b_{short}[d]
1	0.11		270		
2	0.12		260		
3	0.135	$>10^4$	210	~2000	3540
4	0.290	850	56	127	2118
5	0.325	520	45	92	1629
6					
7	0.380	260	32	59	932
8	0.453	130	22	35	551
9					
10	0.560	52	13	17.1	289
11	0.565	48	12.5	16.5	230
12	0.638	25	8.2	10.5	131
13					
14	0.741	12	4.6	5.1	79
15	0.749	10	4.3	4.9	65
16	0.781	7.9	3.4	3.9	59
17					
18	1.00				23
19	1.00				

[a] Calculated from eq 9 and 5. [b] Calculated from eq 10 and 7. [c] Calculated from eq 9 and 6. [d] $b_{short} = b_{total} - b_w$. b_{total} is obtained by interpolation between measured values.

TABLE VIII
BPE-III BRANCH DISTRIBUTION

Fraction	$[\eta]_b/[\eta]_l$	$b_{g^{1/2}}$[a]	b_{h^3}[b]	b_w[c]	b_{short}[d]
1					
2	0.145		190	~900	
3	0.160		160	~650	3100
4					
5	0.220	$>10^3$	96	260	1297
6	0.322	530	45	95	682
7	0.420	180	26	44	419
8					
9	0.438	143	23.5	39	294
10	0.510	76	16.2	23.9	217
11	0.583	42	11.5	14.8	142
12					
13	0.609	32	9.5	12.2	89
14	0.693	16	6.2	7.1	78
15					
16	0.908	2.2	1.1	1.1	46
17	1.00				37
18					
19	1.00				
20	1.00				

[a] Calculated from eq 9 and 5. [b] Calculated from eq 10 and 7. [c] Calculated from eq 9 and 6. [d] $b_{short} = b_{total} - b_w$. b_{total} is obtained by interpolation between measured values.

TABLE IX

Sample		$\overline{M}_{GPC}$[a]	$\overline{M}_{wLS}$[b]	$\langle R_G\rangle_{LS}$,[b] Å
LPE	6	388,000	361,000	460
	8	199,000	172,000	350
	12	94,000	113,000	270
BPE-I	3	520,000	690,000	625
	7	177,000	194,000	370
	11	58,000	82,000	≤250
BPE-II	5	965,000	1,700,000	670
	8	335,000	344,000	280
	12	88,500	82,000	≤250
BPE-III	5	1,090,000	982,000	420
	7	351,000	360,000	≤250
	11	91,800	81,000	≤250

[a] Gel permeation chromatograph data. [b] Light-scattering data.

discarded, the Zimm-plot components are essentially straight lines. Calculations of A_2 for the LPE fractions (not shown) are in fair agreement with those of Chiang, but the values of R_G for the LPE fractions are somewhat higher.[25] Because of the difficulties in obtaining R_G by light scattering, we do not place a great deal of weight on the absolute values, but note that at comparable molecular weights the relative molecular dimensions are LPE ≈ BPE-I > BPE-II ≥ BPE-III. A few calculations from the data indicate g values of ≈0.3–0.4. Comparison with viscosity ratios indicates $[\eta]_b/[\eta]_l \approx g$. This is merely an observation based on very limited data and is not offered as a general relationship.

Discussion

The data from the tables are also presented in Figures 2, 3, and 4. It is obvious that the LCB for BPE-II and -III appear almost directly proportional to M, with some possible deviations at the high and low extremes of molecular weight. The values of LCB are somewhat higher in BPE-III than in BPE-II. The LCB for BPE-I obviously deviate from ideal behavior, exhibiting high branch levels at low molecular weights, falling below the levels observed in BPE-I and BPE-II

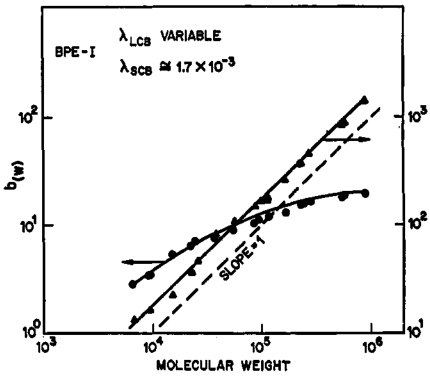

Figure 2. Branch distributions in BPE-I.

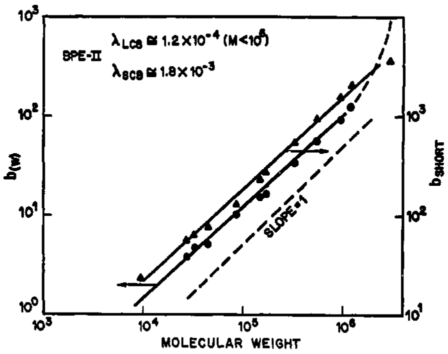

Figure 3. Branch distributions in BPE-II.

