Macromolecules 1991, *24*, 1469–1472 **1469**

Chemical Composition Distribution of Ethylene–1-Hexene Copolymer Prepared with $TiCl_3$–$Al(C_2H_5)_2Cl$ Catalyst

Masahiro Kakugo,* Tatsuya Miyatake, and Kooji Mizunuma

Chiba Research Laboratory, Sumitomo Chemical Co. Ltd., 2-1 Kitasode, Sodegaura-cho, Kimitu-gun, Chiba 299-02, Japan

Received April 26, 1990; Revised Manuscript Received August 28, 1990

ABSTRACT: The temperature-programmed column fractionation (TPCF) technique has been successfully used to investigate the chemical composition distribution of ethylene–1-hexene (EH) copolymer containing 52.0 mol % ethylene which was prepared with $TiCl_3$–$Al(C_2H_5)_2Cl$ catalyst. EH copolymer was fractionated according to only the crystallinity of the ethylene sequence, exhibiting a trimodal distribution: the predominant peak is located at 28 mol % ethylene, the middle peak near 100 mol % ethylene, and the lowest peak at 80 mol % ethylene. The first polymer contains isotactic 1-hexene triads. It has been shown from ^{13}C NMR data and the reactivities of the active centers that a highly isospecific center and a nonstereospecific center produce the first and second polymers, respectively. The last polymer was degraded at 330 °C under pure argon and fractionated again by the TPCF technique. This polymer is a block copolymer consisting of a long copolymer containing 66 mol % ethylene and polyethylene blocks. The formation of the block copolymer is elucidated in terms of the configurational change of the low isospecific center during polymerization. A schematic model of the active center relevant to the block copolymer is shown.

Introduction

Heterogeneous Ziegler–Natta catalysts give ethylene–α-olefin copolymers with a wide chemical composition distribution.[1] We recently studied the origin of such a wide composition distribution by using ^{13}C NMR and temperature-programmed column fractionation (TPCF).[2–4] The wide distribution was found to be primarily due to the presence of multiple active centers residing in the heterogeneous catalysts: isospecific, stereoblock, and nonstereospecific centers produce copolymers with increasing ethylene content in this order.[3] Furthermore, TPCF of ethylene–propylene (EP) copolymers has shown that the copolymers consist of three types polymers, i.e., random copolymer containing a low percentage of ethylene, block copolymer containing a high percentage of ethylene, and polyethylene.[4] From these findings we have concluded that isospecific, stereoblock, and nonstereospecific centers produce random copolymer, block copolymer, and polyethylene, respectively.[4] In addition, we have shown that two isospecific centers reside in the heterogeneous catalysts.[5] We are thus interested in revealing which of the isospecific centers is relevant to the stereoblock center. Fortunately, activity toward ethylene is different between the isospecific centers,[3] which could provide us with valuable information.

The objective of the present study is to know the chemical composition distribution of ethylene–1-hexene (EH) copolymer and specifically to obtain information on the block copolymer fraction. As described previously,[4] TPCF takes place according to the degree of crystallinity of polymer and, therefore, has substantial limitations if applied to copolymers having many crystalline blocks such as EP copolymer. Since isotactic poly(1-hexene) is soluble in hydrocarbon solvent even at room temperature, EH copolymer would be expected to be fractionated only on the basis of ethylene content. As a result, EH copolymer has been successfully fractionated according to expectation, showing a wide chemical composition distribution. The block copolymer fraction obtained has been slightly degraded at elevated temperature and then fractionated again by TPCF. This fraction has been proven to consist of long ethylene and copolymer blocks. On the basis of these results we discuss here the origin of the block copolymer.

