Table VI
Thermal Properties of Aromatic Polybenzoxazoles

polymer	T_g,[a] °C	decomposition temp,[b] °C in air	decomposition temp,[b] °C in nitrogen
9aa	290	570	620
9ba	240	500	530
9ca	260	530	545
9cb	310	545	555
9cc	325	540	560
9cd	300	545	560
9ce	295	525	530
9cf	280	545	555

[a] Determined by TMA at a heating rate of 10 K·min^{-1} in air. [b] The temperature at which 10% weight loss was recorded by TG at a heating rate of 10 K·min^{-1}.

Table VII
Mechanical Properties of Aromatic Polybenzoxazole Films

polymer	tensile strength, MPa	elongation at break, %	tensile modulus, GPa
9aa	198	7	4.5
9ba	53	2	2.9
9cc	93	6	2.4
9cd	96	6	2.4
9ce	43	2	2.1
9cf	68	3	2.6

43–198 MPa, 2–7%, and 2.1–4.5 GPa, respectively.

Thus, the fluorine-containing polybenzoxazoles had high glass transition temperatures and excellent mechanical properties and are promising candidates for new high-temperature materials.

Registry No. **3**, 3743-70-2; **4**, 833-50-1; **8ca** (copolymer), 113753-62-1; **8ca** (SRU), 114533-35-6; **8cb** (copolymer), 113753-63-2; **8cb** (SRU), 114533-36-7; **8cc** (copolymer), 113753-67-6; **8cc** (SRU), 114533-37-8; **8cd** (copolymer), 113753-61-0; **8cd** (SRU), 114533-38-9; **8ce** (copolymer), 113753-66-5; **8ce** (SRU), 114533-39-0; **8cf**, 113753-68-7; **9ca**, 112480-78-1; **9cd**, 112480-83-8; **9ce**, 112480-81-6; benzoxazole, 273-53-0.

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Characteristics of Ethylene–Propylene and Propylene–1-Butene Copolymerization over $TiCl_3 \cdot {}^1/_3AlCl_3–Al(C_2H_5)_2Cl$

Masahiro Kakugo,* Tatsuya Miyatake, Kooji Mizunuma, and Yoshio Kawai

Chiba Research Laboratory, Sumitomo Chemical Co., Ltd., Ichihara, Chiba 299-01, Japan.

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ABSTRACT: An ethylene–propylene (^{13}EP) copolymer containing 0.41 mol % ^{13}C-enriched ethylene has been fractionated on an isotactic basis by a temperature-programmed elution column technique. The ^{13}C NMR analysis of the fractions indicates that the ethylene content decreases as the isotacticity increases. The atactic fraction eluted at 20 °C is about 6 times as high in ethylene content as the isotactic fractions eluted over 110 °C. This fact well accounts for a wide copolymer composition distribution generally found in ethylene–propylene copolymerization prepared with heterogeneous catalysts. A 1-butene–propylene (^{13}BP) copolymer containing 0.20 mol % ^{13}C-enriched 1-butene has been examined similarly. In this case, the 1-butene content of the fractions is almost uniform.

Introduction

In recent years there has been great interest in the control of a composition distribution in the Ziegler–Natta copolymerization. In a previous paper, we determined the triad sequence distributions and monomer reactivity ratio products (r_1r_2) for some ethylene–propylene (EP) copolymers prepared with the $TiCl_3 \cdot {}^1/_3AlCl_3–Al(C_2H_5)_2Cl$ catalyst system by ^{13}C NMR spectroscopy.[1] As a result, it was found that the values of the r_1r_2 products were much greater than unity, and the isolated ethylene unit and three ethylene units were strangely more than predicted by a first-order Markovian scheme. This result strongly suggests that multiple active centers, one center producing an alternating copolymer and the other a block copolymer, may reside in this catalyst system. A similar tendency was found by Soga et al. for EP copolymerizations with $MgCl_2/TiCl_4$-supported catalyst systems.[2,3] On the other hand, Ross suggested that these data may arise from a variation in monomer diffusion within polymer particles to active centers.[4] It is known that the heterogeneous

