^{13}C NMR, GPC, and DSC Study on a Propylene-ethylene-1-butene Terpolymer Fractionated by Temperature Rising Elution Fractionation

Yu-Dong Zhang,[†] Qing-Qiang Gou, Jun Wang, Chang-Jiang Wu, and Jin-Liang Qiao

Beijing Research Institute of Chemical Industry, SINOPEC, 100013, Beijing, P. R. China

ABSTRACT: A terpolymer of propylene with low amounts of ethylene and 1-butene comonomers was fractionated by temperature rising elution fractionation (TREF), and the effect of fractionation experiment was checked through crystallization analysis fractionation (Crystaf). Nuclear magnetic resonance (^{13}C NMR) spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) were used to characterize the set of polymer fractions obtained. Each polymer fraction was composed of long isotactic propylene sequences and low amounts of ethylene and 1-butene comonomers, and had more uniform molecular weight distribution and narrower crystallization temperature distribution (σ, R) than the original sample. The macromolecular chains consisted mainly of PP, PB, and PE dyads with or without the presence of very low amounts of BB, EE, and EB dyads. The terpolymer could be considered a combination of a propylene-ethylene copolymer and a propylene-1-butene copolymer in analyzing the molecular chain microstructure of the terpolymer. The investigation concluded that with increase of elution temperature, ethylene and 1-butene content of the polymer fractions decreased, and the number average sequence length of ethylene ($\overline{n_E}$) and 1-butene ($\overline{n_B}$) decreased, whereas the number average molecular weight (M_n) and number average sequence length of propylene ($\overline{n_P}$) increased. It is ethylene, not 1-butene, that affects linearly the melting temperature at content lower 6.8 mol%. A linear relationship was found between reciprocal number average molecular weight ($1/M_n$) and reciprocal melting temperature ($1000/T$, $1/K$) at number average molecular weight below 1.59×10^5, in good agreement with Flory's theory.
KEY WORDS   1-Butene / ^{13}C NMR / Ethylene / Melting Crystallization Behavior / Terpolymer of Propylene with Low Amount of Ethylene and 1-Butene / Temperature Rising Elution Fractionation /

Molecular microstructure is of significance in its effect on the physical properties of propylene polymers such as melting crystallization, degree of crystallization, rheological, and optical properties. Tacticity is an important factor to determine the properties of propylene polymers. Incorporation of ethylene, 1-butene, or other comonomers into the macromolecular chain of propylene polymers can also adjust macromolecular chain sequence and morphological structure, and make a variety of properties of propylene polymers, like melting crystallization behavior, improved and optimized effectively. So far, random copolymers of propylene with low amounts of comonomer, like propylene-ethylene copolymer,[1,2] propylene-1-butene copolymer,[3] and propylene-α-olefins copolymer,[4] have been investigated to a certain extent. However, owing to much more complicated macromolecular chain sequences and morphological structures than that of random copolymers, the corresponding terpolymers of propylene, for instance, a random terpolymer of propylene with low amounts of ethylene and 1-butene, have received far less attention. Although up to now some work has been done on this topic,[5–8] our knowledge is still limited.

The work carried out by Galland *et al.*[5] on propylene-ethylene-1-butene terpolymers is detailed and in-depth study. In that paper, the samples included a terpolymer of propylene with low amounts of 1-butene and ethylene comonomers and blend of the same terpolymer and an ethylene-1-butene random copolymer. After the terpolymer sample was fractionated by temperature rising elution fractionation (TREF), ^{13}C NMR was used to characterize the polymer fractions. Almost all assignments of ^{13}C NMR were based on a previous study on spectra of ethylene-propylene, ethylene-1-butene and propylene-1-butene copolymers. However, owing to poor resolving power, many important peaks of propylene-ethylene-1-butene terpolymers overlapped and could not be identified distinctly, so the contents of the comonomers, dyads, and triads from these peaks could not be calculated accurately.

To study thoroughly the relationship between properties and molecular microstructure of a terpolymer of propylene with low amounts of ethylene and 1-butene, we first make samples of propylene terpolymer uniform by TREF, which is a very powerful technique to fractionate semi-crystalline polyolefins on the basis

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[†]To whom correspondence should be addressed (Fax: +86-10-64273136, E-mail: YD-Zhang@brici.ac.cn).

Table I. Specifications of terpolymer sample

	T_m °C	T_c °C	M_n g mol^{-1}	M_w/M_n	T_w °C	T_n °C	R	σ	[E] mol%	[B] mol%
terpolymer	130	82.5	67242	3.77	51.4	49.7	3.4	8.2	5.6	3.3

of crystallizability.[9, 10] We obtained a set of polymer fractions with uniform molecular structure including uniform molecular weight distribution and comonomer content, in which the difference between two consecutive elution temperatures (T_e) was kept constant. Crystallization analysis fractionation (Crystaf) was used to check the effects of the fractionation by analyzing such parameters as σ (Variance) and R ($T_w/T_n - 1$)[11] defining the crystallization temperature distribution of the polymers.[11, 12]

The molecular chain structures of the terpolymers were investigated by a ^{13}C NMR spectrometer, the best way to characterize microstructure and sequence distribution of propylene polymers. Each polymer fraction was composed mainly of propylene sequences and low amounts of ethylene and 1-butene comonomers, and a terpolymer may be considered a combination of a propylene-ethylene copolymer and a propylene-1-butene copolymer. Investigation on propylene terpolymers was thus much simplified. The peaks of ^{13}C NMR of the terpolymers were mainly assigned on the basis of studies by Cheng[13, 14] and Randall,[15–18] and important parameters such as contents of comonomers, dyad and others were calculated by referring to these previous studies. The nomenclature defined by Usami and Takayama[19] was used in the present study.

