

Chemical Compositional Distribution of Ethylene-1-Butene Copolymer Prepared with Heterogeneous Ziegler-Natta Catalyst: TREF and Crystaf Analysis

Young Soo Ko* and Jong-Ki Jeon

Department of Chemical Engineering, Kongju National University, Chungnam 314-701, Korea

Jin-Heong Yim

Department of Advanced Materials Engineering, Kongju National University, Chungnam 314-701, Korea

Young-Kwon Park

Faculty of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

Received January 25, 2008; Revised November 1, 2008; Accepted November 3, 2008

Abstract: Ethylene-1-butene copolymers were prepared with SiO₂-supported TiCl₄ catalyst by changing of 1-butene/ethylene molar ratio in feed, and the resulting copolymers were analyzed using temperature rising elution fractionation (TREF) and crystallization fractionation (Crystaf) methods to investigate the influence of C₄/C₂ molar ratio in feed on chemical compositional distribution and other parameters such as molecular weight and its distribution. TREF analysis showed that the copolymers had a broad and bimodal chemical compositional distribution (CCD) regardless of the content of 1-butene in the copolymer. The chemical composition was in the range of 5 to 55 branches per 1,000 carbons for all copolymers prepared in the study. Furthermore, the broader CCD was revealed for the copolymers having the higher content of 1-butene. Crystaf analysis did not show a bimodal CCD for the copolymers having the 1-butene content of less than 5.1 wt%. The lower crystalline part having higher 1-butene content in Crystaf analysis was less than that of TREF analysis.

Keywords: ethylene-1-butene copolymer, LLDPE, TREF, Crystaf, CCD.

Introduction

Since linear low density polyethylene (LLDPE) was commercialized and considered as an important bulk polymer in the mid 70s, the molecular structure of ethylene and α -olefins has been intensively studied due to its commercial importance.¹⁻⁴ In the copolymerization of ethylene with α -olefins such as 1-butene and 1-hexene with heterogeneous Ziegler-Natta catalyst, the chemical compositional distribution (CCD) in the copolymer chains is of significant importance because it reflects the compositional heterogeneity. The properties of LLDPE are dependent on molecular weight, molecular weight distribution (MWD), comonomer content and CCD.¹ Even though molecular weight is also of importance, comonomer content in copolymer and CCD are dominant parameters to determine the final physical and mechanical properties of ethylene- α -olefin copolymers. It has been understood well that heterogeneous Ziegler-Natta catalyst produces ethylene- α -olefin copolymers with a broad

CCD due to its characteristic nature of multi active sites.⁵⁻⁷ Furthermore, the polymerization processes and conditions are influencing on the molecular structure.

Therefore, the importance of characterization of ethylene- α -olefin copolymer with respect to molecular weight and CCD has been growing from both academic and commercial standpoints. Temperature rising elution fractionation (TREF) has been employed since it was developed in 1980s, and crystallization fractionation (Crystaf) method has been developed and studied rather recently to investigate CCD of semicrystalline polyolefins in depth.^{1,8,9}

In this study, ethylene-1-butene copolymers were prepared with SiO₂-supported TiCl₄ catalyst by changing of 1-butene/ethylene (C₄/C₂) molar ratio in feed, and the resulting copolymers were analyzed with TREF and Crystaf methods to observe the influence of C₄/C₂ molar ratio in feed on CCD and other parameters including MWD. In addition, TREF and Crystaf analysis were compared to each other with respect to CCD produced with heterogeneous Ziegler-Natta catalyst.

*Corresponding Author. E-mail: ysko@kongju.ac.kr

Experimental

Materials. All reactions were performed under a purified nitrogen atmosphere using standard glove box and Shlenk technique. Polymerization grade of ethylene was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Organic solvents were distilled from Na/benzophenone and stored over molecular sieves (4A). All other reagents including 1,2,4-trichlorobenzene (TCB) were purchased from Aldrich and used without further purification.