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Table I
Preparation of ^{13}C-Enriched Ethylene–Propylene and ^{13}C-Enriched 1-Butene–Propylene Copolymers with $TiCl_3 \bullet {}^1/_3AlCl_3$–$Al(C_2H_5)_2Cl$

sample	comonomer	monomer feed		feed $TiCl_3 \cdot {}^1/3AlCl_3$ mmol	cat. efficiency, mol/(mol of Ti h)	comonomer content, mol %	AP,[a] %	[η], dL/g
		compositn, vol %	rate, L/h					
^{13}EP	^{13}C ethylene	0.30	10	0.80	113	0.41	2.8	1.6
^{13}BP	^{13}C 1-butene	0.15	15	2.01	61	0.20	2.0	1.7

[a] % Fraction soluble in xylene at 20 °C. Polymerization conditions: 1-L glass flask; solvent, *n*-heptane, 0.5 L; temperature, 60 °C; time, 2 h; $Al(C_2H_5)_2Cl$, 8.3 mmol.

titanium catalysts such as the $TiCl_3$ and $MgCl_2/TiCl_4$ supported catalysts consist of multiple active centers different in stereospecificity, i.e., nonstereospecific, syndiospecific, and isospecific.[5,6] In addition, we found in previous work the presence of two isospecific active centers.[7] Although individual active centers are also expected to be different in copolymerization characteristics, no data have been presented because of a lack of a suitable method.

The objective of the present study is to understand the characteristics of propylene–α-olefin copolymerizations over the individual active centers, which will lead to a comprehensive understanding of a composition distribution of the copolymers prepared with such catalysts. Polypropylene can be satisfactorily fractionated according to tacticity, though really according to crystallinity depending on the tacticity, by a temperature-programmed elution method. This method will also be expected to be available for the fractionation of the copolymer when the comonomer content is so low as to little affect its crystallinity. For this purpose, we have prepared two copolymer samples containing small quantities of ^{13}C-enriched ethylene or 1-butene. These samples have been precisely fractionated, and the microstructure compositions of the fractions have been determined by ^{13}C NMR spectroscopy.

Experimental Section

A. Polymerization. A polypropylene was prepared in *n*-heptane (1.5 L) in an agitated 5-L autoclave at 70 °C for 4 h in the presence of $TiCl_3 \cdot {}^1/_3AlCl_3$ (1.5 mmol, $TiCl_3$AA grade supplied by Toho Titanium Co.) and $Al(C_2H_5)_2Cl$ (12.5 mmol, supplied by Nippon Aluminum Alkyls). Propylene was fed so as to keep the pressure constant at 10 kg/cm^2 G during the polymerization. The control of molecular weight was done by introducing 11 mmol of hydrogen first. The polymerization was terminated by adding iso-butyl alcohol. After the catalyst residues were removed by washing with a mixture of 1 N HCl and methanol (1/1 v/v), the product was obtained by evaporating heptane and drying in vacuo at 50 °C for 4 h. The copolymerization was carried out in a 1-L three-necked glass flask at atmospheric pressure. A gaseous mixture of ^{13}C-enriched ethylene, propylene, and hydrogen (0.3/97.8/1.9 mol %/mol %/mol %) was prepared at 6 kg/cm^2 G in a 20-L steel cylinder in advance. The catalyst $TiCl_3 \cdot {}^1/_3AlCl_3$ (0.81 mmol) and $Al(C_2H_5)_2Cl$ (8.3 mmol) was fed into the flask containing 500 mL of *n*-heptane. The copolymerization was continued for 2 h at 60 °C by feeding continuously the gaseous mixture into the heptane slurry at a rate of 10 L/h, giving 7.7 g of the product. In this experiment the feed rate of the monomers was kept more than 4 times that consumed by polymerization throughout the run to hold the monomer composition constant. The termination and the extraction of the catalyst residues were carried out in a similar manner as above. The whole product was recovered by evaporating *n*-heptane. Propylene and ^{13}C-enriched 1-butene was copolymerized similarly to the copolymerization of ethylene and propylene. A gaseous mixture of propylene, ^{13}C-enriched 1-butene, and hydrogen (97.85/0.15/2 mol %/mol %) was prepared. $TiCl_3 \cdot {}^1/_3AlCl_3$ (2.1 mmol) and $Al(C_2H_5)_2Cl$ (8.3 mmol) were used as a catalyst. The feed rate of the monomers was 15.3 L/h, and the resulting product was 10.7 g. In this case the feed rate of the monomers was more than 5 times that converted into the copolymer. ^{13}C-enriched ethylene (90% $^{13}CH_2{=}^{13}CH_2$) and 1-butene (90% $CH_2{=}CH{-}CH_2{-}^{13}CH_3$) were purchased from MSD ISOTOPES Co. The detailed copolymerization conditions are described in Table I.

