

Characterization of Ethylene-1-Butene Copolymer by Differential Scanning Calorimetry and ^{13}C -NMR Spectroscopy

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Synopsis

Two kinds of ethylene-1-butene copolymers that were produced by the different procedures, that is, the slurry and the high-pressure polymerizations, were characterized by differential scanning calorimetry (DSC) and carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy. The melting points of both copolymers were found to be different in spite of the same 1-butene content. It was deduced that this phenomenon depended upon the subtly different chain structures between these two copolymers from the tetrad monomer sequence analysis by ^{13}C -NMR method. In addition, the behavior of the composition fractionation by temperature rising elution technique was also considered to be affected by the chain structures.

INTRODUCTION

The ethylene-1-butene copolymer (EB) attracts public attention as a novel-type polyethylene, that is, a kind of the linear low density polyethylene. DSC is widely employed as a source of information about the melting behavior of polymers. By this method one can determine the melting point (mp) and the heat of fusion (ΔH_f) of the sample under investigation. Therefore, many works on thermal analysis by DSC or differential thermal analysis (DTA) of ethylene copolymers have been reported up to the present.¹⁻⁶ In particular, the correlations between the mp's and the polymer chain structures of these copolymers reported by Casey et al.¹ and Bastien et al.² are interesting. They reported the fact that the mp's were different even for the ethylene copolymers containing the same comonomer type and content, and assumed that the origin of the difference in mp's was dependent on whether the comonomer units were uniformly distributed or in groups throughout the polymer chain.

We also found the similar phenomena in the cases of the EBs produced by two different polymerization procedures using the same catalyst system. The purpose of this study is to clarify the cause of this difference in the mp's through the tetrad monomer sequence analysis by the ^{13}C -NMR spectroscopy. As a result, it was deduced that the origin of the difference in mp's was due to the mode of 1-butene distribution along the polymer chain.

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EXPERIMENTAL

Samples

The specific characteristics of the EB samples used in this investigation are listed in Table I. Samples A–D were the products of the slurry polymerization (SP) in butane at 70°C under the pressure of 20 kg/cm² using the catalyst system of supported titanium (TiCl₄)–triethyl aluminum in a pilot-plant scale reactor. The other samples, E–G, were produced by an industrial scale high-pressure tubular reactor [the high pressure polymerization (HP)] using the same catalyst system.

In practice, however, the fractions of these samples obtained by the composition fractionation described below, were used.

Composition Fractionation

This procedure is similar to that described by Shirayama et al.⁷ About 400 mL of Celite 545 coated with 8 g of precipitated polymer was introduced into column 55 mm in diameter and 700 mm in length. The polymer was precipitated from 360 mL of xylene solution containing 0.1% (w/v) antioxidant (Irganox 1010) on the Celite 545 by gradually lowering the temperature. A preheated solvent (xylene) was continuously dropped into the Celite column at a previously settled temperature, and the overflow effluent was collected in a beaker. The extraction temperature was raised stepwise in small intervals over the range of 45–97°C. In order to assure temperature equilibrium, the temperature was kept constant at each level for 30 min before the next extraction started. In this study, 500 mL of xylene for each fraction was added during 90 min at each level of temperature, and about 14 fractions were obtained for each run. To prevent oxidative degradation during the fractionation, 0.1% (w/v) Irganox 1010 was added to the solvent, and all operations were carried out under nitrogen. The polymer was recovered by precipitating with methanol, filtering, washing, and drying in a vacuum oven at 40°C overnight.

DSC

The thermal analysis was carried out by a Perkin-Elmer DSC-2 unit on a ca. 10-mg sample in a covered aluminum sample pan.

