Fractionation and Characterization for a Propylene–Ethylene Random Copolymer

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ABSTRACT: A random copolymer of propylene with 3.5 mol% ethylene comonomer is firstly fractionated by temperature rising elution fractionation (TREF). Techniques including ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FT-IR), gel-permeation chromatography (GPC), crystallization analysis fractionation (Crystaf) and differential scanning calorimetry (DSC) are used to characterize the obtained fraction polymers. The results show that each fraction polymer is composed mainly of isotactic propylene sequence plus a small amount of ethylene comonomer and has uniform molecular weight and ethylene content. The PPP, PPE, and PEP are main part of triad sequence unit. As the elution temperature increasing, ethylene content of the fraction polymers decreases, number average molecular weight increases, and meanwhile number average sequence length of propylene, $\overline{n}_P$, increases, while that of ethylene, $\overline{n}_E$, decreases, close to 1. The results show that ethylene content affects linearly the melting temperature (T_m) in a range of ethylene content being as low as less than 10.23 mol%; there is a linear relationship between the reciprocal melting temperature ($1000/T_m$, K^{-1}) and reciprocal number average molecular weight (M_n^{-1}) in a range of number average molecular weight as low as less than 1.7×10^5.

KEY WORDS Elution Temperature / Ethylene Content 1/K / Melting Temperature / Number Average Molecular Weight / Sequence Length / Tacticity / Temperature Rising Elution Fractionation (TREF) /

Polypropylene is a common semi-crystalline synthetic polymer, and its macromolecular chain structure is an important factor to affect such properties of propylene polymers as crystallization behavior, morphologies, melting temperature, degree of crystallization, toughness, and rheological and optical properties. By the way of introducing some comonomers (*e.g.*, ethylene) into its macromolecular chain, the performance of propylene polymers can be improved purposefully and effectively. Because propylene tacticity and ethylene comonomer complicate the macromolecular chain structure, and can farther lead to complex crystallization behaviors and morphologies, it is very important to firstly characterize the macromolecular chain structure well. In order to investigate thoroughly the relationship between performance and macromolecular chain structure, it is necessary to make samples uniform. Temperature rising elution fractionation (TREF)[1—15] has been shown to be a powerful technique to make crystal polyolefins uniform on the basis of their crystallizability and molecular weight. Through TREF experiments, a set of fraction polymers with uniform molecular weight and content of ethylene comonomer can be obtained; hereafter crystallization analysis fractionation (Crystaf) will be used to check the effect of fractionation by analyzing such parameters as σ and R,[16] which can de-fine the broadness of the crystallization temperature distribution of the fraction polymers.[16—22] Up to now most samples of propylene copolymers on investigation are the impact propylene–ethylene copolymers, a very complex blend. Even though after they have been fractionated by TREF,[3—11] each fraction polymer also consists of PE, PP, propylene–ethylene copolymer and so on, so it is difficult to make sure the relationship among performance, macromolecular chain structure and elution temperature. However the corresponding random copolymers of propylene are not blends, but has received much less attention, and our knowledge of the topic is very limited.[23, 24] Brull *et al.*[23] ever made a study on propylene–ethylene random copolymers, in which the samples, with comonomer content as low as less than 3.5 mol%, are obtained by polymerization. The comonomers are considered as defects in propylene long chains, so relationships between melting temperature and content of the comonomers are determined, but the effect of molecular weight on melting temperature is ignored,

The aim of the present study is to first characterize the macromolecular chain structure of uniform propylene polymers, including ethylene content, number average molecular weight, number average sequence length, tacticity and so on, then to study a relation-

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Table I. Quality specifications of the samples

	$\dfrac{T_m}{°C}$	$\dfrac{T_c}{°C}$	$\dfrac{M_n}{g\ mol^{-1}}$	M_w/M_n	$\dfrac{T_w}{°C}$	$\dfrac{T_n}{°C}$	R	σ	$\dfrac{[E]}{mol\%}$
PERC	144.0	98.3	56703	4.76	65.5	63.1	3.8	9.9	3.5
PHP	163.4	114.0	70662	3.67	80.6	79.4	1.4	6.4	0

ship between melting temperature (elution temperature considered as melting temperature in solution) and macromolecular chain structure. In a typical experiment, a copolymer of propylene with 3.5 mol% of ethylene comonomer is first fractionated by using a preparative TREF. Then the fraction polymers are characterized by ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FT-IR), gel-permeation chromatography (GPC), crystallization analysis fractionation (Crystaf) and differential scanning calorimetry (DSC). Finally, the relationships between melting temperature and ethylene content & number average molecular weight will be discussed.

