Sizes of Long-Chain Branches in a High-Pressure Low-Density Polyethylene as a Function of Molecular Weight

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SYNOPSIS

The mean length and the indices of long-chain branches (LCBs) of a high-pressure low-density polyethylene (HPLDPE) as a function of molecular weight have been determined for its molecular-weight-fractionated parts by the ^{13}C-NMR analysis and the viscosity measurements. The mean LCB length of the fractions was of the order of 200–300 carbons in length. The size of LCBs increases with increasing molecular weight, but the size of LCBs relative to the overall macromolecular size decreases with increasing molecular weight. The LCB sizes as a function of molecular weight determined for the fractions of one parent HPLDPE are in good agreement with those previously reported for HPLDPE whole polymers.

INTRODUCTION

Long-chain branches (LCBs) have important effects on the viscoelastic properties like rheological behaviors of polymers.[1] The presence of LCBs in high-pressure low-density polyethylene (HPLDPE) is well known and plays an important role in commercial applications. Considerable efforts have been made for the determination of the LCB concentration in HPLDPEs by the solution methods[2-15] and the ^{13}C-NMR analyses.[13,16-20] However, a complete characterization is still impossible and, especially, little progress was made in the determination of the exact distribution of the LCBs.

Recently, Bugada and Rudin[21,22] have developed an interesting analytical procedure to evaluate the length and architecture of the LCBs by size exclusion chromatography (SEC) and ^{13}C-NMR. They found that the branch length was of the order of 200–300 carbons in length, and the LCB size increases with increasing molecular weight of the whole polymer. Although the averaged figures of whole polymers give some important understandings, polymers should be considered as a mixture of molecules of varied molecular size and structure. Therefore, the investigation of structural parameters as a function of molecular weight for one polymer has been of much more interest in connection with the physical properties and the polymerization mechanisms.[3-6,11,13,20,23,24]

In this report we determine the mean length and the indices of LCBs in one HPLDPE as a function of molecular weight by ^{13}C-NMR spectroscopy, molecular weight, and viscosity measurements for molecular-weight-fractionated parts of one parent HPLDPE.

EXPERIMENTAL

Samples

The characteristics of the parent HPLDPE used for this study are listed in Table I. Molecular-weight-fractionated parts were prepared from the parent HPLDPE by using a solvent gradient elution technique. Details of the fractionation conditions have been described elsewhere.[20]

Molecular Weight and Viscosity Measurements

The number-average molecular weight ($\bar{M}_n$) of the fractions 6, 8, 10, 12, and 15 were determined at

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Table I   Structural Characteristics (Number-Average Molecular Weight, $\bar{M}_n$, Branch and Vinyl Concentrations) of a Parent HPLDPE and Its Molecular-Weight-Fractionated Parts Determined by Osmometer, ^{13}C-NMR, and FT IR

Sample	$10^{-4}\,\bar{M}_n$	Branch Contents/1000C							Vinyl/1000C
		Total	Methyl	Ethyl	Propyl	Butyl	Pentyl	LCB	
Parent HPLDPE	4.00	24.6	2.9	7.5	0.4	7.3	3.0	3.5	—
Fraction 6	1.48	28.1	3.1	9.0	0.9	8.5	3.0	3.6	0.38
Fraction 8	2.75	25.4	2.8	8.0	0.6	7.8	2.9	3.3	0.24
Fraction 10	5.14	22.7	2.5	7.0	0.4	7.1	2.6	3.1	0.16
Fraction 12	10.2	22.2	2.8	6.5	0.6	7.0	2.4	2.9	0.12
Fraction 15	47.0	22.2	3.0	5.7	0.7	7.1	2.6	3.1	0.08

105°C in 1,2,3,4-tetra-hydronaphthalene by using a Hewlett-Packard high-speed membrane osmometer (Type 502). The intrinsic viscosities of the fractions were determined in 1,2,4-trichlorobenzene at 130°C by using an inside dilution type Ubbelohde's viscometer. The intrinsic viscosity of linear polyethylene, $[\eta]_l$, corresponding to the $\bar{M}_n$ were determined by the equation: $[\eta]_l = 6.82 \times 10^{-4}\bar{M}_n^{0.674}$.