B. Elution Column Fractionation. Sample (7–10 g) was dissolved completely at 130 °C in 400 mL of xylene containing 0.2% 2,6-di-*tert*-butyl-*p*-cresol as an antioxidant. The solution was mixed with 1200 g of sea sand (35–48 mesh) kept at 130 °C and then cooled gradually to 20 °C, resulting in the deposition of the higher crystalline polymer on the sea sand first and the lower crystalline one last. This treatment enables satisfactory fractionation. After being maintained at 20 °C for 3 h, the mixture was introduced into a column (74 mm in diameter and 455 mm in height) immersed in an oil bath kept at the same temperature. The first fraction was eluted at 20 °C by dropping xylene (500 mL) into the column. The consective fractions were obtained in a similar manner by increasing the elution temperature stepwise up to 125 °C. The fractions were taken every 10–20 °C in the 20–60 °C region, 2–10 °C in the 60–90 °C region, 1–2 °C in the 90–110 °C, and 0.5–1 °C over 110 °C. The temperature of the bath was controlled within 0.1 °C. The polymers in the eluates were precipitated by adding methanol (2500 mL), filtered, and dried in vacuo at 50 °C.

C. ^{13}C NMR Measurement. ^{13}C NMR spectra were obtained at 135 °C on a JEOL FX-100 pulsed Fourier transform NMR spectrometer at 25 MHz. Experimental procedure and instrumental conditions were described elsewhere.[1] Although ethylene units were presently isolated, the ethylene content (mol % *E*) was calculated by the equation

$$\text{mol \% } E = \frac{\frac{1}{2}(S_{\alpha\gamma} + S_{\beta\beta})(1.1/90)}{\frac{1}{2}(S_{\alpha\gamma} + S_{\beta\beta})(1.1/90) + \frac{1}{3}(T_{\beta\beta} + S_{\alpha\alpha} + P_{\beta\beta})} \times 100$$

where *S*, *T*, and *P* indicate methylene, methine, and methyl carbons and a couple of Greek letters shows the distance in both directions from the nearest tertiary carbons as shown in a previous paper.[1] The value of 1.1 means the percent of natural abundance of ^{13}C. Similarly, the 1-butene content (mol % *B*) was calculated by the equation

$$\text{mol \% } B = \frac{P_{2B}(1.1/90)}{P_{2B}(1.1/90) + \frac{1}{3}(T_{\beta\beta} + S_{\alpha\alpha} + P_{\beta\beta})} \times 100$$

where P_{2B} is the branch methyl carbon in the 1-butene unit.