The principal aims of this study were to obtain a set of uniform samples of propylene terpolymer by TREF, to characterize the molecular microstructure through techniques including ^{13}C NMR, GPC and the melting crystallization behavior by DSC, and to discuss the relationship between melting crystallization and molecular microstructure such as ethylene and 1-butene content and number average molecular weight.

EXPERIMENTAL

Materials

The sample used in the present study was a commercial terpolymer of propylene with low amounts of ethylene and 1-butene comonomers, polymerized by a liquid phase bulk process. Product specifications was listed in Table I. To obtain a set of uniform polymer fractions, TREF was used to fractionate the propylene-ethylene-1-butene terpolymer.

Preparative TREF

The preparative TREF system consisted of a jacketed column thermostated to ± 0.1°C by circulating hot oil and a fractionation column with a free volume of 1250 mL made of a large double-walled glass condenser packed with fine glass beads. A 15 g sample were dissolved in 400 cm^3 of 1,2,4-trimethylbenzene at 140°C and stabilized with antioxidant 2,6-ditertbutylpresol. The solution was transfused to the fractionation column from the top at 140°C. To make polymer molecule deposit around glass beads in layers step by step crystallizability, it took nearly 100 h for the column to cool from 140°C to room temperature. The most easily crystallizable macromolecules precipitated first around the glass beads in the innermost layers. Molecules with least crystallinity precipitated last around the outermost layer. As the column was heated gradually, polymer fractions were eluted continuously from outermost layer to inmost layer, and collected in batches as temperature increased gradually stepwise from room temperature to 140°C. Finally, the polymer fractions obtained from TREF were precipitated into excess acetone at room temperature, filtered and dried in vacuum to constant weight.

^{13}C NMR

^{13}C NMR spectra were measured on a Bruker 400 MHz FT-NMR spectrometer operating at 100 MHz in polymer solutions (less than 20 wt%) with *o*-dichlorobenzene as solvent at 110°C, with the highest single peak as the reference (132.9 ppm). Considering that T_1 of methylene carbons and methine carbons in each location was shorter than 2 s,[15, 16] a pulse program with flip angle of 90°C was used, matching with 2 s acquisition time and 12 s relaxation delay in the sweep width of 180 ppm. To eliminate nuclear Overhauser effect (NOE), an inverse-gate decoupling pulse program was selected, and meanwhile proton broadband decoupling was achieved with the Walth16 program. At least 15000 scans were collected with 64 k points/scan. To identify distinctly and assign correctly response peaks, an experiment of dept-135 was also carried out. Nomenclature and assignments of various carbon atoms along the molecular chain for absorption bands in the NMR spectra were determined on the basis of studies by Cheng,[13, 14] Randall,[15–18] and Usami.[19]

GPC

Gel permeation chromatography (GPC, Waters, Alliance GPCV 2000) with a polystyrene column in the

GPC-viscometer module was used for characterization of molecular weights and weight distributions of the polymer fractions at 140 °C. Molecular weight was calculated with a standard procedure based on the universal calibration curve of polystyrene.

Crystaf

Commercial Crystaf Apparatus, Model 200, manufactured by Polymer Char S.A., was used for crystal fractionation to obtain σ (Variance), R ($T_w/T_n - 1$), T_w, and T_n defining the crystallization temperature distribution of polymers and to check TREF results.[11] Concentrations of 0.1% (w/v) were used, with 30 mg samples in 30 mL 1,2,4-trichlorobenzene. Crystallization was carried out in stirred stainless steel reactors of 60 mL volume, where dissolution and filtration took place automatically. The temperature changed from environment temperature to 160 °C at 30 °C min^{-1}, and after staying at this level for 60 min, the temperature decreased from 160 °C to 95 °C at 30 °C min^{-1}. After staying for 45 min, crystallization started from 95 °C to 25 °C at 0.1 °C min^{-1}. Concentrations of the samples in solution were immediately found from the intensity of C–H stretching frequencies of methylene and methyl group with an infrared detector with fixed wavelength of 3.5 micrometer. As temperature decreased gradually according to a prearranged temperature program, the samples underwent stepwise crystallization. By monitoring on-line intensity of absorbance bands of the polymer fractions, polymer concentrations in solution were measured in time.

DSC

DSC was carried out on a DSC-7 apparatus from PerkinElmer. To ensure identical thermal history, the samples were first heated from 0 °C to 210 °C and kept at this temperature for more than 10 min and subsequently cooled from 210 °C to 0 °C at 10 °C min^{-1}. They were again heated from 0 °C to 210 °C at 10 °C min^{-1}. The maximum point on the exothermic curve in the cooling cycle was utilized to determine crystallization temperature, T_c, from bulk melt. Maximum peak of the second heating cycle was taken as the melting temperature, T_m, of the polymer fraction.