TABLE I
Characteristics of the Samples

Sample ^a	1-Butene content (mol %)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	Density (g/cc)
A (SP)	3.35	11.3	1.68	6.70	0.920
B (SP)	3.04	9.84	1.07	9.22	0.928
C (SP)	2.98	3.73	0.58	6.45	0.923
D (SP)	3.56	30.9	6.13	5.05	0.914
E (HP)	2.92	14.4	1.26	11.4	0.921
F (HP)	3.49	5.35	0.65	8.22	0.927
G (HP)	3.69	7.98	1.11	7.20	0.919

^a SP = slurry polymerization; HP = high-pressure polymerization.

The thermogram was calibrated with indium as a temperature standard. The powdered sample covered with the aluminum disk was gently compressed while molten on the hot plate and sealed tightly to ensure good contact with the detection area after cooling to room temperature. The reference holder, being empty, was also covered and sealed with the aluminum disk.

For the calculation of ΔH_f , the apparatus constant k was determined using benzoic acid ($\Delta H_f = 33.9$ cal/g).⁸ The "no-sample" base line had been previously determined to permit subsequent reliable area measurements. The area measurement was done by weighing the endothermic peak portion cut out from the Xerox copy.

In order to be free from unknown thermal histories, samples were heated to 160°C above their mp's manually, where they were held for 3 min and then cooled to 25°C at a controlled rate of 5°C/min, where they were held for 3 min. Consecutively, the thermogram was recorded by scanning to 160°C at 10°C/min. In this study, the temperature for the endothermic peak top was defined as the mp.

^{13}C - and ^1H -NMR

The ^1H - and ^{13}C -NMR spectra were recorded on a JEOL FX200 NMR spectrometer (^1H : 199.50 MHz; ^{13}C : 50.10 MHz). The contents of 1-butene were determined by the ^1H -NMR method and the tetrad monomer sequence fractions were done by the proton-decoupled ^{13}C -NMR method. Sample measurements were made at 130°C.

Instrumental conditions for ^1H -NMR measurement were as follows: pulse width, 45°; pulse repetition, 10 s; and number of scans, 20–100. Polymer solutions for the ^1H -NMR measurements were prepared in *o*-dichlorobenzene (ODCB)/deuteriobenzene- d_6 (C_6D_6) (80/20 in volume), with octamethylcyclotetrasiloxane (OMCTS) as internal reference. Sample concentration was 5% (w/v). The intensities of the signals of ^1H -NMR spectra were determined by the weights of signals portions cut out from the Xerox copies. The 1-butene (C_4) content was calculated from the intensities of the signals at 1.18 ppm (methylene and methine protons) and 0.80 ppm (methyl protons) from OMCTS according to the following equation:

$$\text{C}_4 \text{ content (mol \%)} = 400 \times \text{I}(0.80 \text{ ppm}) / [3 \times \text{I}(1.18 \text{ ppm}) - \text{I}(0.80 \text{ ppm})]$$

Instrumental conditions for ^{13}C -NMR measurement were as follows: pulse width, 45°; pulse repetition, 10 s; spectral width, 8000 Hz; number of scans, 6400–23,000; number of data points per spectrum, 16K; and double-precision arithmetic. Polymer solutions for ^{13}C -NMR measurements were prepared in ODCB/ C_6D_6 with OMCTS as internal reference, and the sample concentration was 15% (w/v). The intensities of the signals of ^{13}C -NMR spectra were determined by the same method as that of ^1H -NMR mentioned above. The determination of the tetrad monomer sequence fractions was done according to the method reported by Hsieh et al.⁹