Spectroscopic Measurements

The ^{13}C-NMR spectra were obtained with a JEOL FX200 spectrometer at 50.10 MHz with 10-mm outer diameter tubes and about 10% (w/v) of the sample concentrations in orthodichlorobenzene (ODCB). Pulse widths of 45° (9 μs) and pulse delay of 2 s were applied. The branch concentrations were determined by the ^{13}C-NMR results using a calibration technique since the measurement conditions used here do not satisfy the conditions for quantitative branch analysis. Details of the calibration procedure have been described elsewhere.[20] The vinyl concentrations of the fractions were determined from the peak at 910 cm^{-1} by using a Digilab FTS-15C Fourier transform infrared spectrometer in the following equation:

Vinyl (per 1000 carbons) $= 1.22 \times A_{910}/t$

where A_{910} and t are the absorption at 910 cm^{-1} and the thickness (mm), respectively.

RESULTS AND DISCUSSION

Length of LCBs as a Function of $\bar{M}_n$

Table I lists the number-average molecular weight ($\bar{M}_n$), the branch, and the vinyl concentrations per 1000 carbons of the fractions determined by osmometer, ^{13}C-NMR and FT IR, respectively. The branch and the vinyl concentrations in one mole of the fractions are evaluated by multiplying those values by $\bar{M}_n/14{,}000$ as shown in Table II.

The total number of carbons per one mole of the molecule in the fractions (C_T) are obtained by dividing $\bar{M}_n$ by 14 in a good approximation, and the total number of carbons that belong to short-chain branches (C_{SCB}) are given by

$$C_{SCB} = 5[\text{pentyl}] + 4[\text{butyl}] + 3[\text{propyl}] + 2[\text{ethyl}] + [\text{methyl}]$$

Table II   Branch and Vinyl Concentrations per One Mole of the Molecule of the Fractions

Sample	$10^{-4}\,\bar{M}_n/1.4$	Branch Contents/Molecule						Vinyl/Molecule
		Methyl	Ethyl	Propyl	Butyl	Pentyl	LCB	
Fraction 6	1.06	3.3	9.5	1.0	9.0	3.2	3.8	0.40
Fraction 8	1.96	5.5	16	1.2	15	5.7	6.5	0.47
Fraction 10	3.67	9.2	26	1.5	26	9.5	11	0.59
Fraction 12	7.29	20	47	4.4	51	18	21	0.87
Fraction 15	33.6	100	190	24	240	87	100	2.7

Table III   Values of LCB Parameters of the Fractions Determined by the ^{13}C-NMR and the Molecular Weight Measurements

Sample	$10^{-3}\ \bar{M}_n$	C_T	C_{SCB}	C_M	$\bar{L}_n$	$10^{-3}\ \bar{M}_L$	$\bar{M}_L/\bar{M}_n$
Fraction 6	14.8	1060	77	983	234	3.28	0.221
Fraction 8	27.5	1960	130	1830	263	3.68	0.134
Fraction 10	51.4	3670	220	3450	298	4.17	0.081
Fraction 12	102	7290	420	6870	314	4.40	0.043
Fraction 15	470	33600	1900	31700	309	4.33	0.009

where the square brackets represent the concentration of the each branch type per one mole of the molecule given in Table II.