RESULTS AND DISCUSSION

Fractionation

By the method mentioned, a terpolymer of propylene with low amounts of ethylene and 1-butene comonomers was fractionated by preparative TREF. Ten fractions were collected from 45 °C to 100 °C. The difference between two consecutive elution tempera-
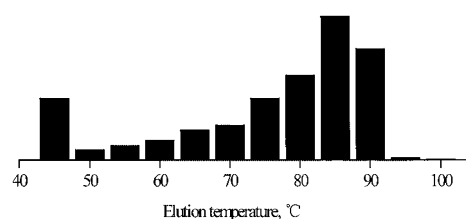
Figure 1. Diagram of weight distribution of temperature rising elution fractionation for the propylene-ethylene-1-butene terpolymer, showing relative weight of the fraction polymers as a function of the elution temperature (°C).
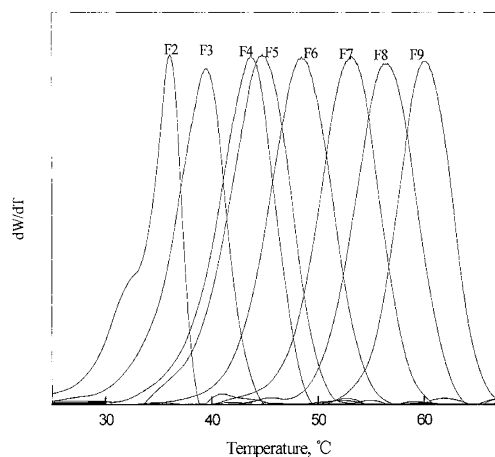
Figure 2. The concentration distribution determined by Crystaf of the polymer fractions in solution as a function of temperature (°C).

tures was kept at 5 °C. About 80 wt% of the sample was fractionated from 50 to 90 °C. At elution temperatures lower than 45 °C or higher than 95 °C, only residual elastic polymers with lower melting temperatures or very low amounts of polymers were fractionated, respectively (Figure 1). Figure 2 shows the results of Crystaf, a group of curves of differential weight versus crystallization temperature of propylene polymers. The polymer fractions had narrower crystallization temperature distribution than the original sample, suggesting that results of TREF were excellent and polymer fractions uniform. Important data for the set of polymer fractions are summarized in Table II, including elution temperature (T_e, as melting temperature in solution), melting temperature (T_m, as bulk melting temperature), number average molecular weight (M_n), molecular weight distribution (M_w/M_n), weight average crystallization temperature (T_w, °C), number average crystallization temperature (T_n, °C), and parameters σ (Variance) and R ($T_w/T_n - 1$) defining the crystallization temperature distribution. As seen from Figure 1 and Table II, at lower elution temperatures, polymer fractions F2, F3, and F4 had relatively larger polydispersity (M_w/M_n) and broader crystallization temperature distribution (σ, R). Based on previous study,[2] at
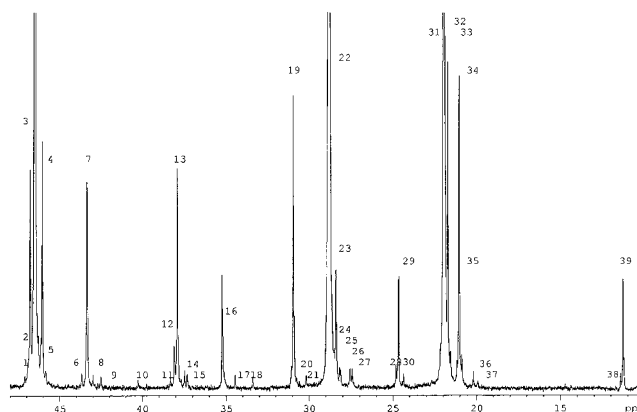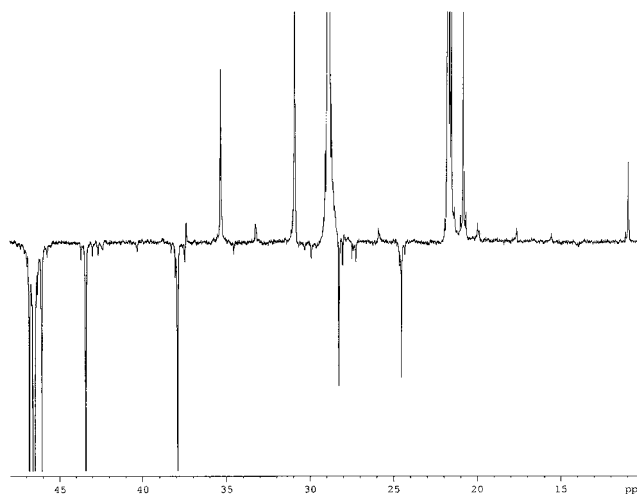
Table II. Characteristics of fraction polymers

Frac. No. T_e, °C	T_m °C	M_n g mol^{-1}	M_w/M_n	T_w °C	T_n °C	σ	R
F1 (50)	103	32995	2.8				
F2 (55)	106	42574	3.0	34.3	33.9	3.4	1.1
F3 (60)	111	49681	2.8	38.2	37.9	3.7	1.0
F4 (65)	114	62894	2.8	42.7	42.3	4.0	0.9
F5 (70)	118	70445	2.8	44.5	44.5	4.2	1.0
F6 (75)	122	86183	2.6	48.4	48.4	4.2	0.7
F7 (80)	127	98256	2.5	52.9	52.6	3.9	0.5
F8 (85)	132	129462	2.2	56.4	56.4	3.8	0.4
F9 (90)	136	158794	2.2	60.6	59.8	3.2	0.3

Figure 3. ^{13}C NMR spectrum of a terpolymer.