EXPERIMENTAL

Materials

The samples used in this study are a commercial copolymer of propylene with a small amount of ethylene comonomer (PERC) and a commercial propylene homopolymer (PHP) initiated with Z-N Ti-catalyst by a liquid phase bulk polymerization process. The product quality specifications are listed in Table I. Before being used, the polypropylene homopolymer is treated with *n*-heptane for more than 10 h to extract and remove the low stereoregular and small molecular weight polymer. The propylene–ethylene random copolymer is fractionated by TREF to obtain a set of fraction polymers. In the Table I, T_w is the weight average crystallization temperature; T_n is the number average crystallization temperature; σ and R are parameters defining the broadness of the crystallization temperature distribution of the fraction polymers.[16]

Preparative TREF

A preparative TREF is used to carry out fractionation of the propylene–ethylene random copolymer sample. The preparative TREF system consists of a jacketed column thermo-stated to $\pm 0.1°C$ by circulating heated oil and a fractionation column with free volume of 1240 mL made of a large double-walled glass condenser and packed with fine glass beads. About 15 g of sample is first dissolved in 400 cm^3 of 1,2,4-trimethylbenzene at 140°C, and stabilized with the antioxidant 2,6-di-*t*-butyl-*p*-cresol (3 g/1000 mL). Then the solution is transferred into the fractionation column from the top end of the column at 140°C. In order to

make polymer deposit around the glass beads in layers step by step on the basis of the crystallizability, it takes more than 70 h for the column to be cooled to room temperature. With this process, the most easily crystallizable polymers precipitate first and deposits on the glass beads in the innermost layer. On the contrary, the polymers with the least crystallinity precipitate last and deposit on the outermost layer. As the column is heated, and the elution temperature increases, the polymers on the outermost layer is first eluted with 1,2,4-trimethyl benzene, and subsequent polymers are collected. While increasing the elution temperature stepwise from room temperature to 140°C, a set of fraction polymer will be obtained. The fraction polymers obtained from TREF are precipitated into a large excess of acetone at room temperature, then filtered and dried in vacuum at 60°C to constant weight.

Crystaf

Commercial Crystaf equipment, Model 200, manufactured by Polymer Char S.A., is used to check the effect of TREF experiment to obtain such parameters as σ, R, T_w, and T_n.[16] Concentrations of 0.1% (w/v) are used in this experiment, with 30 mg of samples in 30 mL of 1,2,4-trichlorobenzene solvent. The crystallization process is carried out in stirred stainless steel reactors of 60 mL volume where dissolution and filtration takes place automatically. The whole process of temperature changes during the experiments is as follows: from room temperature to 160°C at rate of 30°C m^{-1}, after staying for 60 min at 160°C, the temperature decreases to 95°C at rate of 30°C m^{-1}, staying 45 min, then the experiments begin from 95°C to 25°C at rate of 0.1°C m^{-1}. In order to monitor the concentration for the samples in solution *in situ*, an infrared detector with a fixed wavelength of 3.5 μm is used to detect the intensity of the C–H stretching frequencies of methylene and methyl group. As temperature decreases according to the temperature program, the samples experience the stepwise crystallization. By monitoring on-line intensity of absorbance peak of the fraction polymers, the polymer concentration in solution is measured in time, which can reveal the crystalline process.

^{13}C NMR Analysis

^{13}C NMR spectra are measured on a Bruker

Table II. Fractionation of the propylene–ethylene random copolymer

Fraction No.	T_e (°C)	W_i (mg)	$W_i/\Delta T_i$ (mg °C^{-1})	W_i (%)	$\sum W_i$ (%)
F1	26.98	553.5		3.57	3.57
F2	52	583.7	23.33	3.91	7.48
F3	65	608.7	46.82	4.08	11.56
F4	75	670.9	67.01	4.49	16.05
F5	85	1296	129.6	8.68	24.73
F6	90	924.2	184.8	6.19	30.92
F7	95	1781.9	356.38	11.94	42.86
F8	100	3350.1	670	22.44	65.3
F9	102	569.4	284.7	3.81	69.11
F10	105	1506	502.1	10.09	79.2
F11	107	1227.1	613.55	8.22	87.42
F12	110	1780.5	593.5	11.93	99.35
F13	112	46.9	23.45	0.31	99.66
F14	115	8.8	2.67	0.06	99.72
F15	117	3.7	1.85	0.02	99.74
F16	120	3.8	1.27	0.03	99.79
F17	123	1.1	0.3	0.01	99.80
F18	140	10.7	1.53	0.07	99.87
F19	>140	20.6			

Weight of sample used: 14996.8 mg. Total recovery: 14898.9 mg (99.35%, ≦ 110°).