Experimental Section

Sample Preparation. The EH copolymer was prepared in an agitated 1-L autoclave at 60 ± 1 °C for 1 h in the presence of 0.65 mmol of δ-$TiCl_3$ (TAC-131 grade, supplied by Toho Titanium Co.) and 12.5 mmol of $Al(C_2H_5)_2Cl$ (supplied by Nippon Aluminum Alkyls). 1-Hexene (0.5 L) dried over molecular sieves 13X was fed into the autoclave, which was heated to the prescribed temperature. After a gaseous mixture of ethylene and hydrogen as a chain-transfer agent (96/4 mol/mol) was fed to a pressure of 3.5 atm, the catalysts were added to initiate the polymerization. Additional ethylene was fed so as to keep the pressure at 3.5 atm, and the copolymerization was terminated at 10% conversion of 1-hexene into the copolymer by the addition of isobutanol. The catalyst residue was extracted with a mixture of 1 N HCl and methanol (1/1 (v/v)). Thermal degradation of the polymer was carried out at 330 °C for 7 h in an atmosphere of pure argon. Ten grams of the sample was put into a 100-mL glass flask. The atmosphere was replaced with argon by evacuation and filling with argon several times before degradation.

Temperature-Programmed Column Fractionation (TPCF). Forty grams of the sample was dissolved at 130 °C in xylene, and then 1200 g of sea sand (35–48 mesh) kept at 130 °C was put into the solution. The mixture was cooled gradually to −30 °C and then put into a column (74 mm in diameter and 435 mm in height) immersed in an oil bath kept at −30 °C. The first fraction was eluted at −30 °C by dropping xylene into the column. Five hundred milliliters of xylene was used to elute each fraction. However, when a precipitate or milky turbidity appeared by addition of the last several droplets of the eluate into methanol, some additional xylene was used until one or the other did not appear. The consecutive fractions were obtained by raising stepwise the elution temperature to 100 °C. The elution temperature was controlled within ±0.1 °C. Each polymer fraction was precipitated by addition of the eluate into 2.5 L of methanol, recovered by filtration, and dried in vacuo. The elution temperature was raised stepwise from 0 to 100 °C. The degraded sample was fractionated in a similar manner, but the amounts of the sample and sea sand were reduced to 5 and 700 g, respectively, and the first fraction was eluted at 0 °C.

Characterization of Polymer. Intrinsic viscosity ([η]) was measured at 135 °C in tetralin. The number-average molecular weight was calculated by the equation $[\eta] = 4.60 \times 10^{-4} M^{0.725}$.[6] GPC measurements were carried out at 140 °C in *o*-dichlorobenzene on a Waters 150C GPC using two Shodex M-80 mixed

0024-9297/91/2224-1469$02.50/0

Table I
Fractionation of Ethylene–1-Hexene Copolymer Containing 52 mol % Ethylene Prepared with $TiCl_3$–$Al(C_2H_5)_2Cl$ Catalyst

frac no.	elution temp, °C	amt, wt %	ethylene content, mol %	obsd triads HHH	HHE	EHE	HEH	EEH	EEE
O-1	-30	79.8	28	0.50	0.16	0.06	0.08	0.11	0.09
O-2	0	1.5	60	0.16	0.13	0.11	0.07	0.20	0.33
O-3	30	1.4	73	0.08	0.08	0.11	0.06	0.19	0.48
O-4	50	1.1	78	0.06	0.06	0.10	0.04	0.17	0.51
O-5	60	1.4	82	0.05	0.05	0.08	0.03	0.15	0.64
O-6	70	2.0	84	0.04	0.04	0.07	0.02	0.13	0.69
O-7	80	1.8	92	0.02	0.02	0.06	0.01	0.12	0.79
O-8	90	1.9	95	0.01	0.01	0.03	0	0.06	0.89
O-9	95	5.8	100						1.00
O-10	100	2.9	100						1.00

