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Generation Mechanism of Short-Chain Branching Distribution in Linear Low-Density Polyethylenes

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ABSTRACT: Some linear low-density polyethylenes (LLDPEs) have been examined in detail by temperature rising elution fractionation (TREF), size exclusion chromatography (SEC), ^{13}C NMR analysis, differential scanning calorimetry (DSC), and FTIR spectroscopy. From the results, the following have been concluded: (i) LLDPEs manufactured by four different processes have in common a characteristic intermolecular bimodal short-chain branching (SCB) distribution; (ii) the bimodal SCB distribution is caused by two kinds of active sites in Ti-based heterogeneous Ziegler catalysts, identified by the values of the reactivity ratio product (r_1r_2 = 0.5–0.6 and r_1r_2 = 1.0, respectively); (iii) one kind of active site, having an alternating character in the copolymerization (identified by r_1r_2 = 0.5–0.6), gives the higher SCB concentration peak in the bimodal SCB distribution and the lower molecular weight polymer, while the other kind of active site, having a random character (identified by r_1r_2 = 1.0), gives the lower SCB concentration peak and the higher molecular weight polymer.

Introduction

Since the commercial introduction of linear low-density polyethylene (LLDPE), which is produced by copolymerizing ethylene with 1-olefins using a Ziegler catalyst, there has been great interest in the properties of LLDPE as a third type of polyethylene. LLDPE shows some characteristic properties not only in viscoelastic behavior, due to little or no long-chain branching (LCB), but also in melting and impact strength behavior, due to short-chain branching (SCB).

A few studies on SCB sequential analysis[1,2] have been conducted on LLDPE whole polymer by ^{13}C nuclear magnetic resonance (NMR) assuming that LLDPE has a homogeneous character. In this sense, homogeneity should be understood to mean that the SCB distribution in the molecule and the related single-peak sequence length distribution can be described by one set of reactivity ratios, that is, no difference between individual molecules. However, it seems difficult to explain all the structural characteristics by only this kind of short-range intramolecular SCB distribution analysis, because a very wide intermolecular SCB distribution due to the diversity of the active sites in heterogeneous Ziegler catalysts is expected to exist.[3] This heterogeneous character of the SCB distribution in LLDPE is a remarkable phenomenon. It can be observed, for instance, in the melting behavior as the appearance of several peaks in differential scanning calorimetry (DSC). This suggests that LLDPE is not uniform in composition.

The cause of this nonuniformity in melting behavior might be due to a heterogeneous SCB distribution which gives a multipeak ethylene sequence length distribution. Moreover, a question that comes up is whether the observed heterogeneity exists within individual molecules (intramolecular) or between different molecules (intermolecular). Unequivocal answers to these problems can be provided by cross-fractionation. This method involves first separating molecules according to ethylene sequence length and next separating them by molecular size. Such a fractionation was carried out by Wild et al.[4,5] and by Nakano and Goto,[6] using temperature rising elution fractionation (TREF) and size exclusion chromatography (SEC).

Recently, Wild et al.[5] reported that some LLDPEs had a characteristic bimodal intermolecular SCB distribution compared with a conventional high-pressure, low-density polyethylene (HP-LDPE), which had a single-peak SCB distribution. From these results, it seems important to consider the intermolecular SCB distribution in discussing the properties of LLDPEs. However, there have been very few studies that deal in detail with the characteristic intermolecular SCB distribution of LLDPE and its generation mechanism. In the present work, we have investigated the intermolecular SCB distribution of LLDPE and its generation mechanism by TREF, SEC, ^{13}C NMR, DSC, and FTIR. We then discuss the molecular weight of the polymer based on the mechanism.

Experimental Section

The six LLDPEs and one HP-LDPE that have been examined are listed in Table I along with their characteristic properties. LLDPE-A, -B, -C, and -D are manufactured by gas,[7a] slurry,[7b] bulk,[7c] and solution[7d] processes, respectively, while HP-LDPE is a conventional high-pressure polyethylene. The polymerization of the LLDPEs was carried out in the presence of MgCl$_2$-supported, TiCl$_4$- or TiCl$_3$-based heterogeneous Ziegler catalysts with triethylaluminum or diethylaluminum chloride as cocatalyst.