The total number of carbons in the main chain of the molecule (C_M) including methyl and vinyl chain ends group are given in the difference between C_T and C_{SCB}:

$$C_M = C_T - C_{SCB}$$

Finally, average number of carbons in a LCB $(\bar{L}_n)$ is determined from

$$\bar{L}_n = C_M/([LCB] + [vinyl])$$

Here the denominator is the chain ends concentration, which is determined as the sum of the LCB and the vinyl concentrations in Table II. The number-average molecular weight of LCBs $(\bar{M}_L)$ is given by:

$$\bar{M}_L = 14 \times \bar{L}_n$$

The values of C_T, C_{SCB}, C_M, $\bar{L}_n$, $\bar{M}_L$, $\bar{M}_L/\bar{M}_n$, and $\bar{M}_n$ are listed in Table III and the correlation between $\bar{L}_n$ versus $\bar{M}_n$ is plotted in Figure 1.

It is clear that the size of LCBs $(\bar{L}_n)$ generally increases with increasing molecular weight in one HPLDPE. However, $\bar{L}_n$ seems to stay relatively constant at very high $\bar{M}_n$ and the value is around 300. It is interesting that the $\bar{L}_n$ values as a function of molecular weight found for the fractions of one parent HPLDPE are in good agreement with those obtained for whole HPLDPEs by Bugada and Rudin.[21]

The ratios of the mean LCB length to the number-average molecular weight $(\bar{M}_L/\bar{M}_n)$ of the fractions shown in Table III are plotted in Figure 2 as a function of $\bar{M}_n$. Since the increase in the length of LCBs with increasing $\bar{M}_n$ is only below one and a half times in the $\bar{M}_n$ range between 1.48×10^4 and
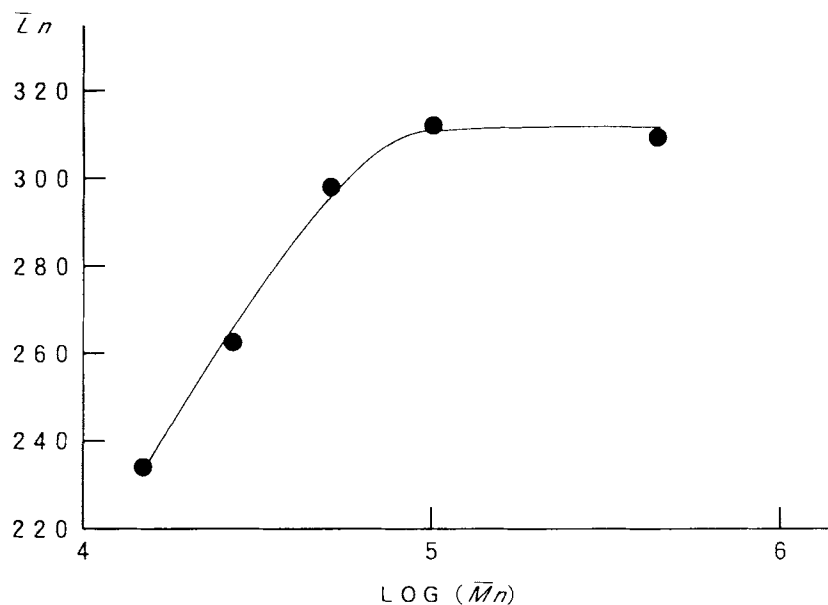
Figure 1   The mean LCB length $(\bar{L}_n)$ as a function of $\bar{M}_n$.