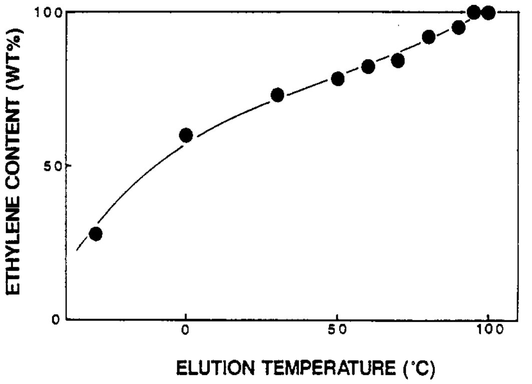


Figure 1. Ethylene content of the fractions obtained from ethylene–1-hexene copolymer containing 52 mol % ethylene vs elution temperature.

columns. ^{13}C NMR spectra were obtained at 135 °C on a JEOL FX-100 pulsed Fourier transform NMR spectrometer. Samples were prepared as 10% (w/v) solutions of polymer in *o*-dichlorobenzene. Tetramethylsilane was added to the solutions as an internal chemical shift reference. The pulse interval was 10 s, the acquisition time was 4.2 s, the pulse angle was 45°, and the number of transients accumulated was 2000. The signal assignment was made according to Hsieh and Randall.[7] The triad sequence distributions were calculated from the resonances of the methine and the methylene carbons.

Results and Discussion

Fractionation of EH Copolymer. The EH copolymer containing 52 mol % ethylene was fractionated by TPCF. Table I summarizes the fractionation data and the triad distributions of the fractions obtained. As plotted in Figure 1, the ethylene content of the fractions increases monotonically from 28 to 100% ethylene with an increase in elution temperature. This shows that the fractionation was carried out on the basis of ethylene content according to expectation and the chemical composition distribution is very broad. The molecular weight distribution of each fraction obtained was measured by GPC. From these data, a bird's-eye view of the chemical composition and the molecular weight distribution is depicted in Figure 2, where three peaks can be seen. The highest peak (peak 1), the abundance of which reaches 80 wt % of the whole polymer, is located at ca. 28% ethylene, the middle one (peak 3) near 100% ethylene, and the lowest one (peak 2) at ca. 80% ethylene. This trimodal distribution apparently resembles that observed by Hosoda for ethylene–1-butene copolymers (linear low-density polyethylene) produced with heterogeneous catalysts.[8]

The catalyst system used here is highly isospecific, producing more than 90% isotactic polypropylene. As described previously,[3] the highly isospecific active center is the lowest in relative activity toward ethylene among the active centers, i.e., both the high and low isospecific, the stereoblock, and the nonstereospecific active centers. The most abundant polymer (peak 1) contains the lowest ethylene and isotactic HHH sequence as seen in the ^{13}C NMR spectrum shown in Figure 3. That is, the strong signals seen at 33.65 and 35.34 ppm are assigned to the methine and methylene resonances in the central monomer unit of the isotactic HHH sequence, respectively.[9,10] This finding leads us to the conclusion that the peak 1 polymer was produced with the highly isospecific active center. On the other hand, we have shown that the nonstereospecific center is the most active toward ethylene.[3] Therefore, the nonstereospecific center probably produced the peak 3 polymer containing the highest ethylene. The peak 2 polymer has a wide composition distribution ranging from 60 to 95 mol % ethylene. This polymer will be assumed to be produced with the stereoblock active center. To make this point clear, we have characterized a more detailed molecular structure of the peak 2 polymer.

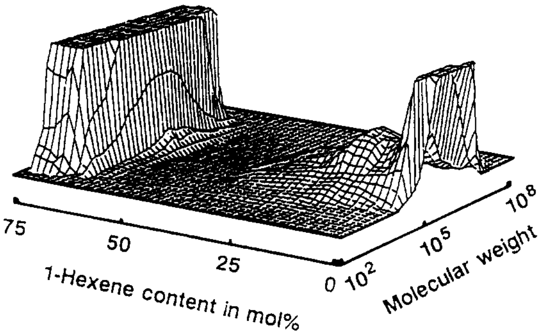


Figure 2. Bird's-eye view of the chemical composition and the molecular weight distribution for ethylene–1-hexene copolymer containing 52 mol % ethylene.