The analytical TREF–SEC system, the fractionation procedure, and the data-processing procedure used have been described previously in detail.[6] A schematic diagram of the system is shown in Figure 1. The fractionation technique involves loading a small sample of polymer (2 mg) onto a column of inert packing by slow cooling[6] a 0.4% *o*-dichlorobenzene solution. The polymer is then eluted stepwise from the column at 40, 50, 60, 65, 70, 73, 76, 80, 84, 88, 90, 92, 95, 98, 101, 105, 110, 120, 130, and 140 °C at a flow rate of 1 mL/min. Each eluted polymer solution is automatically introduced into the SEC part of the system, which has an infrared detector.

LLDPE-A was subjected to preparative TREF. The preparative TREF system (Figure 2) was constructed in our laboratory based on the analytical TREF system, and the procedure was as follows. About 2.5 g of LLDPE-A was loaded onto the column in the same way as the analytical TREF. The polymer was then eluted stepwise at 40, 64, 74, 84, 91, and 97 °C. These six fractions (F1 to F6) are schematically shown in Figure 3 with the elution curve. Detailed analyses by ^{13}C NMR, DSC, and FTIR were performed on F1 to F6. Another preparative TREF was carried out in the following manner. LLDPE-A loaded onto a glass wool cloth was eluted stepwise at 40, 82, and 97 °C. These three fractions (F′1 to F′3) are also schematically shown in Figure 3. Only ^{13}C NMR measurement was conducted on F′1 to F′3.

^{13}C NMR spectra were obtained at 120 °C and 50.1 MHz with a JEOL-FX200 spectrometer equipped with a JEC-980B minicomputer operating with quadrature detection. Measurements were made on ca. 7% (w/v) sample solutions in a mixed solvent of 70% (v/v) *o*-dichlorobenzene and 30% (v/v) perdeuteriobenzene in a 10-mm sample tube. Measurements were performed for 40–60 h for the TREF fractions and HP-LDPE and for 7–8

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Table I
Characteristics of LDPEs Examined in This Work

sample	comonomer	$\sum CH_3$[a]	density, g/cm^3	$\bar{M}_w \times 10^{-4}$	polymerization conditions: process	temp, °C	press, kg/cm^3
LLDPE-A	1-butene	19.0	0.920	8.3	gas	85	21
LLDPE-B	1-butene	20.0	0.920	8.9	slurry	85	21
LLDPE-C	1-hexene	19.5	0.920	9.7	bulk	230	1200
LLDPE-D	1-butene	17.0	0.921	7.4	solution	145	30
LLDPE-E	1-butene	17.0	0.921		solution	145	30
LLDPE-F	1-butene	20.0	0.920		solution	145	30
HP-LDPE		26.8	0.920	27.1[b]	bulk	300	2000

[a] Per 1000 C; determined by ^{13}C NMR. [b] Determined by Drott–Mendelson method.

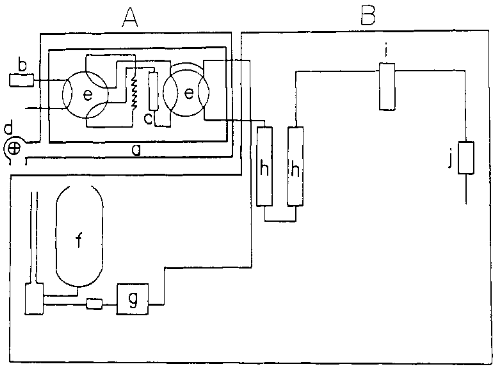

Figure 1. Schematic diagram of the analytical TREF–SEC system. (A) TREF part: (a) block heater; (b) syringe; (c) column; (d) fan cooler; (e) valve. (B) SEC part: (f) solvent tank; (g) pump; (h) column; (i) detector; (j) siphon.