Polymerization and Characterization. A 3 L autoclave reactor was used for ethylene-1-butene copolymerization. Detailed polymerization and polymer workup procedures were described elsewhere.¹⁰ A SiO₂-supported TiCl₄ catalyst, containing 2.0 wt% of Ti was employed for the copolymerization. The more detail information on catalyst employed was provided elsewhere.¹⁰ Melting point and crystallinity for the copolymer were measured by DSC. DSC measurements were made by a Dupont DSC thermal analyzer at a heating rate of 10 °C/min. Comonomer contents in the copolymers were measured by FTIR method using the absorbance ratios.¹¹ Crystaf analysis was performed using CRYSTAF model 200 manufactured by PolymerChar S.A. The polymer was dissolved in TCB at a concentration of 0.1 mg/mL. During the dissolution step, the polymer solution was kept at a temperature of 160 °C for 1 h, then decreased to 95 °C and kept for 45 min. The polymer solution was then cooled at a constant rate of 0.1 °C/min to 30 °C. During the cooling process, aliquots of the polymer solution were collected and transferred to the in-line infrared detector. The infrared detector monitored the change in polymer concentration in solution with temperature, giving intergral Crystaf curve. The differential curve of Crystaf as reported in this article is obtained by numerical differentiation of the intergral curve. The molecular weight and its distribution was measured by gel permeation chromatography (Waters 150CV) at 135 °C with TCB as solvent. Fractionation of the PE samples was achieved by using analytical TREF. The TREF elution profiles were generated using a home-made instrument. The sample was dissolved in xylene at a concentration of 2-4 mg/mL at 130 °C and injected into the col-

umn at the same temperature, and the latter was then cooled to 20 °C at a rate of 1.5 °C/h. The column was subsequently eluted with 1,2,4-trichlorobenzene (TCB) at a flow rate of 0.5 mL/min while the temperature was increased from 20 to 130 °C over 4.5 h. The output, detected with an IR detector, was presented as a fractogram normalized to constant area. Molecular weights were calculated with a calibration curve established using polystyrene standards.

Results and Discussion

Copolymerization of Ethylene and 1-Butene. Table I summarizes the results of copolymerizations and the properties of resulting ethylene-1-butene copolymer. The polymerization time was not fixed, but changed to feed the same amount of ethylene gas into the reactor for all copolymerizations to compare microstructures of the resulting copolymers. C₄/C₂ molar ratio was changed by changing the amount of 1-butene in feed, and it was 0.0, 0.28, 0.75, 1.06 and 1.50 mole/mole. The activity showed the maximum at C₄/C₂ molar ratio of 0.75. Density and comonomer content were decreased and increased, respectively, as C₄/C₂ molar ratio increased. At C₄/C₂ molar ratio of 1.50 the copolymer was not produced in a powder form due to higher content of 1-butene and quite low crystallinity in the copolymer. The higher content of 1-butene in the copolymer, the lower melting point of the polymer, but it was not lower than 120 °C. However, the crystallinity of copolymer calculated with DSC analysis decreased as the 1-butene content increased.

The molecular weight of copolymer was decreased as 1-butene/ethylene molar ratio in feed was increased. This was coincided with the previous reports that claimed the role of comonomer as chain terminating agent, and lowering the polymerization propagation in the case that 1-butene was just inserted into the polymer chain.² Different from the molecular weight, molecular weight distribution (MWD) showed an opposite behavior in the copolymerization. The homopolyethylene produced in this study had MWD of 4.6, and it was down to 3.1 in the presence of 1-butene during the polymerization with C₄/C₂ molar ratio of 0.28. However, it was increased as 1-butene/ethylene molar ratio increased up to 6.2. A broad MWD of polyolefin produced with heteroge-

Table I. Ethylene-1-Butene Copolymers Prepared Using Ziegler-Natta Catalyst

C ₄ /C ₂ Molar Ratio in Feed (mol/mol)	Activity (kg-PE/g-cat hr)	Density (g/cm ³)	Comonomer Content in Polymer (wt%)	T _m (°C)	Crystallinity (%)	M _w (g/mol)	MWD
0.00	2.2	0.956	0.0	134.4	70.0	273,000	4.6
0.28	7.0	0.937	1.1	125.2	53.2	195,000	3.1
0.75	8.9	0.928	3.3	121.7	46.7	181,000	3.8
1.06	7.9	0.923	5.1	120.4	45.5	154,000	4.2
1.50	- ^a	0.906	13.8	119.7	28.6	126,000	6.2