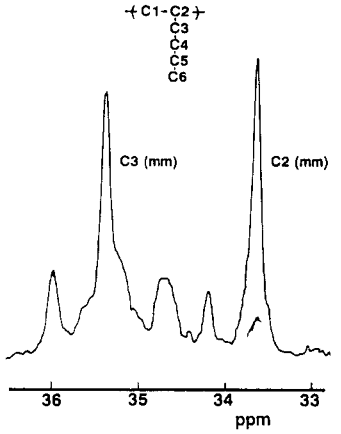


Figure 3. ^{13}C NMR spectrum of fraction O-1 obtained from ethylene–1-hexene copolymer containing 52 mol % ethylene.

Fractionation of Thermally Degraded Polymer. If the peak 2 polymer was produced with the stereoblock center, it will be expected to consist of different long blocks.

Table II
Refractionation of the Block Copolymer Fractions[a] of the Ethylene–1-Hexene Copolymer after Thermal Degradation

frac no.	elution temp, °C	amt, wt %	ethylene content, mol %	obsd triads HHH	HHE	EHE	HEH	EEH	EEE
D-1	0	10.6	66	0.09	0.11	0.14	0.08	0.21	0.37
D-2	30	3.0							
D-3	50	10.6	90	0.02	0.03	0.06	0.01	0.12	0.77
D-4	60	18.2	93	0.01	0.01	0.05		0.11	0.82
D-5	70.1	26.2	95		0.01	0.04		0.09	0.86
D-6	80.1	28.3	97			0.03		0.07	0.90
D-7	above 90	3.0	100						1.00
original			88	0.03	0.03	0.06	0.02	0.13	0.74

[a] A mixture of the O-6 and O-7 fractions in Table I; average ethylene content, 87.8 mol %.

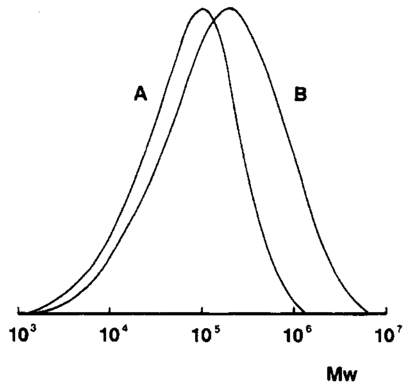
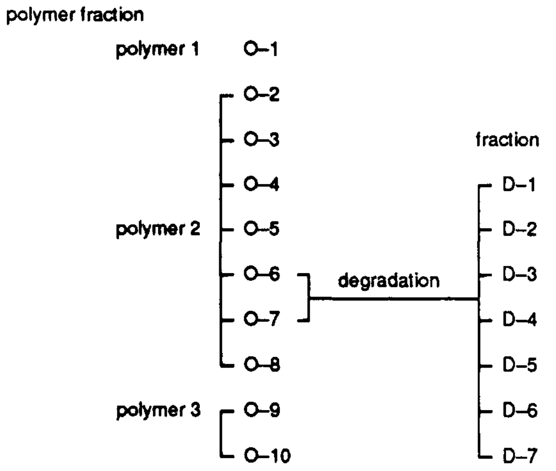


Figure 4. GPC curves of ethylene–1-hexene copolymer containing 52 mol % ethylene before and after thermal degradation: (A) after degradation; (B) original sample.

Therefore, there is a possibility that one can separate the constituent blocks by refractionation of slightly degraded fractions. Thus, we have intended to conduct such experiment.



Fractions O-6 (84 mol % ethylene) and O-7 (92 mol % ethylene), after being completely mixed in hot xylene, were recovered by precipitating with an excess of methanol and dried in vacuo. The mixture wad degraded under an inert atmosphere from 1.8 to 1.0 dL/g in intrinsic viscosity. The number-average molecular weight (M_n) calculated from the intrinsic viscosity decreased from 9.0×10^4 to 4.0×10^4, which means that the average number of chain scissions per polymer chain was ca. 1.3. The GPC curves measured before and after degradation are shown in Figure 4. M_n on a polystyrene basis changes from 2×10^5 to 1×10^5. This change is compatible with the result calculated from the change in viscosity. The fractionation data on the degraded sample are summarized in Table II with the ^{13}C NMR analytical data.