$(\bar{M}_L/\bar{M}_n)$

LOG $(\bar{M}n)$
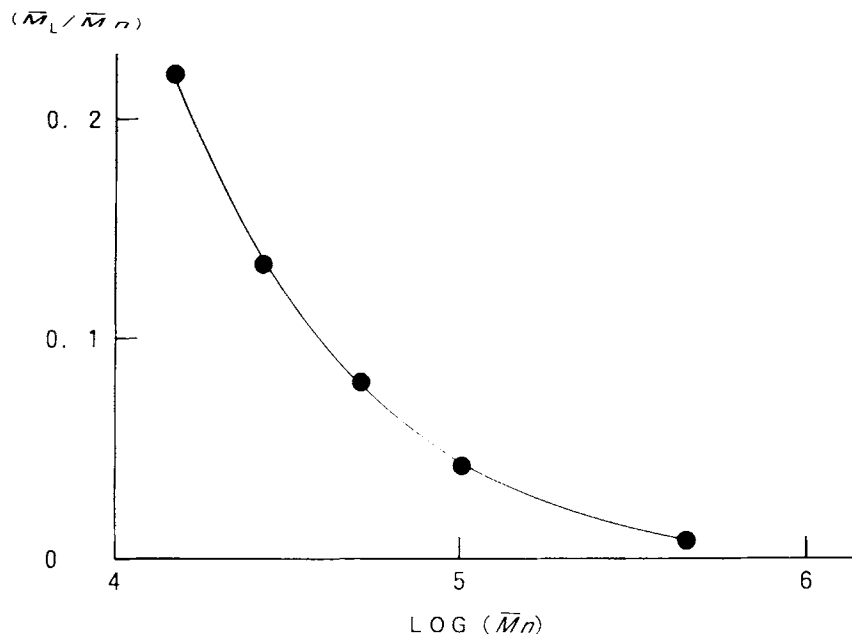
Figure 2 The ratio of LCB size to the parent molecular size $(\bar{M}_L/\bar{M}_n)$ as a function of $\bar{M}_n$.

47.0×10^4, the ratio decreases with increasing $\bar{M}_n$. The size of LCBs, on the average, becomes only about one percent of parent molecular size at very high $\bar{M}_n$.

LCB Indices Determination by ^{13}C-NMR and Intrinsic Viscosity

LCB indices can be determined by combining the ^{13}C-NMR and the intrinsic viscosity results. Solution viscosity is related to molecular structure by $g^\epsilon = [\eta]_b/[\eta]_l,$[25] where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosities of branched and linear molecules at the same molecular weight, respectively, g is the ratio of the mean-square radius of gyration of the branched molecules to that of the linear molecules,

and the exponent ϵ, the LCB index, is a variable parameter ranging from 0.5 to 1.5 depending on the shape of the molecule. For example, ϵ is 0.5 for star-shaped molecules[26] and 1.5 for linear-shaped molecules.[27] For randomly branched molecules with trifunctional branch points, Zimm and Stockmayer[28] have derived the following equation:

$$g = [(1 + m/7)^{1/2} + 4m/9\pi]^{-1/2}$$

where m is the average number of LCBs per one mole of molecule. Although there might be an argument on using the equation for trifunctional branch points, LCBs of HPLDPE seems to have a trifunctional character as pointed out by Bugada and Rudin.[22] The values of m were determined by ^{13}C-NMR. Table IV lists the values of m, g, $[\eta]_b/[\eta]_l$, and ϵ of the fractions. By considering the experimental uncertainty of the measurements, ϵ values in the low $\bar{M}_n$ range fall into around 0.5 and slightly increase and reach to around 0.78 in the very high $\bar{M}_n$ range. The ϵ values 0.5–0.78 seem to be inconsistent with the results of $(\bar{M}_L/\bar{M}_n)$ because the size of LCBs is only several percent or below of the parent molecular size and, in such case, the shape of the molecule can be expected to be comblike rather than starlike. Therefore, a very wide or bimodal distribution in length might be assumed in the architecture of the LCBs to explain the rheological properties of HPLDPE.

Table IV **LCB Indices of the Fractions Determined by the ^{13}C-NMR and the Intrinsic Viscosity Measurements**

Sample	m	g	$[\eta]_b/[\eta]_l$	ϵ
Fraction 6	2.2	0.83	0.85	0.87
Fraction 8	5.0	0.70	0.85	0.46
Fraction 10	9.6	0.59	0.78	0.47
Fraction 12	20	0.46	0.69	0.48
Fraction 15	100	0.24	0.33	0.78

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