D. Measurement of Intrinsic Viscosity. Intrinsic viscosities were measured with a Ubbelohde-type viscometer in tetralin at 135 °C. Molecular weights were calculated by the following equation[8]

$$[\eta] = 0.917 \times 10^{-4} M_n^{0.8}$$

Results and Discussion

Preparation of ^{13}C-Enriched Ethylene–Propylene (^{13}EP) and ^{13}C-Enriched 1-Butene–Propylene (^{13}BP) Copolymers. The analytical data of the ^{13}EP and ^{13}BP copolymers are summarized in Table I. The proton-decoupled ^{13}C NMR spectra of the ^{13}EP and ^{13}BP copolymers are shown in Figure 1. In an usual EP copolymer the $S_{\alpha\gamma}$ and $S_{\beta\beta}$ NMR resonances appear at 37.8 and 24.4 ppm, respectively. However, in the spectrum of the ^{13}EP copolymer, the individual peaks appeared not as a single peak but as a set of a small peak from the isolated $-^{13}CH_2-$ units and two large splitting peaks ($J(^{13}C-^{13}C)$ = 34.8 Hz) from the $-^{13}CH_2-^{13}CH_2-$ units in each position. The

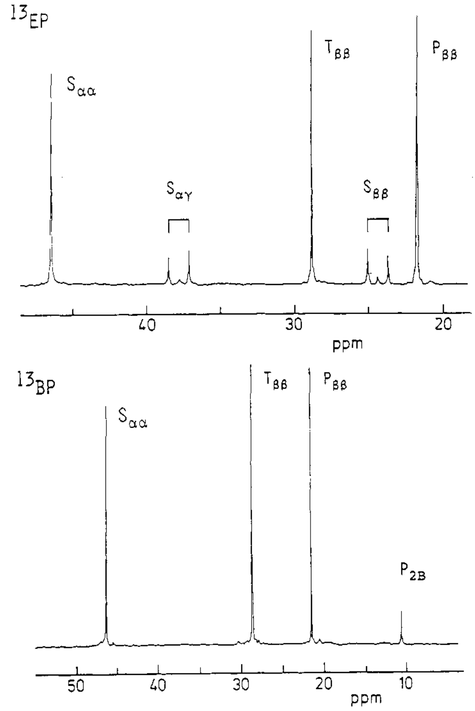

Figure 1. ^{13}C NMR spectra of ^{13}EP (0.41 mol % ethylene) and ^{13}BP (0.20 mol % 1-butene) copolymers.

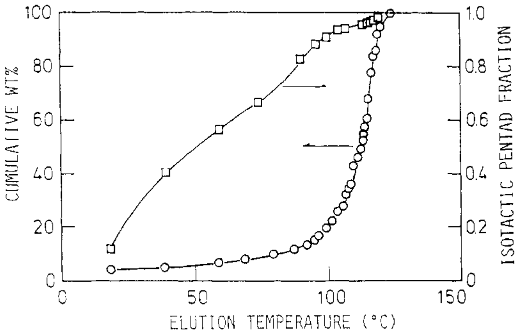

Figure 2. Fractionation curve of polypropylene: ○, cumulative wt %; □, isotactic pentad fraction.

ethylene content was determined to be 0.41 mol % from the total intensity of these peaks. In the ^{13}BP copolymer a single-resonance ^{13}C methyl peak of the 1-butene units, $-CH_2-CH(CH_2-^{13}CH_3)-$, appeared at 11.1 ppm.

Fractionation of Polypropylene. For a comparative purpose, we first fractionated polypropylene ([η] is 1.6 dL/g and the atactic polymer is 4.4% as a fraction soluble in xylene at 20 °C). Thirty fractions were obtained, and the ^{13}C NMR analysis was carried out on 14 fractions. The fractionation data are summarized in Table II. The cumulative weight percent and the isotactic pentad fraction are plotted against the elution temperature in Figure 2. The isotacticity increased monotonously from 0.12 to 0.98 with the increasing elution temperature. The ^{13}C NMR data indicated that the fraction eluted at 20 °C (mm:mr:rr = 0.27:0.36:0.37) was the so-called atactic polymer though it was not completely random. The fractions at temperatures of 40–100 °C were stereoblock-type polymers. Indeed, both the mmmm and rrrr pentad were found in these fractions. The fractions at temperatures of 100 °C or above were isotactic polymers. The expansion of the isotactic region is shown in Figure 3. The fractionation took place on the basis of a slight difference of 0.005 in the isotactic pentad fraction. Therefore, it can be concluded that the present fractionation method gives a precise isotacticity distribution. The observed distribution curve indicated not a normal s-shape curve but a stepwise curve. The distribution was obviously broader than predicted by a Bernoullian statistics model. These data strongly suggest the presence of two isotactic active centers, which will be discussed elsewhere.[7]