^aNot available due to the incomplete collection of sticky polymer.

neous Ziegler-Natta catalyst is considered to be an indicator of the presence of multi-active site in the heterogeneous polymerization catalyst.^{5,12}

Analysis of Copolymer. The chemical compositional distribution (CCD) or short chain branch (SCB) distribution of the copolymers was analyzed by both analytical TREF and Crystaf methods. Figures 1 and 2 show TREF and Crystaf curves of polymer samples, respectively, and the curve shape and peak position are dependent upon the content of 1-butene in copolymer. The SCB content was reported to influence the melting and crystallization behavior of ethylene- α -olefin copolymer significantly, but the effect of molecular weight on them were negligible.^{13,14} TREF curve of homopolyethylene has the maximum peak at 103.8 °C. However, the copolymer molecules with the lowest 1-butene contents were eluted in the range of 97-98 °C, although those contained quite small amount of 1-butene and were highly crystalline. At below 95 °C, broad distributions of the curves are corresponding to the lower crystalline copolymer

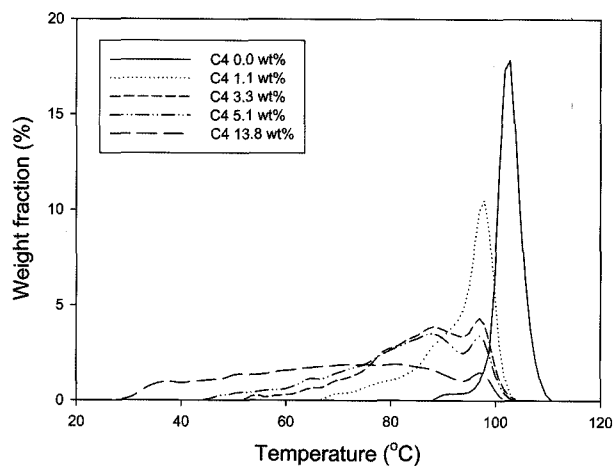


Figure 1. TREF curves of ethylene-1-butene copolymers; see Table I.

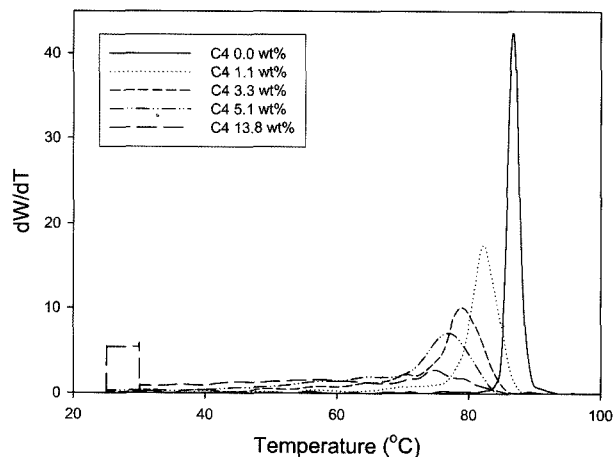


Figure 2. Crystaf curves of ethylene-1-butene copolymers; see Table I.

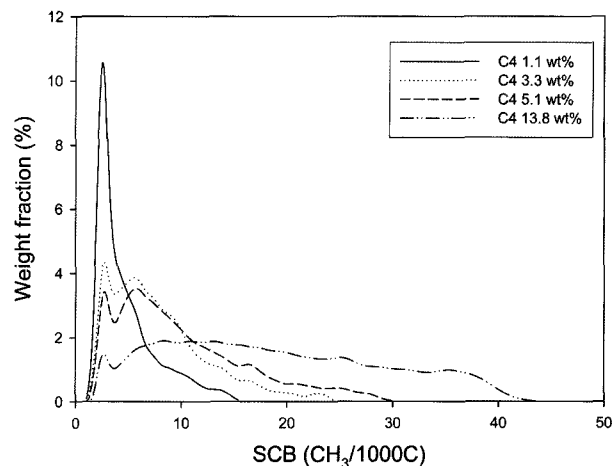


Figure 3. Short chain branch distribution of ethylene-1-butene copolymers calculated from TREF curve.