Figure 4. Dept-135 spectrum of a terpolymer.

least two kinds of macromolecular chains could be fractionated at lower elution temperatures, that is, macromolecular chains with low molecular weight and those with high comonomers content, but macromolecules with various molecular microstructures behaved very differently in undercooling. Crystallization temperature distribution of the polymers was far different from melting temperature distribution, which would lead to broader crystallization temperature distribution of polymer fractions obtained at lower temperatures. As elution temperature increased, molecular weight distribution (M_w/M_n) and crystallization temperature distribution (σ, R) of the polymer fractions became narrower, suggesting that macromolecular chains were more regular and uniform (F8 and F9). In Table II and Table V, only macromolecular chains with higher molecular weight and lower comonomers contents have higher melting temperature. Thus, the higher the regularity and uniform of macromolecular chains and larger the molecular weight, the higher is the melting temperature of polymers.
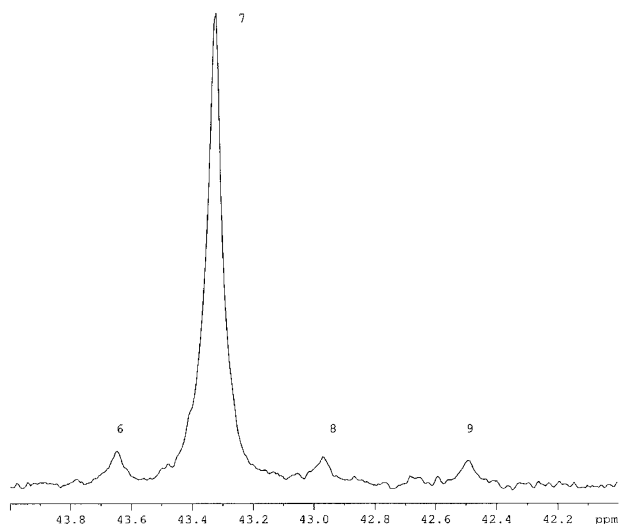
^{13}C NMR Study

Because of the complexity of the molecular microstructure of random propylene-ethylene-1-butene terpolymer, assignment of ^{13}C NMR peaks was difficult. For a random terpolymer, there should have been six unique dyads and eighteen unique triads.[15] But in the present study, each polymer fraction was a terpolymer consisting mainly of propylene monomer with low amounts of ethylene and 1-butene comonomers. thus, macromolecular chains mainly consisted of PP, PB, and PE dyads, in the absence or presence of very low amounts of BB, EE, and EB dyads. A random terpolymer may thus be a combination of a propylene-ethylene random copolymer and a propylene-1-butene random copolymer so as to make the analysis of molecular microstructure more easy and the study of macromolecular structure simple. ^{13}C NMR peaks of the terpolymer were assigned according to Cheng[13, 14] and Randall,[15–18] using the nomenclature of Usami and Takayama.[19]

Figures 3 and 4 show ^{13}C NMR and dept-135 spectra, respectively, of the terpolymer. Nearly all peaks could be found in the studies of Cheng[13, 14] and Randall,[15–18] thus thinking the teropolymer to combination of a propylene-ethylene random copolymer and a propylene-1-butene random copolymer. We found two new peaks at 42.97 ppm and 42.50 ppm, shown in Figure 5. In view of the two new peaks near the response peak of the $\alpha\alpha B_1 B_2$ carbon of PB dyad, we supposed the two peaks should have a relationship with the $\alpha\alpha B_1 B_2$ carbon of PB-center and involve the P, E, and B comonomers simultaneously. The two peaks may be n-ads peaks from the $\alpha\alpha B_1 B_2$ carbon of PB dyad. According to Lindeman and Adams[20] and previous work on binary copolymers,[2] in tetrads sequences, substituting P with E would shift the chemical shift of $\alpha\alpha B_1 B_2$ carbon to the right. Thus, the two peaks at 42.97 ppm and 42.50 ppm were considered the $\alpha\alpha B_1 B_2$ carbon response peaks of EPB(P) and EPB(E) tetrads, respectively. Assignments and chemical shifts of carbon atoms in the ^{13}C NMR spectra of the terpolymer are listed in Table III.

Figure 5. Expanded plot of the $\alpha\alpha B_1 B_2$ region.