TABLE II
Analytical Data of the Compositional Fractions

Fraction No.	Extraction temp (°C)	C ₄ content (mol %)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	mp (°C)	ΔH_f (cal/mg)
Sample B (SP)							
1	Room temp	20.79	5.01	0.73	6.88	65.8	0.0036
2	45	12.11	6.94	0.74	8.99	76.9	0.0103
3	50	10.39	7.27	0.86	8.44	87.9	0.0139
4	55	7.58	6.62	1.01	6.57	95.1	0.0183
5	60	6.19	7.48	1.21	6.19	100.6	0.0190
6	65	5.65	8.67	1.21	7.15	105.3	0.0229
7	69	4.34	8.16	1.29	6.35	109.9	0.0261
8	73	3.82	8.59	1.35	6.34	115.2	0.0296
9	77	2.68	8.31	1.36	6.09	118.8	0.0307
10	81	2.35	8.15	1.43	5.72	121.6	0.0352
11	85	1.46	8.07	1.44	5.61	125.2	0.0378
12	89	1.30	9.14	1.88	4.87	126.7	0.0409
13	93	0.78	10.5	1.98	5.29	127.8	0.0405
14	97	0.55	13.7	3.22	4.26	129.4	0.0414
Sample G (HP)							
1	45	9.43	2.24	0.42	5.27	84.2	0.0182
2	50	7.13	2.44	0.63	3.85	93.7	0.0210
3	55	5.47	3.20	0.97	3.30	99.3	0.0240
4	60	5.05	4.10	1.15	3.58	101.0	0.0249
5	65	4.21	5.99	1.65	3.64	104.5	0.0262
6	69	3.37	6.57	1.82	3.61	108.8	0.0286
7	73	2.44	7.59	2.61	2.91	112.5	0.0284
8	77	1.93	9.54	3.22	2.96	116.6	0.0313
9	81	1.58	11.0	3.75	2.93	120.1	0.0327
10	85	1.35	12.3	4.30	2.85	122.4	0.0361
11	89	1.03	14.9	4.45	3.34	125.2	0.0346
12	95	0.56	19.2	7.16	2.68	128.4	0.0362

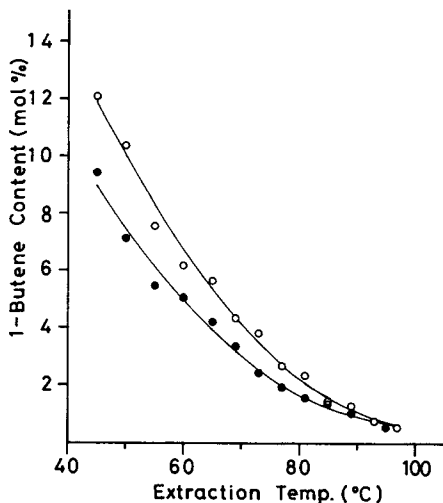


Fig. 1. Relationships between 1-butene contents and extraction temperatures for compositional fractions: (○) sample B (SP); (●) sample G (HP) in Table II.

Molecular Weight Determination

The molecular weights, M_w and M_n , of samples were determined by gel permeation chromatography (GPC) utilizing the universal calibration method.^{10,11} The chromatogram was recorded at 135°C on a Waters ALC/GPC 150C GPC instrument with a two-column Shodex A-80M (Showa Denko Co.) arrangement using ODCB as the carrier solvent. Solution concentration was 0.1% (w/v). M_w and M_n were calculated using the chromatogram data and Mark-Houwink-Sakurada constants, K and a . The constants K and a were determined from the chromatogram data and intrinsic viscosities of two samples which had the same C'_4 content but different molecular weights, according to the method reported by Zhongde et al.¹²

RESULTS AND DISCUSSION

Composition Fractionation

Two typical examples of the data on the composition fractionation (samples B and G) are given in Table II together with the values of mp 's and ΔH_f 's for the fractions. In Figure 1, the C'_4 contents of fractions are plotted against the extraction temperatures of those for two samples.

These results show that the C'_4 content of fraction decreases smoothly with a rise of the extraction temperature. From the multiple regression analysis using a computer, both curves as a function of the extraction temperature (t) can be approximately represented as: $C'_4 = At^2 - Bt + C$, where A, B , and C are the constants. However, two curves of samples B and G are not in agreement. It is supposed that this phenomenon is closely related to the differences in the mp 's and the polymer chain structures between these two kinds of samples, mentioned below.