having a highly short-branched molecules, giving information on the CCD. As the content of 1-butene increased, the TREF curve became broader and broader. The TREF curve can be converted to the short chain branch (SCB) distribution using the calibration curve reported by Zhang.¹ The SCB distribution in Figure 3 shows the bimodal curve with SCB concentration in the range from 5 to 55 branches per 1,000 carbons for all copolymers. The sharp peak of copolymer with a SCB content of less than 3 branches per 1,000 carbons was shown for all copolymers as well as homopolyethylene. The higher concentration of 1-butene was contained in the copolymers, the broader SCB distribution was revealed. It can be said that the higher content of 1-butene in the copolymer results in the more heterogeneous distribution of SCB in case of Ziegler-Natta catalyst.

In the case of Crystaf curves, different behavior from TREF curve was observed, and homopolyethylene had the maximum peak at 86.7 °C. However, as the content of 1-butene

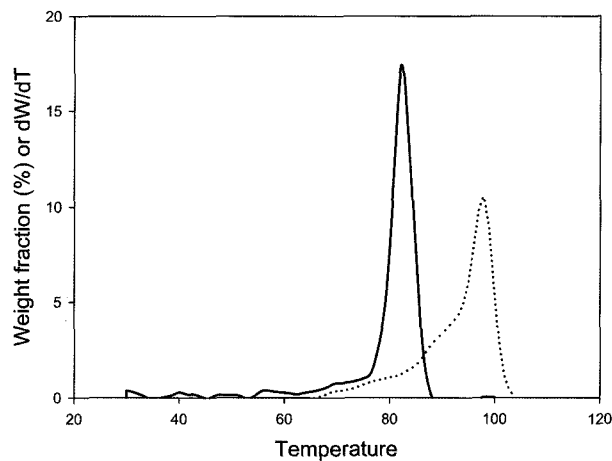


Figure 4. Comparison of TREF and Crystaf curves for the copolymers having 1-butene content of 1.1 wt%; — Crystaf, ... TREF.

increased in the copolymer, the peak temperature was lowered. The Crystaf curves became broader as Sarzotti *et al.* reported previously.¹⁵

Figures 4 to 7 show the difference between TREF and Crystaf curves for the same copolymer sample. All peaks in Crystaf curves were lower than that of TREF curve, resulting from the supercooling effect, similar to what could be observed between the heating and cooling cycles in DSC. It is because Crystaf curve was measured during the process of crystallization, whereas TREF was measured during the process of melting and dissolution.¹⁶ In the case of copolymer with 1-butene content of 1.1 wt% both TREF and Crystaf analysis showed broadening of peaks and growing of lower crystalline part. TREF gives more prominent broad peak in comparison to Crystaf curve. At the higher content of 1-butene in the copolymer such as 3.3 and 5.1 wt%, Crystaf curve did not show the bimodal shape and the fraction of lower crystalline part was observed to be low compared to TREF curve as shown in Figures 5 and 6. However, TREF

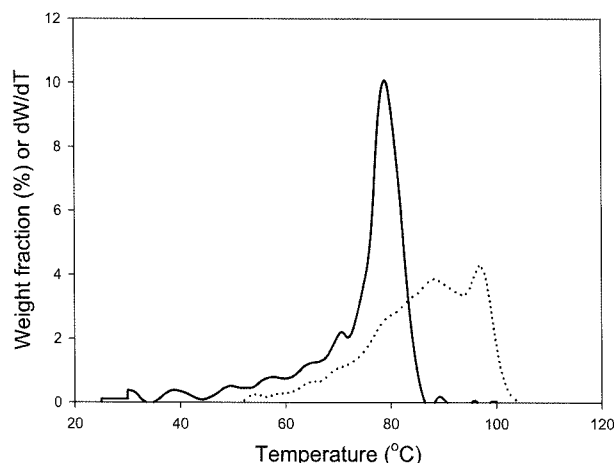


Figure 5. Comparison of TREF and Crystaf curves for the copolymers having 1-butene content of 3.3 wt%; — Crystaf, TREF.