Table III. Chemical shifts and triad carbon assignments

Peaks No.	Chem. Shift, PPM	Triads	Carbon
1	47.01	BPP(B)(m)	$\alpha\alpha B_1$
2	46.76	BPP(P)(mm)	$\alpha\alpha B_1$
3	46.45	PPP(P)(mmm)	$\alpha\alpha B_1$
4	46.03	EPP(P)(mm)	$\alpha\alpha B_1$
5	45.83	EPP(E)(m)	$\alpha\alpha B_1$
6	43.67	BPB(P)	$\alpha\alpha B_1 B_2$
7	43.32	PPB(P)(m)	$\alpha\alpha B_1 B_2$
8	42.97	EPB(P)(m)	$\alpha\alpha B_1 B_2$
9	42.50	EPB(E)	$\alpha\alpha B_1 B_2$
10	40.29	BBB	$\alpha\alpha B_2$
11	38.29	(P)PEP(r)	$\alpha\gamma B_1$
12	37.89	(P)PEP(m)	$\alpha\gamma B_1$
13	37.54	(P)PEE(r)	$\alpha\delta B_1$
14	37.45	(P)PEE(m)	$\alpha\delta B_1$
15	37.35	EBB	brB_2
16	35.30	PBP	brB_2
		BBP	brB_2
		BBB	brB_2
17	34.51	BEB	$\alpha\gamma B_2$
18	33.31	EPE	brB_1
19	30.93	PPE(m)	brB_1
20	30.39	PEE	$\gamma\delta B_1$
21	30.00	EEE	$\delta\delta B_1 + \delta\delta B_2$
22	28.87	BPB	brB_1
		PPB(m)	brB_1
		PPP(mm)	brB_1
23	28.30	PBP	$2B_2$
24	28.09	PBB	$2B_2$
25	27.89	BBB	$2B_2$
26	27.51	(E)PEE	$\beta\delta B_1$
27	27.31	(P)PEE(m)	$\beta\delta B_1$
28	24.71	PEP(E)	$\beta\beta B_2$
29	24.57	PEP	$\beta\beta B_1$
30	24.35	BEB	$\beta\beta B_1$
31	21.95	PPP(mm)	$1B_1$
32	21.87	PPB(m)	$1B_1$
33	21.73	BPB	$1B_1$
34	21.06	EPP(m)	$1B_1$
35	20.87	PPP(mr)	$1B_1$
36	20.19	PPP(rr)	$1B_1$
37	19.92	EPE	$1B_1$
38	11.40	EBE	$1B_2$
39	11.27	PBP	$1B_2$
		BBE	$1B_2$
		BBP	$1B_2$

B_1, propylene; B_2, 1-butene.

In characterizing molecular microstructure, it was necessary to calculate monomer content, dyad and triad sequence distribution and number average sequence length of the terpolymers. On the basis of ^{13}C NMR spectrum of propylene-ethylene-1-butene terpolymers, monomer content was calculated from contents of dyads. Figure 3 shows that the corresponding peaks related to dyads are relatively simple and isolated, and unlikely to overlap, so error by overlapping of peaks is low enough to be ignored. For example, the content of PP dyad could be obtained from a group of peaks 1–5, the content of PE dyad from a group of peaks 11–14, the content of PB dyad from a group of peaks 6–9, the content of EE from a group of peaks 21, 26, and 27 through equation [EE] = [EEE] + ([PEE] + [BEE])/2, the content of BE from peak 17 and the content of BB from peak 10. As seen from Figure 3, a dyad consists of many tetrads, so each peak of dyad could be further divided into many peaks. The peak of $\alpha\alpha B_1$ carbon included peaks from 1 to 5, by which tetrad content could be estimated. Considering overlapping of peaks related to triads and an enormous difference of intensities of triad peaks, for example, PPP, PPE, BPP, BBB, the content of monomer obtained from triads should bring about larger error. If we calculated monomer content by methylene peaks and methine peaks at the same time, the veracity would be debased. To minimize error, only methylene peaks were used. Based on Randall[15] and our previous study,[2] formulae to calculate the dyad content, monomers content and number average sequence length wase summarized in Table IV. The E and B were considered comonomers, with B_1 and B_2 standing for propylene and 1-butene monomers, respectively.