Table II
Fractionation Data on the Polypropylene Prepared with $TiCl_3\cdot{}^1/_3AlCl_3-Al(C_2H_5)_2Cl$[a]

fract no.	extr, °C	extr, mg	intg, %	[η]	[mmmm]
1	20	433.3	4.43		0.120
2	40	98.8	5.44		0.408
3	60	195.6	7.44		0.567
4	70	125.6	8.72		0.669
5	80	175.8	10.52		
6	88	180.6	12.37		0.830
7	92.5	156.2	13.97		
8	95.2	156.9	15.57		0.882
9	97	174.5	17.35		
10	100	292.0	20.34		0.910
11	102.1	260.6	23.00	0.50	
12	104	349.6	26.57	0.60	0.941
13	106	158.8	28.19		
14	107.1	450.6	32.80	0.72	0.946
15	108	156.5	34.40		
16	109	184.0	36.28		
17	110	685.1	43.28	1.20	
18	111	263.6	45.97		
19	112	67.6	46.66		
20	113	319.6	49.93		0.959
21	114	301.0	53.01		
22	114.5	478.4	57.90	1.40	0.965
23	115.5	269.0	60.65		
24	116	725.9	68.07		0.971
25	117	941.4	77.69	2.00	0.975
26	118	621.5	84.04		
27	119	184.4	85.93		
28	119.5	618.3	92.25	3.20	0.980
29	120.6	246.1	94.77		
30	125	509.1	99.97	4.85	

[a] Abbreviations: fract, fraction; extr, extraction; intg, integration.

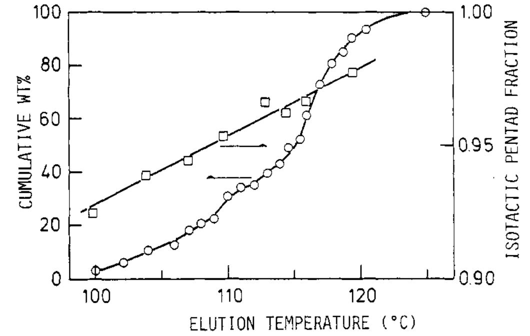

Figure 3. Expansion of the isotactic region of polypropylene: ○, cumulative wt %; □, isotactic pentad fraction.

Fractionation of ^{13}EP and ^{13}BP Copolymers. The ^{13}EP copolymer was fractionated into 27 fractions, and the ^{13}C NMR analysis was carried out on 23 fractions. The fractionation data are summarized in Table III, and the fractionation curve is illustrated in Figure 4. As expected, the isotacticity increased monotonously with the increasing elution temperature. On the other hand, the ethylene content decreased markedly from 1.29 to 0.23 mol %. As described in the Experimental Section, this copolymer was prepared by bubbling a large excess of the monomers into the slurry at a low polymerization rate (113 mol of propylene/(mol of Ti h)). The productivity was also suppressed to 24 g of polymer/g of catalyst. Therefore, the monomer diffusion, we believe, had not any influence on the copolymerization. Even if there was any influence, it

Table III
Fractionation Data on the ^{13}EP Copolymer Prepared with $TiCl_3 \bullet {}^1/_3AlCl_3$–$Al(C_2H_5)_2Cl$[a]