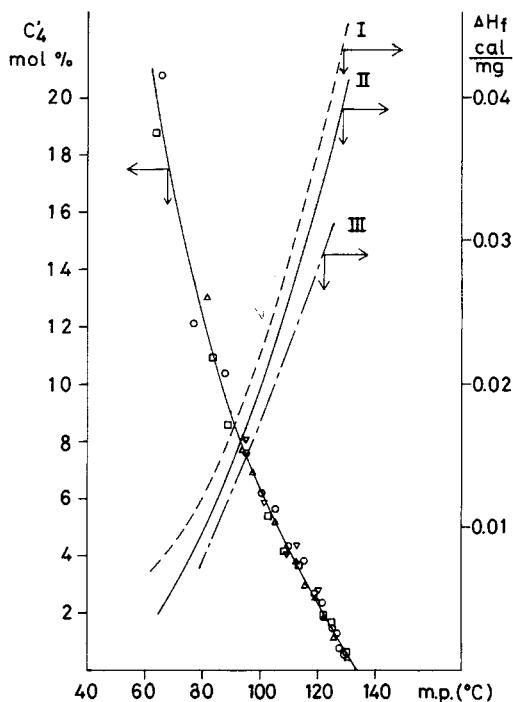


Fig. 2. 1-Butene content-melting point and ΔH_f -melting point relationships for slurry polymerization polymers (samples A-D in Table I): (\square , I) sample C; (\circ , II) sample B; (\triangle , II) sample A; (∇ , III) sample D.

Relationships between 1-Butene Content and Melting Point

In Figure 2, the C_4 contents, as determined by $^1\text{H-NMR}$ method, are plotted against the mp's on the compositional fractions of the samples produced by the slurry polymerization procedure. Also included in Figure 2 are the three lines showing the relations between the ΔH_f 's and the mp's of the fractions. These four curves were obtained by the multiple regression analysis. It is pointed out that the molecular weight in the range examined does not affect the mp, although it has a potent influence upon the ΔH_f ; that is, the relation between the mp and the C_4 content results in a single curve irrespective of the molecular weight. These results were also found in the case of the HP samples. As to the ΔH_f , it decreases as the molecular weight becomes larger. These facts indicate that higher molecular weight affects crystallinity more than the mp because the polymer chains cannot completely crystallize through chain entanglements and remain partially in the amorphous state.^{5,13} The relation between the mp and the C_4 content, shown in Figure 2, does not necessarily follow Flory's copolymer melting equation,¹⁴ because in this study the mp has not been measured in the equilibrium state and none of samples is the ideal random copolymer from the results of the sequence analysis by the $^{13}\text{C-NMR}$ method mentioned below.

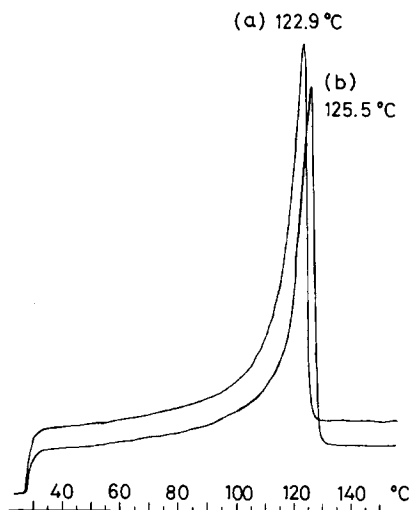


Fig. 3. DSC curves of fractions of slurry polymerization (SP) and high-pressure polymerization (HP) polymers: (a) HP, $C_4 = 1.51$ mol %, $M_w = 15.2 \times 10^4$, $M_w/M_n = 3.41$; (b) SP, $C_4 = 1.46$ mol %, $M_w = 17.7 \times 10^4$, $M_w/M_n = 5.15$