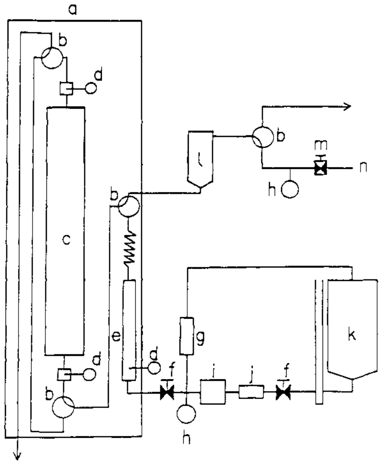

Figure 2. Schematic diagram of the preparative TREF system: (a) oven; (b) three-way valve; (c) column (70-mm i.d., 1000 mm); (d) thermoelectric couple; (e) preheating column; (f) stop valve; (g) relief valve; (h) pressure gauge; (i) pump; (j) filter; (k) solvent tank; (l) solution tank; (m) constant-pressure valve; (n) N_2 inlet.

h for LLDPE whole polymers. The FIDs were accumulated and Fourier-transformed with a 12-bit A/D converter and a 16-bit minicomputer. The data processing was carried out in double precision (32 bit) to obtain a wider dynamic range. A pulse width of 45° (7 μs) and a pulse delay of 2 s were applied. Quantitative analysis can be done under those measurement conditions as shown before.[8] Details of the quantitative analysis are described later.

A Perkin-Elmer Type II instrument was used for DSC measurement. Cooling and heating speeds of 10 °C/min were used with 5-mg polymer samples.

FTIR spectra were recorded on a Digilab FTS-15C FTIR system equipped with a mercury–cadmium telluride detector. A typical measurement was performed under the following conditions: the number of scans was 100, the digital spectral resolution was 4 cm^{-1}, and a double-precision data-processing program was used. For the measurements, films about 0.1 mm thick were

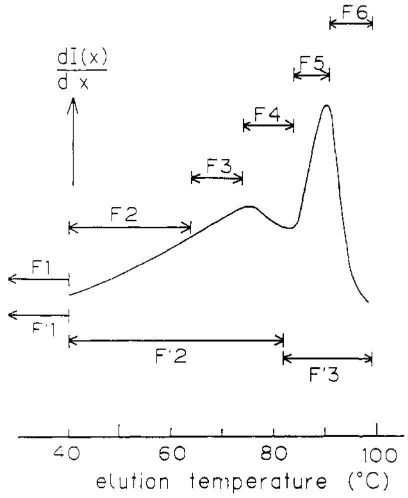

Figure 3. TREF diagram of LLDPE-A showing the preparative TREF fractions.

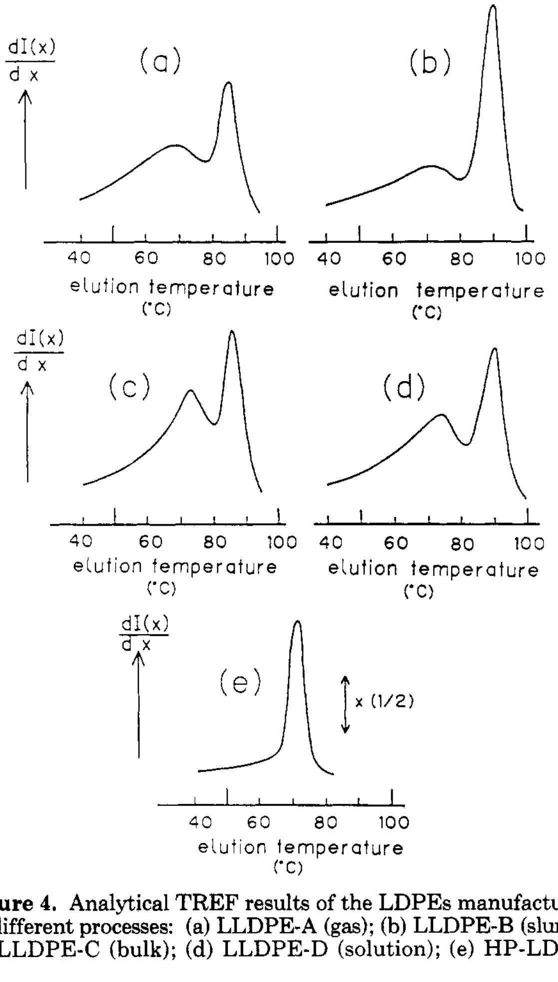

Figure 4. Analytical TREF results of the LDPEs manufactured by different processes: (a) LLDPE-A (gas); (b) LLDPE-B (slurry); (c) LLDPE-C (bulk); (d) LLDPE-D (solution); (e) HP-LDPE.