Table V summarizes dyad content, comonomer content, and number average sequence length of the polymer fractions. As seen from Table V, in macromolecular chains of propylene terpolymers, PP, PE, and PB dyads were the majority of molecular sequences. The EE, BB, and BE dyads were very low, even close to zero in some fractions, such as F8 and F9. As elution temperature increased, the PP dyad and number average sequence length of propylene ($\overline{n_P}$) increased, while PE, PB, BB, EE, and EB, decreased, number average sequence length of ethylene ($\overline{n_E}$) and 1-butene ($\overline{n_B}$) decreased.
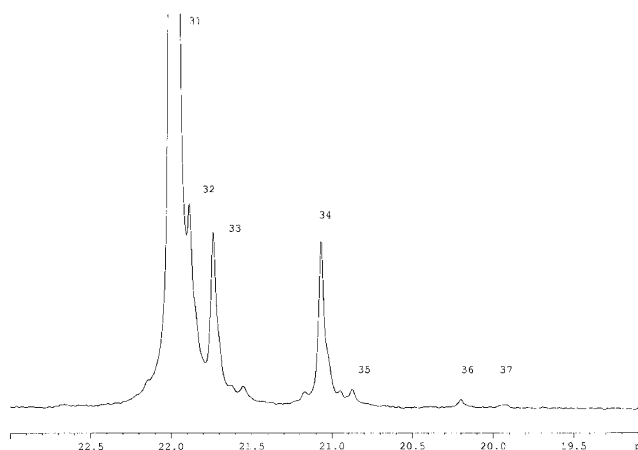
With regard to a macromolecular chain of propylene, if incorporation of ethylene and 1-butene comonomers and racemic structure of propylene sequence are the factors affecting tacticity of the macromolecular chain of propylene, all peaks related to methyl group in the range of 18 ppm to 23 ppm in Figure 6 should be investigated. According to Cheng[13, 14] and Randall,[15−18] peaks from 31 to 37 were assigned as follows: PPP(mm), PPB(m), BPB, PPE(m), PPP(mr), PPP(rr), and EPE. Table VI summarizes PPP(mm) triad content in polymer fractions. As seen from Figure 6 and Table VI, PPP(mm) is the majority of triads sequences in polymer fractions, suggesting that the polymers were terpolymers with high isotactic propylene sequences. Table VI shows that with increase of elution temperature, the tacticity of propylene sequence of the fraction polymers increased.

Melting Crystallization

For terpolymers of propylene with low amounts of ethylene and 1-butene, macromolecular chain length and comonomer content are considered to affect melting crystallization of terpolymers. DSC endothermic curves of the polymer fractions are depicted in Figure 7 in conformity with the number of polymer fractions, from which melting temperature of each polymer fraction could be obtained. The maximum endothermic curve was recorded as the melting temperature (T_m). To ensure identical thermal history, only melting temperatures for the second heating cycle were considered. Figure 7 indicates that all the DSC curves are not symmetric in the neighborhood of the maximum. The melting process sets out at a lower temperature, and the curve rises slowly at the begin. Beyond the maximum the curve drops abruptly, because the comonomers, especially 1-butene, brought about defects in the polypropylene crystal lattice. Thus with increase of comonomer

Table IV. Formulae for calculating dyads content, monomers content, and number average sequence length

|	Formula
PP	$\alpha\alpha B_1$
PE	$\alpha\gamma B_1 + \alpha\delta B_1$
PB	$\alpha\alpha B_1 B_2$
EE	$\delta\delta + (\beta\delta B_1 + \beta\delta B_2)/2$
EB	$\alpha\gamma B_2$
BB	$\alpha\alpha B_1$
P	$PP + PB/2 + PE/2$
E	$EE + BE/2 + PE/2$
B	$BB + PB/2 + BE/2$
$\overline{n_P}$	$2P/(PB + PE)$
$\overline{n_E}$	$2E/(PE + BE)$
$\overline{n_B}$	$2B/(BE + PB)$

Figure 6. Expanded plot of the methyl region.

Table V. Sequence distribution, monomers content, and number average sequence length of polymer fractions

	F2	F3	F4	F5	F6	F7	F8	F9
PP	77.9	79.3	81.1	82.3	84.2	85.7	88.0	90.0
PB	9.2	8.9	8.6	8.6	7.8	7.3	6.7	5.4
PE	11.3	10.5	9.2	8.3	7.3	6.4	5.0	4.5
BB	0.2	0.2	0.2	0.1	0.1	0.1	0	0
BE	0.3	0.3	0.2	0.1	0.1	0.1	0	0
EE	1	0.9	0.7	0.6	0.5	0.4	0.2	0.1
P	88.2	88.9	90.0	90.7	91.7	92.6	93.9	95
E	6.8	6.3	5.4	4.8	4.2	3.6	2.7	2.3
B	5.0	4.8	4.6	4.5	4.1	3.8	3.4	2.7
$\overline{n_P}$	8.57	9.20	10.1	10.7	12.2	13.5	15.9	19.2
$\overline{n_E}$	1.17	1.17	1.15	1.14	1.14	1.13	1.06	1.03
$\overline{n_B}$	1.05	1.04	1.04	1.03	1.03	1.03	1.01	1.0