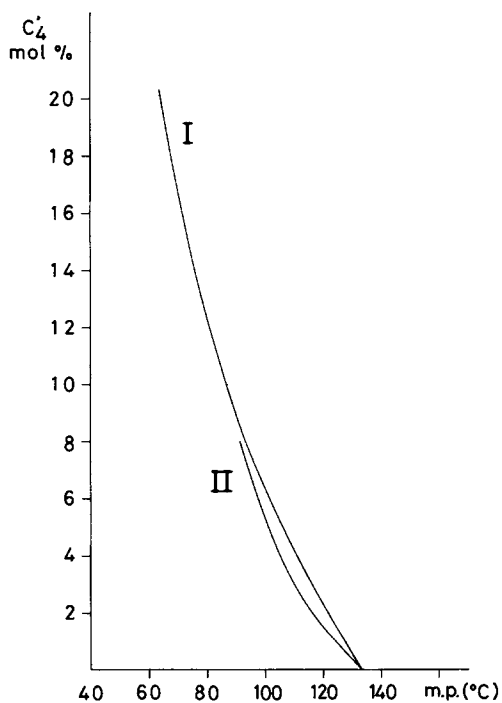


Fig. 4. 1-Butene content-melting point relationship: (I) slurry polymerization polymers (samples A-D); (II) high-pressure polymerization polymers (samples E-G).

TABLE III
Results of Tetrad Monomer Sequence Fractions of Several Pairs of Samples

Pairs of samples	Mole fractions										
	S_{EEEE}	S_{EEEB}	S_{EEER}	S_{EEER}	S_{EEEB}	S_{EEBE}	S_{EEBB}	S_{EEBE}	S_{EEBB}	S_{EEBE}	S_{EEBB}
E-8 (HP) ^a mp = 112.0°C C ₄ = 3.32 mol %	obs	0.879	0.054	0.0007	0.061	0.0013	0.0026	0	0.0007	0	0
	calcd ^b	0.874	0.060	0.0010	0.060	0.0021	0.0021	~0	0.0010	~0	~0
	obs/calcd	1.007	0.902	0.700	1.020	0.619	1.238		0.700		
D-12 (SP) ^a mp = 120.1°C C ₄ = 3.04 mol %	obs	0.889	0.050	0.0023	0.051	0.0023	0.0044	0	0.0012	0	0
	calcd ^b	0.884	0.055	0.0009	0.055	0.0017	0.0017	~0	0.0009	~0	~0
	obs/calcd	1.006	0.895	2.556	0.921	1.353	2.588		1.333		
F-6 (HP) ^a mp = 107.2°C C ₄ = 4.48 mol %	obs	0.827	0.081	0.0017	0.085	0.0015	0.0028	0	0.0007	0	0
	calcd ^b	0.833	0.078	0.0018	0.078	0.0037	0.0037	0.0002	0.0018	0.0002	~0
	obs/calcd	0.994	1.041	0.944	1.083	0.405	0.757		0.389		
A-10 (SP) ^a mp = 113.4°C C ₄ = 4.58 mol %	obs	0.835	0.076	0.0046	0.074	0.0046	0.0037	0	0.0023	0	0
	calcd ^b	0.829	0.080	0.0019	0.080	0.0038	0.0038	0.0002	0.0019	0.0002	~0
	obs/calcd	1.007	0.956	2.421	0.933	1.211	0.974		1.211		
G-5 (HP) ^a mp = 101.0°C C ₄ = 6.33 mol %	obs	0.773	0.100	0.0037	0.107	0.0045	0.0096	0	0.0023	0	0
	calcd ^b	0.770	0.104	0.0035	0.104	0.0070	0.0070	0.0005	0.0035	0.0005	~0
	obs/calcd	1.007	0.959	1.057	1.028	0.643	1.371		0.657		
A-8 (SP) ^a mp = 106.1°C C ₄ = 6.23 mol %	obs	0.783	0.090	0.0048	0.101	0.0050	0.0133	0	0.0025	0	0
	calcd ^b	0.773	0.103	0.0034	0.103	0.0068	0.0068	0.0005	0.0034	0.0005	~0
	obs/calcd	1.013	0.877	1.412	0.982	0.735	1.956		0.735		

^a HP = high-pressure polymerization; SP = slurry polymerization.