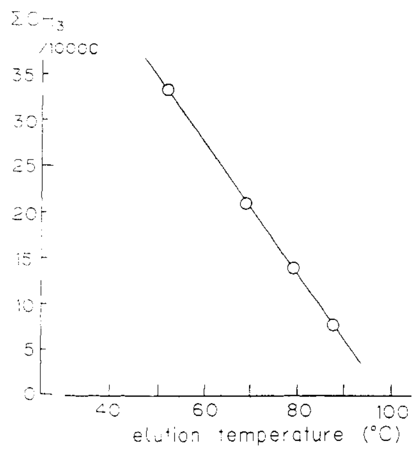

Figure 5. Relationship between the SCB concentration and the elution temperature.

prepared by hot pressing at 180 °C. The film thickness was measured by a micrometer, and the densities were measured by the density-gradient column method.

Results and Discussion

A. Analytical TREF Results for LDPEs. Figure 4 shows the results of analytical TREF for LDPEs. There is a linear relationship between the elution temperature and the SCB concentration, as shown in Figure 5. Figure 4 provides the SCB distribution curves. Comparison of the curves indicates that LLDPEs manufactured under very different conditions of temperature, pressure, and solvent have in common a characteristic bimodel SCB distribution, while HP-LDPE exhibits a single-peak SCB distribution. Similar phenomena were observed by Wild et al. for some LDPEs.[5]

B. Cause of the Bimodal SCB Distribution. There seem to be two possible explanations for the bimodal distribution of LLDPEs. One is the existence of two kinds of active sites in Ti-based heterogeneous Ziegler catalysts which have different characters in the copolymerization of ethylene and 1-olefin. The other is a discontinuous change in monomer concentration which exists in common in the four polymerization processes. However, the latter case in unlikely because such a common feature does not seem to exist among those processes owing to the very different polymerization conditions. For example, the polymer and solvent are in a homogeneous state in the solution and bulk processes, while they are in a heterogeneous state in the slurry and gas processes. Moreover, since the polymerization is carried out continuously in these processes, the time-dependent change of monomer concentration seems improbable. This was ensured by the fact that the bimodal SCB distribution did not change with the polymerization time in the solution process, as shown in Figure 6. Therefore, the possibility of a discontinuous change in monomer concentration depending on the polymerization state and the polymerization time can be ruled out. Consequently, the bimodal SCB distribution is expected to be caused by two kinds of active sites in Ti-based heterogeneous Ziegler catalysts.

C. Identification of the Active Sites. 1. Problems in Applying Copolymerization Theory. In characterizing the two different active sites, the most effective way is the sequential analysis based on the copolymerization theory. However, further difficult problems remain to be solved in applying copolymerization theory to copolymers prepared by Ti-based heterogeneous Ziegler catalysts:

(a) If there exist at least two kinds of active sites in the catalyst, the correct copolymerization parameters cannot be derived from the sequential analysis for a whole polymer.

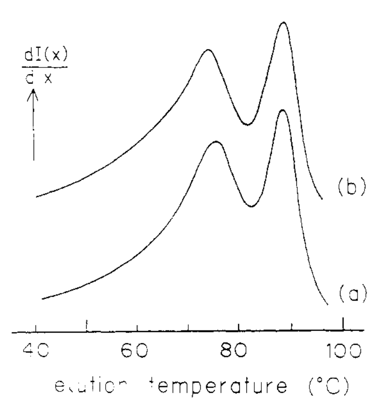

Figure 6. Change of the TREF diagrams with the polymerization time: (a) 3 min (LLDPE-E); (b) 18 min (LLDPE-F).