400 MHz FT NMR spectrometer operating at 100 MHz on polymer solutions (< 20 wt%) in *o*-dichlorobenzene at 110°C, the highest single peak of which is considered as the reference (132.9 ppm). A program with pulse angle of 90° is used, matching with 2 s acquisition time and 10 s relaxation delay, so as to attain conditions far from any saturation but close enough to the maximum signal-to-noise ratio. In order to eliminate the NOE, an inverse-gate decoupling pulse program is selected, and meanwhile proton broad-band decoupling is achieved with the walth 16 sequence. Due to the high resonance, 5000–15000 scans are collected with 64 k points/scan. The nomenclature and assignments of the different carbon atoms along the molecular chain adopted for the absorption bands in the NMR spectra are those of Carman & Wilkes, Randall and Cheng.[25–28]

FT-IR

FT-IR spectra are measured with a Nicolet Fourier transform infrared spectrophotometer (MAGNA-IR 760). The samples are first compression-molded into films in 10–100 μm thick. Then the absorption bands are observed and analyzed.

GPC

A gel-permeation chromatography (GPC, waters, Alliance GPCV 2000), equipped with a polystyrene column in the GPC-viscometer module, is used for the characterization of the molecular weight and molecular weight distribution of the fraction polymers at 140°C.

The molecular weight obtained is calculated by a standard procedure based on the universal calibration curve of polystyrene.

DSC

DSC measurement is carried out on a DSC-7 from Perkin–Elmer. In order to ensure an identical thermal history, the sample is heated from 0°C to 190°C at a rate of 10°C min^{-1} and subsequently cooled down from 190°C to 0°C at same rate. The maximum of the exotherm in the cooling cycle is utilized to determine the crystallization temperature, T_c. The melting endothermic changes are recorded while heating the sample from 0°C to 190°C at a heating rate of 10°C min^{-1}, and the peak maximum of the second heating cycle is used to determine the melting temperature, T_m.

RESULT AND DISCUSSION

Fractionation and Characterization

TREF.   A copolymer of propylene with a small amount of ethylene comonomer is fractionated by using a preparative TREF as described above, and 18 fraction polymers are collected from room temperature (about 26°C) to 140°C. Important data of the fractionation experiment are summarized in Table II, including elution temperature (T_e, °C), the weight of fraction polymers (W_i for the ith fraction), the differential weight to temperature ($W_i/\Delta T_i$), the accumulative weight (ΣW_i) and so on. Figure 1 shows the curves of the accu-