^b Bernoullian results.

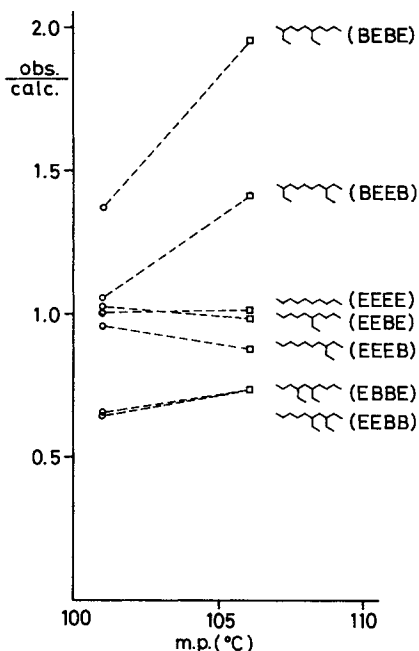


Fig. 5. Normalized observed tetrad monomer sequence fraction (obs/calcd)-melting point relationships. (○) Fraction G-5 (HP); (□) fraction A-8 (SP) in Table III.

Difference of Melting Points

Figure 3 shows the thermograms of two kinds of samples, the fractions of HP and SP polymers, which have the comparable C'_4 content and molecular weight. In spite of the similar C'_4 content, the mp's of both samples are different; the SP polymer shows a higher mp than the HP one. The relationships between the mp's and the C'_4 contents of the fractions of these two kinds of polymers are shown in Figure 4. Evidently, the deviation of the mp of SP polymer to higher temperature was observed over a fairly broad range of C'_4 contents.

Therefore, several pairs of these two kinds of compositional fractions were selected, and those tetrad monomer sequence fractions were determined by the ^{13}C -NMR method. The results are listed in Table III, and those of the pair of fractions having about 6.3 mol % of C'_4 content (fractions G-5 and A-8 in Table III) are illustrated in Figure 5. The observed fraction of each tetrad monomer sequence was normalized in such a way of dividing itself by the calculated one based on Bernoullian statistics.

In any pair, the normalized observed fractions (obs/calcd) that the C'_4 units (B) are present in the neighboring or the nearest neighboring arrangements (i.e., EBEB and BEEB, or EEBB and EBBE) are larger in the SP polymer than in the HP one. On the contrary, those of the C'_4 unit being present isolated (EEBE and EEEB) are smaller. From these results, it is deduced that the SP polymer has longer sequence length of ethylene than the HP one, assuming that the C'_4 contents of both polymers are identical. Therefore, the origin of the higher mp of the SP polymer, in comparison with the HP one, may be attributed to the existence of longer ethylene sequence in its polymer chain. In other words, it may be considered that

the C'_4 units, being present in the neighboring or the nearest neighboring arrangements, act as a single crystallite interruption zone like the isolated C'_4 units, and then, the depressing of the mp of the SP polymer is low, as mentioned by Casey et al.¹

The difference between the results of the composition fractionations shown in Figure 1 is assumed to be due to the subtly different chain structures of two kinds of polymers; that is, the sample B which has a longer ethylene sequence compared with the sample G has to be dissolved at rather high temperature, even though both the samples have the same content of C'_4 .

Moreover, as shown in Figure 5, either value of obs/calcd's of BEBE and BEEB is larger than 1.0 and that of EBBE and EEBB is less than 1.0. These results may be attributed to the fact that the C'_4 unit has a tendency to be isolated in the copolymer chain rather than to be present in the ideal random monomer distribution. This trend is also found in the cases of other ethylene-1-olefin copolymers.¹⁵

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