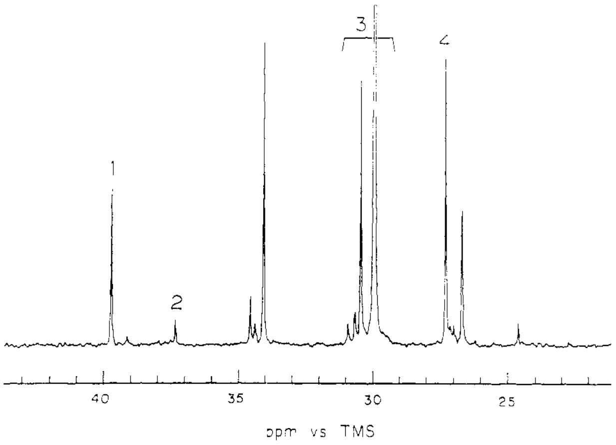

Figure 7. ^{13}C NMR spectrum of F1 showing the key signals: (1) CH(39.6), (2) CH(37.4), (3) main-CH_2; and (4) β-CH_2.

(b) It is doubtful whether the monomer concentration in the feed is identical with those at the active sites because of the extremely fast polymerization rate. Therefore, the copolymerization analysis using the monomer concentration in the feed is not reliable.

These problems were reflected, for example, in the fact that ethylene–propylene rubber prepared by Ti-based heterogeneous Ziegler catalysts shows a very broad compositional distribution.[3]

2. Solution for Those Problems. In order to solve the problems, the following procedure for sequential analysis has been adopted in this work: (a) the use of the LLDPE manufactured by the continuous polymerization process to minimize the change of the monomer concentration with polymerization time; (b) preparation of the LLDPE which is produced from only one kind of active site using the preparative TREF system; (c) determination of the copolymerization parameters which identify the two kinds of active sites, based on the information derived only from the polymer.

3. Procedure of Identification. Specifically, LLDPE-A was subjected to preparative TREF, and the reactivity ratio product (r_1r_2) was determined for each fraction by ^{13}C NMR with the equation[9]

$$r_1r_2 = 1 + f(\chi + 1) - (f + 1)(\chi + 1)^{1/2} \qquad (1)$$

Here, f is the mole ratio of ethylene to 1-butene in the copolymer and χ is the mole ratio of 1-butene in sequences of two or more to isolated 1-butene in the copolymer. Since there is no appreciable signal due to the contiguous trimers

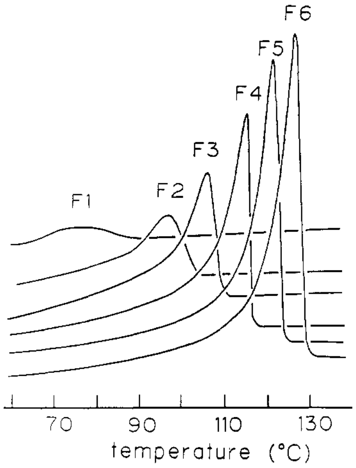

Figure 8. DSC melting curves of F1 to F6.

Table II
Values of *f*, χ, and r_1r_2 for F1 to F5 and F′1 to F′3

fraction	f	χ	r_1r_2
F1	6.51	0.170	0.49
F2	14.0	0.0686	0.45
F3	22.9	0.0530	0.59
F4	34.7	0.0347	0.59
F5	62.4	0.0313	0.97
F′1	6.45	0.217	0.63
F′2	14.7	0.0956	0.67
F′3	32.0	0.0643	1.00

of 1-butene units (BBB triad) around 35 ppm[1] even for the fraction with the highest 1-butene concentration (F1) (Figure 7), f and χ can be determined by ^{13}C NMR with the equation.

$$f = \frac{I_{\text{main}} + (3/2)I_\beta + 2I_{\text{BEB}}}{\left(\dfrac{1}{\chi + 1}\right)I_\beta + 2\left(\dfrac{\chi}{\chi + 1}\right)I_\beta} \tag{2}$$

I_{main} is the integral intensity of the main-CH$_2$ signal at 30.0 ppm, I_β is the integral intensity of the β-CH$_2$ signal at 27.3 ppm, I_{BEB} is the integral intensity of the CH$_2$ signal due to the isolated ethylene units (BEB triad) at 24.7 ppm, and

$$\chi = I_{\text{CH(37.4)}}/I_{\text{CH(39.6)}} \tag{3}$$

where $I_{\text{CH(37.4)}}$ is the integral intensity of the CH signal from the 1-butene unit in sequences of two or more at 37.4 ppm and $I_{\text{CH(39.6)}}$ is the integral intensity of the CH signal from the isolated 1-butene unit at 39.6 ppm. These key signals are shown in Figure 7.