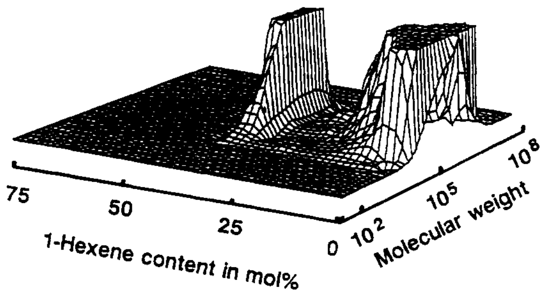


Figure 5. Bird's-eye view of the chemical composition and the molecular weight distribution for the block copolymer fractions of ethylene–1-hexene copolymer after slight thermal degradation.

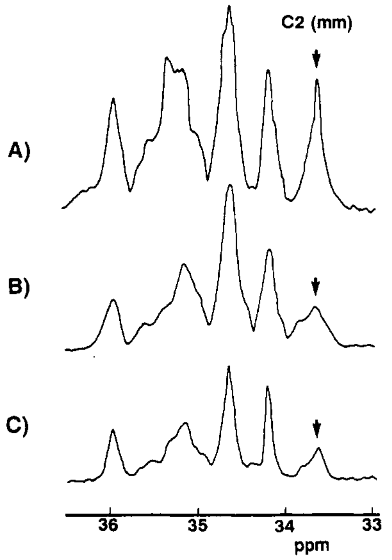


Figure 6. ^{13}C NMR spectra of fractions O-2 (spectrum A), O-3 (spectrum B), and D-1 (spectrum C) obtained from ethylene–1-hexene copolymer.

The degraded sample showed again a broad chemical composition distribution ranging from 66 to 100 mol % ethylene. The molecular weight distributions of these fractions were measured by GPC. A bird's-eye view of the chemical composition and the molecular weight distribution is depicted in Figure 5, showing a bimodal distribution. The higher peak is located near 100% ethylene and the lower one at ca. 70 mol % ethylene. This figure clearly shows that this sample consists of long ethylene and long copolymer blocks, the lengths of which correspond to half of the original polymer chain length. Fraction D-1, viz., the copolymer block, which contains 66 mol % ethylene, is much higher in ethylene than fraction O-1 of the original sample, 28 mol %, and close to those of fractions O-2 and O-3 of the original sample, 60 and 73 mol %, respectively. The triad distribution is also very close to those of fractions O-2 and O-3. As shown in Figure 6, the ^{13}C NMR spectra of fractions O-2, O-3, and D-1 show the