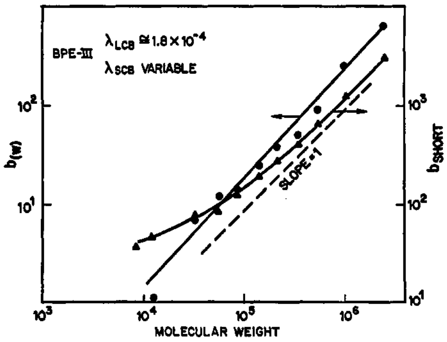

Figure 4. Branch distributions in BPE-III.

at the upper end of the MWD. As limited by the accuracy of our viscosity measurements, it is worthwhile to note that there is no "linear" polymer in BPE-I, while BPE-II and BPE-III contain about 15% "linear" polymer each at the low end of the MWD. The same trends may be followed in branching values calculated using the other equations.

We can now speculate on the cause of departure from ideal polymerization behavior, particularly in BPE-I and BPE-III. A growing chain with the normal terminal $R(CH_2)_xCH_2\cdot$ can disappear by addition with monomer, by termination, or by either of the two chain-transfer mechanisms leading to branching. Other transfer reactions occur but are not of interest here. The *intramolecular* transfer would probably be assisted by increasing the temperature and by increasing the conversion if the latter proceeded to the point of significant monomer depletion. Again, the *intermolecular* transfer to polymer is assisted by increased temperature and assuredly by higher conversion.

It would be helpful if we could associate molecular weight with degree of conversion or residence time, but the assumptions necessary are obviously unrealistic. The following brief comments are therefore strictly qualitative and oversimplified.

In stirred autoclaves, polymerization conditions in terms of T, P, and [M] are likely to be the most constant. The greatest variable would be the residence time of a given polymer molecule. Thus, for BPE-II, the increase in LCB at very high molecular weight would represent molecules with the longest residence time, and the apparently "linear" low molecular weight end would represent the shortest residence times. The SCB levels would be unaffected by residence time.

Tubular reactors, on the other hand, vary widely in T and P, with less variation in residence time, and unusual distributions might be expected. For BPE-I the reactor temperature was apparently uniform enough to maintain normal levels of SCB. This leaves pressure perhaps as the main variable, with monomer depletion a secondary factor. Applying the same line of reasoning, perhaps temperature is the major variable in the manufacture of BPE-III in light of the wide variation in SCB.

Based on experimental data, some authors have indicated that a single gel permeation chromatography calibration curve may be used to provide true molecular weight distributions for a variety of branched polyethylenes.[7,11] Two conditions must be met for this to be strictly true. The variations in λ_{LCB} within a sample must be negligible, and variations between different samples must not be greater than, say, a factor of 3. Our data indicate that the first condition will not be met by a wide population of representative commercial polyethylenes. Thus, while a branched-polymer calibration curve will give truer values of MWD than a linear-polymer calibration, precise MWD analysis requires prior knowledge of the type of branch distribution.

Conclusions

Application of the universal calibration concept to gel permeation chromatography data allows relatively reliable measurement of LCB in commercial polyethylenes. When combined with infrared analysis of the total methyl group content, reasonable values for SCB may also be derived. Acceptance of a molecular-weight-independent branching coefficient for all commercial branched polyethylenes seems an oversimplification, especially in the case of tubular reactor products. This limits the applicability of a single gel permeation chromatography calibration curve where precise MWD is sought.

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Notes

Desorption of Polystyrene from Silica Gel Thin Layer Chromatography Substrates

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It has recently been found that synthetic polymers can be effectively fractionated by thin layer chromatography (tlc).[2,3] This work further explores the mechanisms by which such fractionation occurs.

Both solubility and adsorption effects have been identified as playing a role in the tlc fractionation of polymers. For successive adsorption–desorption cycles to play a major part in separation of molecules according to their molecular weight, the rates of these processes must be quite rapid, since the experimental time is less than 1 hr. Normally determined desorption rates are orders of magnitude slower,[4] which suggests that desorption cannot play a significant role in the tlc fractionation of polymers.

The following method was employed to examine desorption rates of polystyrene from tlc substrates. Commercial precoated plastic-backed tlc plates of silica gel with zinc silicate fluorescent indicator (Brinkmann Instrument Co.) were cut into 3 × 8 cm sections. Aliquots (15 μl) of anionically polymerized polystyrenes (Pressure Chemical Co.) in CCl_4 (1 mg/ml) were applied as $\sim 0.3 \times 1.0$ cm streaks to give a calculated average adsorbent coverage of 4×10^{-4} mg cm^{-2}.

The plates were not given any special drying treatment. While this results in a small amount of water adsorbed on the plate, our previous experience indicates that the removal of water by standard activating procedures does not markedly decrease R_f values observed during elution. The plates employed in earlier work were not activated.[2]

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(1) (a) Bell Telephone Laboratories; (b) State University of New York.

(2) (a) E. P. Otocka and M. Y. Hellman, *Macromolecules*, **3**, 362 (1970); (b) E. P. Otocka, *ibid.*, **3**, 691 (1970).

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