4. Preparative TREF Results for LLDPE-A. DSC results of F1 to F6 are shown in Figure 8. From these results, it is demonstrated that TREF was well performed and the bimodal SCB distribution has an intermolecular character because each fraction gives a sharp melting curve. The values of f and χ for F1 to F5 and F′1 and F′3 are shown in Table II.

5. Reactivity Ratio Product (r_1r_2). The reactivity ratio products have been determined from eq 1 by ^{13}C NMR analysis for F1 to F5 and F′1 and F′3. These values are listed in Table II and are plotted against the elution temperature in Figure 9, showing the bimodal SCB distribution curve. The active sites giving the higher SCB concentration peak of the bimodal SCB distribution (F1 to F4 and F′1 and F′2) have an alternating character of copolymerization, identified by r_1r_2 = 0.5–0.6. On the other hand, the active sites giving the lower SCB concentration peak (F5 and F′3) have a random character, identified by r_1r_2 = 1.0. From these results, it is concluded that the bimodal SCB distribution is caused by two kinds of active sites in Ti-based heterogeneous Ziegler catalysts, identified by r_1r_2 = 0.5–0.6 and r_1r_2 = 1.0, respectively. Since two different stereospecific (isotactic and atactic) active sites are generally recognized in the polymerization of propene using Ti-based heterogeneous Ziegler catalysts, the existence of two kinds of active sites in the copolymerization of ethylene and 1-olefin is also reasonably probable.

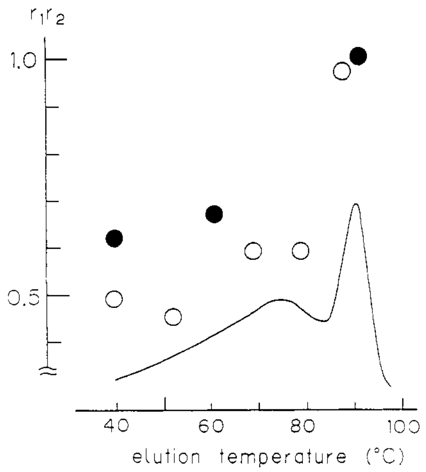

Figure 9. Plots of r_1r_2 values against the elution temperature for the preparative TREF fractions showing the TREF diagram: (○) F1 to F5; (●) F′1 to F′3.

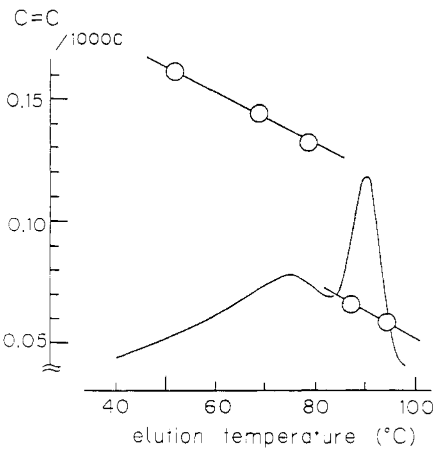

Figure 10. Plots of the vinyl concentrations against the elution temperature for the preparative TREF fractions (F2 to F6) showing the TREF diagram.

D. Molecular Weights of the Polymers Produced by the Two Kinds of Active Sites. Vinyl concentrations were determined for the five fractions (F2 to F6) from the peak at 910 cm^{-1} in the IR spectra. In Figure 10, the vinyl concentrations are plotted against the elution temperature, showing the bimodal SCB distribution curve. It is clearly demonstrated that there is a discontinuity in vinyl concentrations between the polymers produced by the two kinds of active sites. The discontinuity means that the molecular weights of the polymers produced by the two different active sites are different. Since the bimodal SCB distribution can be separated into each peak at a boundary elution temperature T_b (~84 °C extrapolated for LLDPE-A), the molecular weight distributions of the polymers eluted below and above that temperature were determined by the analytical TREF–SEC system. The results are shown in Table III and Figure 11. From these results, it is clear that the sites of r_1r_2 = 0.5–0.6 give the lower molecular weight polymer and the sites of r_1r_2 = 1.0

Table III
Molecular Weights of the Polymers Eluted below and above the Boundary Temperature (T_b) of the Bimodal SCB Distribution for LLDPE-A to LLDPE-D

	$\bar{M}_w \times 10^{-4}$			
	LLDPE-A	LLDPE-B	LLDPE-C	LLDPE-D
whole polymer	8.3	8.9	9.7	7.4
polymer below T_b[a]	7.0	5.6	8.0	6.6
polymer above T_b	11.1	12.0	12.2	9.1

[a] T_b is the boundary elution temperature between the two peaks of the bimodal SCB distribution curve.