Table VI. PPP(mm) content as function of fractions

|	F2	F3	F4	F5	F6	F7	F8	F9
PPP(mm) mol%	66.3	66.5	66.9	70.1	72.2	77.1	80.1	80.9
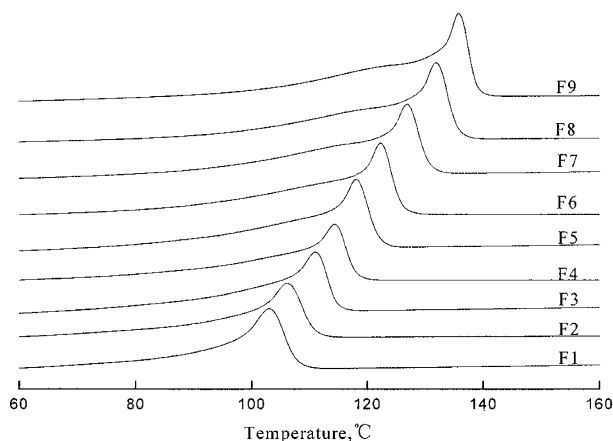
Figure 7. DSC endothermal curves (2nd heating cycle) of the polymer fractions of the propylene-ethylene-1-butene terpolymer, measured at a heating rate at $10\,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$.
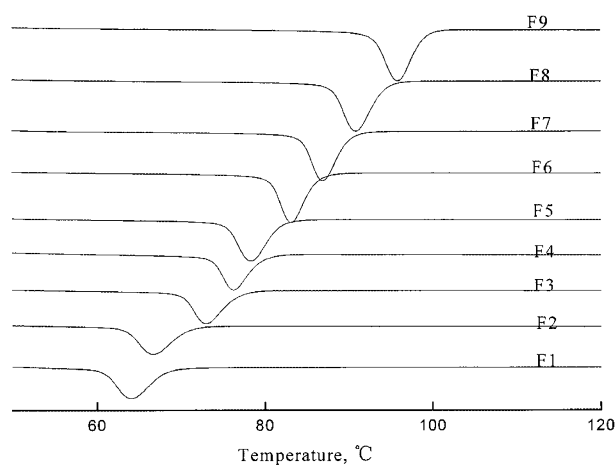
Figure 8. DSC exothermical curves of the polymer fractions of a propylene-ethylene-1-butene terpolymer, obtained at a cooling rate at $10\,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$.

content, the top part of curve become narrower. Figure 8 depicts crystallization curves of the polymer fractions, without long tails.

Brull[4] considered macromolecular chains of propylene as long crystallizable chains, and comonomers as non-crystallizable defective comonomers. Therefore, according to Monrabal[11] and Brull,[4] the classical Flory eq 1[21] simplified to eq 2, formerly applied to explain the relationship between melting temperature and ethylene content for propylene-ethylene random copolymer.[2] This study extends the application of eq 2 from copolymers to terpolymers. To analyze the effect of comonomer of terpolymer on melting temperature, we first considered this comonomer as a defective comonomer. In the equations, T_{m} and T_{m}^{0} stand for melting temperature of the copolymer and homopolymer, and R, ΔH_{u}, P, and X_{C} are the gas constant, heat of fusion per propylene comonomer, molar fraction of propylene comonomer and molar fraction of
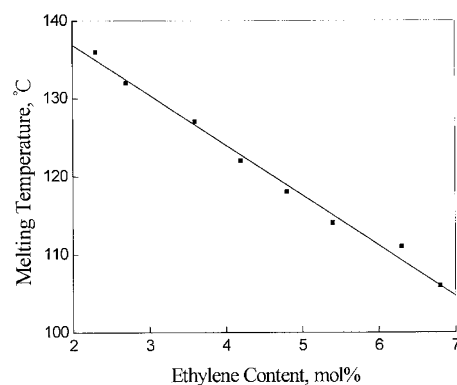
Figure 9. Melting temperature (T_{m}, $^{\circ}\mathrm{C}$) determined by DSC for the fraction polymers of the propylene-ethylene-1-butene terpolymer as a function of ethylene content (mol%).

comonomer, respectively.

$$\frac{1}{T_{\mathrm{m}}} - \frac{1}{T_{\mathrm{m}}^{0}} = \frac{-R}{\Delta H_{\mathrm{u}}} \ln p \qquad (1)$$

$$T_{\mathrm{m}} \cong T_{\mathrm{m}}^{0} - \frac{R(T_{\mathrm{m}}^{0})^{2}}{\Delta H_{\mathrm{u}}} X_{\mathrm{C}} \qquad (2)$$

Figure 9 shows plots of the melting temperature as a function of ethylene content. Eq 2 is in good agreement with the relationship between melting temperature and ethylene content. The ethylene content increases, the melting temperature of terpolymers decreases linearly. However, we do not think that the proposal by Monrabal[11] and Brull[4] is correct in explaining decline of the melting temperature due to the comonomer ethylene unit excluded from the polypropylene crystal lattice, because Alamo has expressed that in 3_{1} helical structure of polypropylene crystal lattice, few small branches such as methyl, chlorine and others could be included in the crystalline lattice. But larger branches would be excluded.[22] Thus, as for the propylene terpolymer, ethylene comonomer could incorporate into the polypropylene crystal lattice to form hole space without destroying the crystal architecture. The holes unavoidably cause depression of crystallization and melting temperature. According to previous papers[2] and Brull,[4] the lower the content of comonomer, the better the linearity of the curve. The $T_{\mathrm{m}} - X_{\mathrm{C}}$ linear relationship is thus applicable.