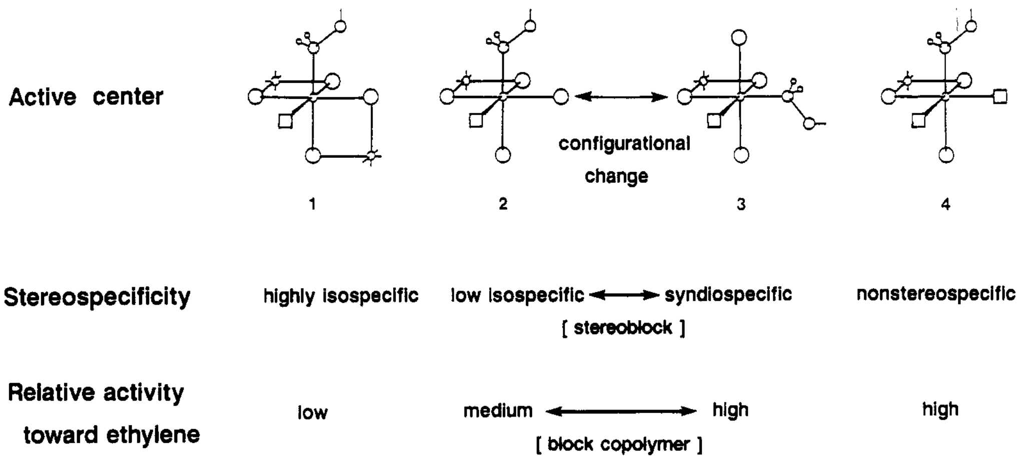


Figure 7. Relationship among the active centers, the stereospecificities, and the relative activity toward the ethylene–α-olefin copolymers obtained.

presence of the signal at 33.65 ppm (central tertiary carbon in the isotactic HHH sequence), which indicates that these fractions were formed with the isospecific center.

In a previous paper,[3] we have shown that the low isospecific center is about twice as active toward ethylene as the highly isospecific one. As described above, the most predominant fraction O-1 of the original sample can be considered to be formed with the highly isospecific center. The ethylene contents of fractions O-2, O-3, and D-1 are about double that of fraction O-1, which suggests that the low isospecific center is relevant to the formation of the block copolymer. On the basis of the Cossee and Arlman model,[11,12] we have proposed that (1) the highly isospecific center consists of four firmly bound Cl ions, an alkyl group, and a Cl vacancy (model 1), (2) the low isospecific center consists of at least a loosely bound Cl ion, an alkyl group, and a Cl vacancy (model 2), and (3) the nonstereospecific center consists of two firmly bound Cl ions, a Cl ion, an alkyl group, and two Cl vacancy (model 4) as shown in Figure 7.[13] In addition, we have considered that the low isospecific active center, when there is no steric hindrance, will become syndiospecific (model 3).[13] A configurational change of the Cl ion, the alkyl group, and the vacancy during polymerization, model 2 ↔ model 3 in Figure 7, likely leads to the formation of isotactic–syndiotactic stereoblock polymer in homopolymerization.[13] Moreover, we have showed that the stereoblock active center increases in relative activity toward ethylene with a decrease in isotacticity, which indicates that the syndiospecific configuration is more active toward ethylene than the isospecific configuration.[13] Thus, the change of the stereoblock active center during polymerization very likely produces block copolymer in ethylene–α-olefin copolymerization. The conclusion to be drawn from these results is also shown in Figure 7.

References and Notes

(1) Lukach, C. A.; Spurlin, H. M. *Copolymerization*; Ham, G. E., Ed.; Wiley-Interscience: New York, 1964; Chapter IVA.
(2) Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. *Macromolecules* **1982**, *15*, 1150.
(3) Kakugo, M.; Miyatake, T.; Mizunuma, K.; Kawai, Y. *Macromolecules* **1988**, *21*, 2309.
(4) Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. *Makromol. Chem.* **1989**, *190*, 849.
(5) Kakugo, M.; Miyatake, T.; Naito, Y.; Mizunuma, K. *Macromolecules* **1988**, *21*, 314.
(6) Tung, L. H. *J. Polym. Sci.* **1959**, *36*, 287.
(7) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 1402.
(8) Hosoda, S. *Polym. J.* **1988**, *20*, 383.
(9) Soga, K.; Yanagihara, H. *Makromol. Chem.* **1988**, **189**, 2839.
(10) Nishiyama, Y.; Asakura, T. *Polym. Prepr., Jpn.* **1987**, *36*, 2408.
(11) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.
(12) Arlman, E. J. *J. Catal.* **1966**, *5*, 178.
(13) Kakugo, M.; Miyatake, T.; Naito, Y.; Mizunuma, K. *Makromol. Chem.* **1989**, *190*, 505.

Registry No. EH (copolymer), 25213-02-9; δ-$TiCl_3$, 7705-07-9; $Al(C_2H_5)_2Cl$, 96-10-6.