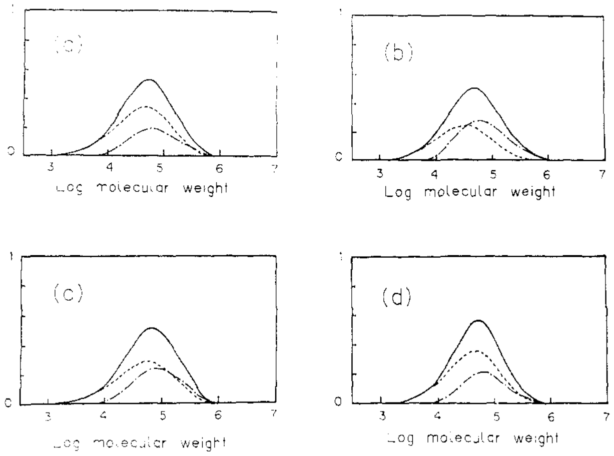

Figure 11. Molecular weight distribution curves of the polymers eluted below and above the boundary temperature (T_b) of the bimodal SCB distribution: (—) whole polymer; (- - -) polymer eluted below T_b; (-·-) polymer eluted above T_b. (a) LLDPE-A; (b) LLDPE-B; (c) LLDPE-C; (d) LLDPE-D.

give the higher molecular weight polymer.

Conclusion

Four LLDPEs manufactured by different processes and one HP-LDPE have been examined by TREF, SEC, ^{13}C NMR, DSC, and FTIR. From these results, the following conclusions were derived:

(1) LLDPEs have an intermolecular bimodal SCB distribution in common.

(2) The bimodal SCB distribution is caused by two kinds of active sites in Ti-based heterogeneous Ziegler catalysts.

(3) One kind of active site has an alternating character of copolymerization, identified by $r_1r_2 = 0.5–0.6$, and the other has a random character, identified by $r_1r_2 = 1.0$.

(4) The sites of $r_1r_2 = 0.5–0.6$ give the higher SCB concentration peak of the bimodal SCB distribution and lower molecular weight polymer, while the sites of $r_1r_2 = 1.0$ give the lower SCB concentration peak and higher molecular weight polymer.

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Registry No. (1-Butene)(ethylene) (copolymer), 25087-34-7; (1-hexene)(ethylene) (copolymer), 25213-02-9.

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Crystal Lattice Modulus of Polyethylene Calculated As Functions of Crystallinity and Molecular Orientation by Linear Elastic Theory

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ABSTRACT: A mathematical representation based on a linear elastic theory is proposed by which one may investigate the dependence of the crystal lattice modulus in the chain direction on molecular orientation and crystallinity. This description indicates that the crystal lattice modulus as measured by X-ray diffraction is different from the intrinsic crystal lattice modulus. However, the numerical calculation indicates that the calculated value is almost independent of the molecular orientation and crystallinity except in the case of a low degree of molecular orientation and low crystallinity, although the calculated Young's modulus is strongly affected by them. Thus it turns out that X-ray diffraction has advantages in measuring the crystal lattice modulus exactly.

Introduction

The elastic moduli of a crystal lattice in the direction of the molecular chain axis have been reported from the theoretical and experimental viewpoints. Lyons,[1] Treloar,[2] Shimanouchi et al.,[3,4] and Miyazawa[5,6] have carried out theoretical treatments for various polymers using reliable force constants obtained mainly from infrared spectroscopy. Odajima et al.[7] calculated the elastic constants, C_{ij}, of polyethylene on the basis of Born's dynamical theory[8] for a model of interatomic interactions representing inter- and intramolecular force fields.

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