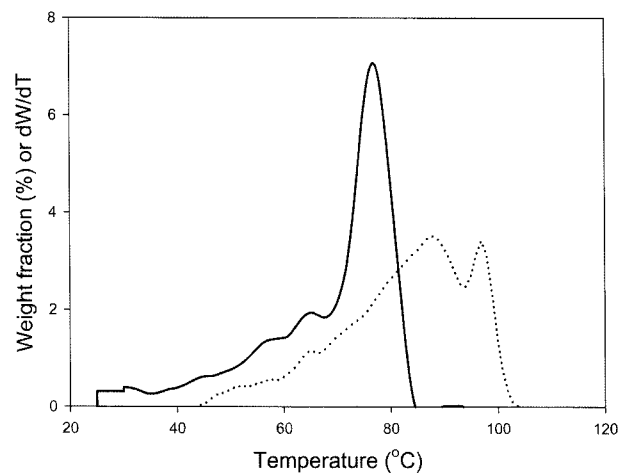


Figure 6. Comparison of TREF and Crystaf curves for the copolymers having 1-butene content of 5.1 wt%; — Crystaf, TREF.

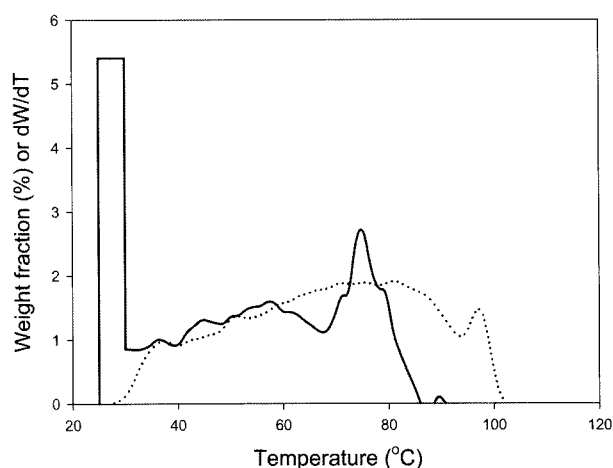


Figure 7. Comparison of TREF and Crystaf curves for the copolymers having 1-butene content of 13.8 wt%; — Crystaf, TREF.

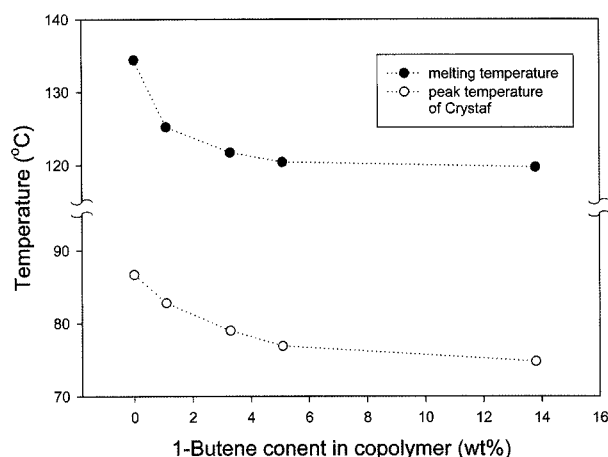


Figure 8. Melting temperature determined by DSC and peak temperature of Crystaf curve as a function of 1-butene content in the copolymer.

and Crystaf curves started to show the similar curve pattern at the higher 1-butene content of 13.8 wt%, but Crystaf analysis gave the distinct soluble part in solvent at room temperature as shown in Figure 7. The peak temperature was not decreased drastically in Crystaf curves, but rather slightly at the higher 1-butene content, similar to the trend of melting point in DSC analysis as shown in Figure 8.

The purpose of both TREF and Crystaf methods is to analyze and compare CCD of copolymers. It could be summarized from this study that TREF can give the more detail and distinct information on CCD of copolymer compared to Crystaf in the lower comonomer content such as the range of 0 to 5 wt%.

As C_4/C_2 molar ratio in feed was increased from 0.28 to 1.5, the lower crystalline copolymer was revealed, and its fraction was also increased and SCB distribution was broadened. Figure 9 shows the lower molecular weight fraction is also increased as C_4/C_2 molar ratio in feed was increased.