fract no.	extr, °C	extr, mg	intg, %	[η]	[mmmm]	^{13}E content, mol %
1	20	182.5	2.85	0.30	0.165	1.26
2	40	41.3	3.50		0.506	1.29
3	60	115.4	5.29		0.646	1.18
4	70	77.5	6.50			1.00
5	80	109.8	8.21		0.788	0.94
6	88	161.9	10.73		0.825	0.70
7	92.5	156.5	13.16		0.924	0.60
4	95.1	112.8	14.92		0.932	0.53
9	97.1	105.6	16.56		0.925	0.45
10	100	237.5	20.26	0.55	0.944	0.44
11	102	202.1	23.40			0.42
12	104	264.7	27.52	0.65	0.952	0.39
13	106	286.1	31.97		0.954	0.39
14	107	128.3	33.97		0.964	0.37
15	108.1	106.8	35.63	0.7	0.957	
16	109	153.7	38.02	0.8	0.964	0.35
17	110.1	148.0	40.32	0.9		0.32
18	111	286.4	44.78	1.2	0.961	0.32
19	112.1	692.1	55.55	1.4	0.971	0.29
20	113	368.4	61.28	1.6	0.962	0.27
21	114	752.5	72.99	2.0	0.968	0.26
22	114.5	24.1	73.36			
23	115.5	763.2	85.24	2.4	0.970	0.27
24	116	246.8	89.08	3.1	0.972	0.23
25	117	79.0	90.30			
26	118.1	158.8	92.77	5.5		
27	123.2	464.4	100		0.982	0.23

[a] See footnote *a* in Table II.

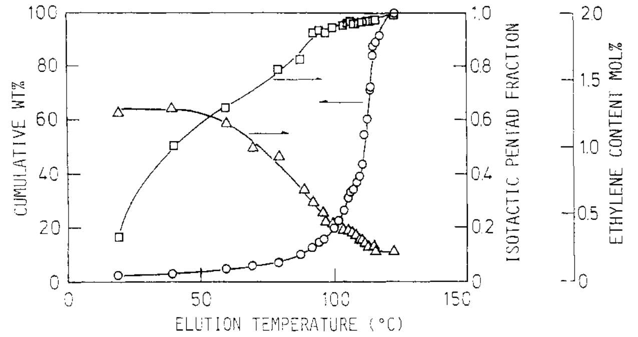

Figure 4. Fractionation curve of the ^{13}EP copolymer (0.41 mol % ethylene): ○, cumulative wt %; □, isotactic pentad fraction; △, ethylene content mol %.

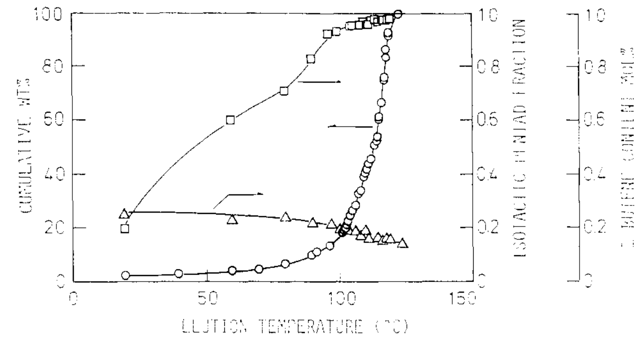

Figure 5. Fractionation curve of the ^{13}BP copolymer (0.20 mol % 1-butene): ○, cumulative wt %; □, isotactic pentad fraction; △, 1-butene content mol %.

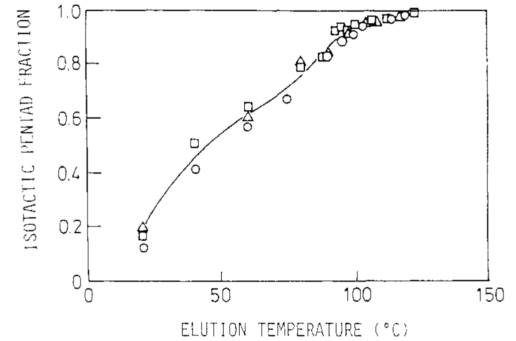

Figure 6. Plots of isotactic pentad fractions against the elution temperatures: ○, polypropylene; □, ^{13}EP copolymer; △, ^{13}BP copolymer.