Figure 10 does not show a linear relationship between melting temperature and 1-butene content at 1-butene content below 5.0 mol%. As 1-butene content increases, the curve bends down gradually. The rate of depression of melting temperature increases more and more rapidly. Without question, the effect of 1-butene comonomer on melting temperature is far different from that of ethylene,[2,4] so eq 2 is no longer applicable to explain the phenomenon for propylene terpolymers. If 1-butene monomer was forced to be incorporated into the crystal lattice, it would cause the crystal
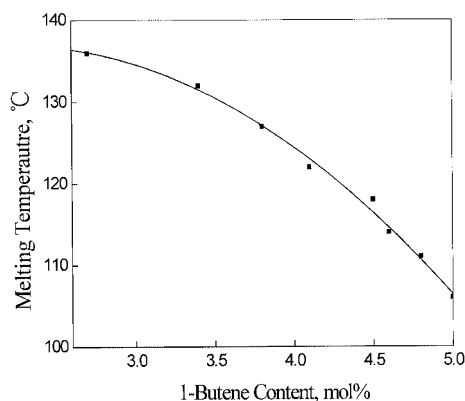
Figure 10. Melting temperature (T_m, °C) determined by DSC for the fraction polymers of the propylene-ethylene-1-butene terpolymer as a function of butene-1 content (mol%).

Figure 11. Reciprocal melting temperature determined by DSC, ($1/T_m$, $1/K$) versus reciprocal number average molecular weight ($1/M_n$) for the fraction polymers of the propylene-ethylene-1-butene terpolymer.
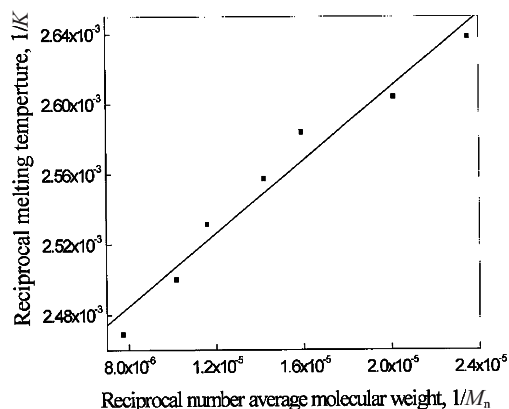
swelling, even rupture, with depression of crystallization of propylene polymers and melting temperature. At lower amounts of 1-butene comonomer, the hole space owing to the presence of ethylene comonomer may debase the breakage from 1-butene to protect the crystal architecture. As comonomer contents increased to a threshold, not only would 1-butene comonomer causes more breakage, but the hole space of ethylene comonomer in the crystal architecture would not prevent crystal architecture breakage.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{2R}{\Delta H_u} \times \frac{1}{i} \qquad (3)$$

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{2Rm}{\Delta H_u} \times \frac{1}{\overline{M_n}} \qquad (4)$$

Macromolecular chain length affects melting crystallization of polymers. Flory[23] presented eq 3 to relate melting temperature (T_m) to number average degree of polymerization (i).[23] If the number average degree of polymerization (i) is transformed to the number average molecular weight (M_n) by assuming $M_n/m = i$ (m, molar mass of propylene monomer), eq 3 could be replaced by eq 4. Eq 4 has been applied to explain the $T_m - M_n$ relationship of random copolymers of propylene with low amounts of ethylene (<10.23 mol%) by assuming weight of the ethylene comonomer identical to that of propylene.[2] For terpolymers of propylene with low amounts of ethylene and 1-butene, the same method was used to analyze the $T_m - M_n$ relationship. The macromolecular chain of the terpolymer was assumed identical to that of propylene homopolymer.

Figure 11 indicates the effect of number average molecular weight on melting temperature. An approximately linear relationship exists between reciprocal melting temperature ($1000/T$, $1/K$) and the reciprocal number average molecular weight ($1/M_n$), even though there is relatively large difference between actual data and the fitting line. Thus, eq 4 may be applied to explain the $T_m - M_n$ relationship for terpolymers at number average molecular weight lower than 1.59×10^5. As number average molecular weight increases, the melting temperature increases, suggesting that when the sum of all comonomers content is below 12 mol%, the melting temperature (T_m) depends on macromolecular chain length, even though the number average molecular weight is close to 1.59×10^5.

CONCLUSIONS

Polymer fractions with uniform molecular weight and comonomers content were obtained by TREF. Macromolecular chains with higher content of ethylene and 1-butene or lower molecular weight were fractionated at lower elution temperatures. Macromolecular chains with higher molecular weight and lower ethylene and 1-butene content had to be fractionated at higher elution temperatures. Macromolecules with various molecular microstructures behaved very differently in undercooling, so that crystallization temperature distribution of polymers is far different from melting temperature distribution. Crystallization temperature distribution and molecular weight distribution of polymer fractions obtained at lower temperature are thus broadened. ^{13}C NMR showed polymer fractions to consist mainly of isotactic propylene sequences with low amounts of ethylene and 1-butene comonomers. Two new response peaks at 42.97 ppm and 42.50 ppm were supposed to be response peaks of the $\alpha\alpha B_1 B_2$ carbon of EPB(P) and EPB(E), respectively. As elution temperature increased, the content of PP dyad, number average sequence length ($\overline{n_P}$) of propylene, and tacticity of macromolecular chain increased. Other dyads such as PE, PB, BB, EE, and EB decreased, and number average sequence length of ethylene ($\overline{n_E}$) and 1-

butene ($\overline{n_B}$) decreased. Investigation on melting crystallization showed that it was ethylene, not 1-butene, that affects linearly the melting temperature at content lower 6.8 mol%. A liner relationship between reciprocal number average molecular weight ($1/M_n$) and reciprocal melting temperature ($1000/T$, $1/K$) was noted.

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