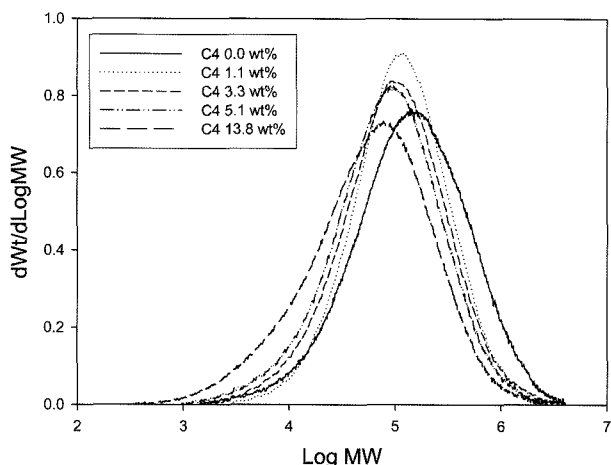


Figure 9. GPC curves of copolymer samples with respect to the 1-butene content in the copolymer; see Table I.

Taking GPC, TREF and Crystaf results into consideration, the lower crystalline or the higher 1-butene fraction in copolymer should have rather lower molecular weight. It could be explained the broader distributions of molecular weight and chemical composition result from the role of 1-butene as terminating agent and the retarding effect of chain propagation during copolymerization.

Conclusions

Ethylene-1-butene copolymers with different 1-butene content were prepared with SiO₂-supported TiCl₄ catalyst, and analyzed to investigate chemical compositional distribution in detail using TREF and Crystaf methods. TREF analysis showed that the copolymers had a broad and bimodal CCD regardless of the content of 1-butene in the copolymer. The SCB concentration was in the range of 5 to 55 branches per 1,000 carbons for all copolymers prepared in the study. Furthermore, the broader CCD was revealed with the higher content of 1-butene in the copolymer. Crystaf analysis did not showed a bimodal CCD for the copolymers having the

1-butene content of less than 5.1 wt%. The lower crystalline or higher SCB fraction in Crystaf analysis was less than that of TREF analysis. The trend of peak temperature in Crystaf analysis was similar to that of melting temperature in DSC.

Acknowledgements. This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-20144-0).

References

- (1) M. Zhang, D. T. Lynch, and S. E. Wanke, *J. Appl. Polym. Sci.*, **75**, 960 (2000).
- (2) F. M. Mirabella, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 2800 (2001).
- (3) L. Wild, *Adv. Polym. Sci.*, **98**, 1 (1991).
- (4) C. Gabriel and D. Lilge, *Polymer*, **42**, 297 (2001).
- (5) Y. S. Ko, T. K. Han, H. Sadatoshi, and S. I. Woo, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 291 (1998).
- (6) Y. S. Ko, T. K. Han, J. W. Park, and S. I. Woo, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 2769 (1997).
- (7) Y. V. Kissin, F. M. Maribella, and C. C. Meverden, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 4351 (2005).
- (8) L. J. D. Britto, J. B. P. Soares, A. Penlidis, and B. Monrabal, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 539 (1999).
- (9) Y. V. Kissin and H. A. Fruitwala, *J. Appl. Polym. Sci.*, **106**, 3872 (2007).
- (10) Y. S. Ko and J.-K. Jeon, *Catal. Today*, **132**, 178 (2008).
- (11) T. E. Nowlin, Y. V. Kissin, and K. P. Wagner, *J. Polym. Sci. Part A: Polym. Chem.*, **26**, 755 (1988).
- (12) Y. V. Kissin, F. M. Mirabella, and C. C. Meverden, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 4351 (2005).
- (13) M. Peeters, B. Goderis, H. Reynaers, and V. Mathot, *J. Polym. Sci. Part B: Polym. Phys.*, **37**, 83 (1999).
- (14) M. Zhang, D. T. Lynch, and S. E. Wanke, *Polymer*, **42**, 3067 (2001).
- (15) D. M. Sarzotti, J. B. P. Soares, L. C. Simon, and L. J. D. Britto, *Polymer*, **45**, 4787 (2004).
- (16) S. Anantawarskul, J. B. P. Soares, and P. M. Wood-Adams, *Adv. Polym. Sci.*, **182**, 1 (2005).