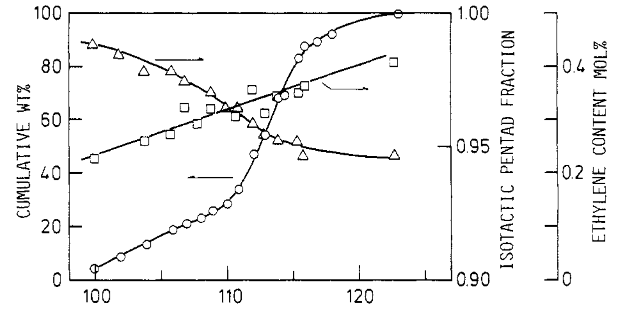

Figure 7. Expansion of the isotactic region of the ^{13}EP copolymer: ○, cumulative wt %; □, isotactic pentad fraction; △, ethylene content mol %.

is reasonably expected that all of the active centers were similarly influenced. We, therefore, interpret this finding as showing that the individual active centers are different from each other in monomer reactivity. The atactic fraction was about 6 times as high in ethylene content as the highly isospecific one, which indicates that the atactic active center is much more active toward ethylene than the isotactic one. In the stereoblock region a steep decrease in ethylene content was seen. The stereoblock polypropylene is generally accepted as the polymer consisting of the isotactic and syndiotactic blocks.[5] Therefore, this variation implies that the syndiotactic active center may also be active toward ethylene over the isotactic one. As a result, a wide composition distribution generally seen in the EP copolymers prepared with the heterogeneous catalysts can ascribe to the presence of multiple-active centers. Here, we examined only the EP copolymer containing a small amount of ethylene, less than 1 mol %. In the case of EP copolymers containing much more ethylene such as the copolymers (15–75 mol %) previously examined,[1] the atactic active center will give a copolymer containing very long sequences of the ethylene units, whereas the isospecific active center will give a copolymer containing short sequences of the ethylene units. Consequently, the ^{13}C NMR analysis of whole copolymers indicates the strange phenomenon that ethylene may copolymerize either in alternation or in runs as pointed out previously.

Next, the ^{13}C BP copolymer was fractionated into 37 fractions, and 24 fractions obtained were analyzed by ^{13}C NMR spectroscopy. The fractionation data are summarized in Table IV and shown in Figure 5. It is clear that fractionation was similarly carried out on an isotacticity basis. In this case a copolymer composition distribution was considerably narrow. The 1-butene content of the atactic fraction was only twice that of the isotactic one. This evidence supports the earlier findings that the comonomer sequences in BP copolymers closely conform to a Bernoullian statistical model.[4,9,10]

Figure 6 shows the plots of isotactic pentad fraction vs the elution temperature for the polypropylene and the ^{13}EP and ^{13}BP copolymers. One can find hardly a difference between the samples. It is obvious, therefore, that the comonomers incorporated to the extent of 0.4 mol % or below had little influence on fractionation as we would expect. As described above, it is very likely that two kinds

Table IV
Fractionation Data on the ^{13}BP Copolymer Prepared with $TiCl_3 \bullet {}^1/_3AlCl_3–Al(C_2H_5)_2Cl^a$

fract no.	extr, °C	extr, mg	intg, %	[η]	[mmmm]	^{13}B content, mol %
1	20	161.6	2.02	0.27	0.196	0.253
2	40	68.8	2.88			
3	60	96.5	4.09		0.600	0.226
4	70	76.1	5.04			
5	80	167.9	7.14		0.809	0.240
6	90	279.8	10.64	0.42	0.826	0.221
7	92.5	39.0	11.13			
8	97	211.8	13.78		0.920	0.215
9	100	345.1	18.10	0.48	0.929	0.194
10	101	52.6	18.76			
11	102	92.0	19.91			
12	103	56.3	20.61			
13	104.2	204.2	23.16	0.71		0.192
14	105.1	148.6	25.02		0.949	0.181
15	106.1	155.1	26.96		0.953	0.188
16	107	137.4	28.68			0.178
17	108.4	405.4	33.75	0.84	0.951	0.146
18	109.2	49.0	34.37			
19	110.3	445.2	39.94	0.91	0.963	0.180
20	110.9	61.6	40.71			
21	111.5	161.5	42.73			0.180
22	112	111.2	44.12		0.953	0.156
23	113	175.6	46.32		0.969	0.156
24	113.5	24.1	46.62			
25	114.2	329.7	50.74	1.28	0.973	0.171
26	114.8	188.4	53.10			0.182
27	115.4	143.4	54.89			0.164
28	116	457.2	60.61	1.69	0.964	0.168
29	116.5	43.4	61.15			
30	117	449.9	66.78	1.94		0.141
31	117.6	702.4	75.57	2.24	0.971	0.146
32	118	36.0	76.02			
33	118.4	546.2	82.85	2.60	0.970	0.166
34	119	290.7	86.49	3.05		
35	119.5	391.8	91.39	3.46	0.975	0.155
36	120.5	67.0	92.23		0.975	
37	124	621.3	100.00	4.75		0.133

[a] See footnote *a* in Table II.

of isotactic polymers are present in polypropylene. The distribution curves for the ^{13}EP copolymer shown in Figure 7 seem also to change in curvature near the elution temperature of 115 °C just as in the case of polypropylene. In the ^{13}EP copolymer the copolymer composition considerably changes also in this region. Since the present fractionation did not occur on a compositional basis, such a variation in composition cannot be found in the case of the presence of only a single isotactic center. As shown in Figure 8, an observed composition distribution shows a shoulder that cannot be obviously interpreted by a Bernoullian scheme based on the presence of a single active center. This evidence suggests that lowly isospecific centers may be more active toward ethylene. Consequently, these data show that the active centers become more active toward ethylene with a decrease in isotacticity. In other words, catalysts highly active toward ethylene may be generally less isospecific. On the other hand, the ^{13}BP copolymer showed only a slight change as shown in Figure 9, suggesting both active centers have rather similar activities toward α-olefins.

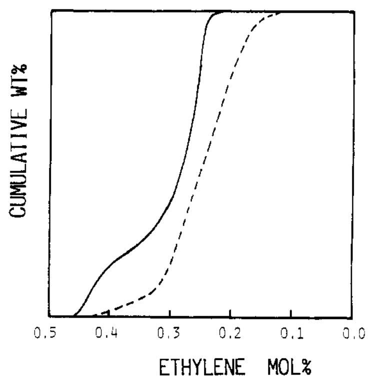

Figure 8. Ethylene content distribution curves of the isotactic region of the ^{13}EP copolymer: —, observed curve; - - -, calculated curve (ethylene content = 0.25 mol %, M_n = 315 000).

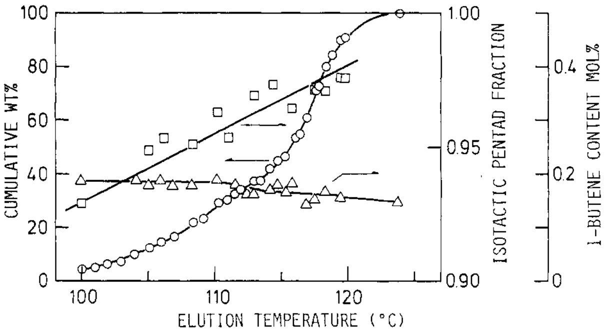

Figure 9. Expansion of the isotactic region of the ^{13}BP copolymer: ○, cumulative wt %; □, isotactic pentad fraction; △, 1-butene content mol %.

Conclusion

The EP and BP copolymers containing only less than 0.4 mol % ^{13}C-enriched comonomer prepared with the $TiCl_3 \cdot {}^1/_3AlCl_3–Al(C_2H_5)_2Cl$ catalyst was satisfactorily fractionated on the basis of tacticity by a temperature-programmed elution method. The ^{13}C NMR analysis of the fractions showed that the lower isospecific active centers are much more active toward ethylene, whereas their activities toward 1-butene does not change so much.

Registry No. EP (copolymer), 9010-79-1; $TiCl_3$, 7705-07-9; $AlCl_3$, 7446-70-0; $Al(C_2H_5)_2Cl$, 96-10-6; (1-butene)(propylene) (copolymer), 29160-13-2.

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