Table III. Characteristics of Fraction Polymers

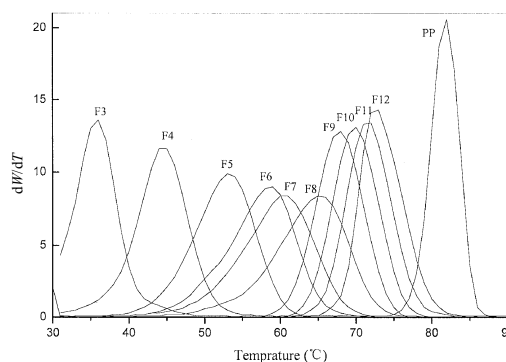| Fraction No.	T_m °C	T_c °C	M_n g mol^{-1}	M_w/M_n	T_w °C	T_n °C	R	σ
F2	97.9	58.3	20989	3.5				
F3	114.0	75.6	30566	3.295	35.9	35.6	0.7	3.0
F4	123.4	84.6	44642	3.529	44.1	43.8	0.7	3.2
F5	132.2	92.6	52243	3.705	52.1	51.7	0.8	4.4
F6	136.9	95.5	60542	3.273	56.8	56.3	0.9	5.1
F7	141.9	100.0	87164	2.850	59.1	58.4	1.1	6.0
F8	146.2	102.5	105040	2.795	63.2	62.5	1.0	5.8
F9	147.7	105.6	101123	2.928	67.6	67.4	0.4	3.5
F10	150.5	105.5	126632	2.705	69.6	69.1	0.7	4.4
F11	150.5	107.1	151702	2.643	71.8	71.7	0.1	2.8
F12	152.7	107.3	169953	2.645	73.8	74.1	−0.4	2.0
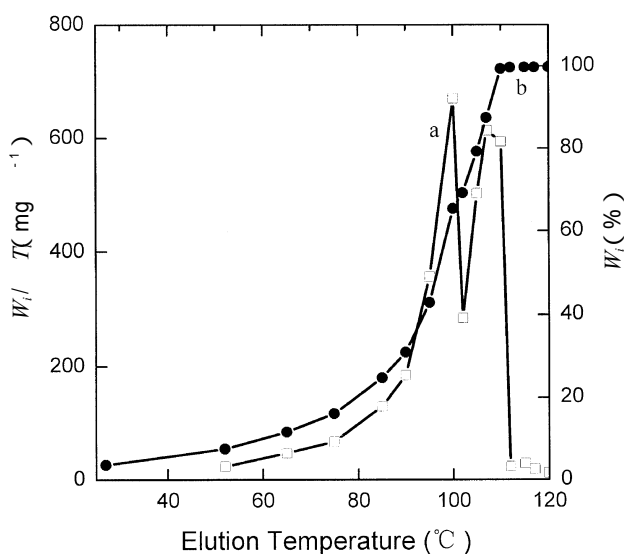
Figure 1. The curves of temperature rising elution fractionation for the propylene–ethylene random copolymer. The weight of the fraction polymers as a function of the elution temperature (°C) (a) the differential weight to temperature, $W_i/\Delta T_i$ (mg °C^{-1}), (b) accumulative weight, $\sum W_i$ (%).

Figure 2. The concentration in solution determined by Crystaf of the fraction polymers as a function of the temperature.

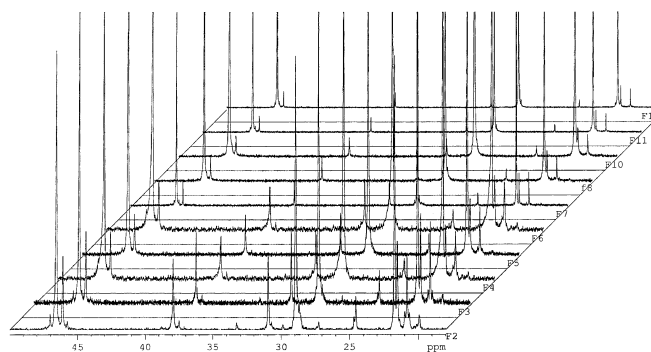**Figure 3.** ^{13}C NMR spectra of fraction polymers.

mulative weight and the differential weight to temperature against elution temperature. From the curve of the differential weight to temperature, $W_i/\Delta T_i$, against temperature, we can observe two peaks at 95–100°C and 105–107°C, respectively, implying the fractionation process is complicated. The curve of accumulative weight indicates that at elution temperatures below 85°C or above 110°C, the weight of each fraction polymer is low, though most fractions occur over a narrow temperature region, 85–110°C, suggesting that macromolecular chain structure of the copolymer is uniform. The curves of accumulative weight appears nearly a straight line in a range from 85°C to 110°C.

Crystaf

Through Crystaf experiment, the effect of fractionation by TREF can be checked up. Table III summarizes the characteristics of the fraction polymers. Figure 2

shows the curves of the crystallization temperature distribution from the Crystaf experiment. In the experiment, the concentration of the corresponding fraction polymers in solution is determined as a function of temperature. By analyzing such parameters put forward by B. Monrabal as T_w, T_n, R, and σ,[16] the uniform of crystallization temperature distribution of the fraction polymers can be characterized. The results indicate that the broadness of the crystallization temperature distribution of the fraction polymers becomes narrower than that of rude samples, and the fraction polymers at low or high elution temperature have narrower distribution than at middle area of elution temperature, showing that the effect of fractionation is good.

Table IV. Chemical shifts and intensities for the carbon atom in propylene–ethylene copolymer in ^{13}C NMR

Chemical shift		Peak intensity(%)									
	ppm	F2	F3	F4	F5	F6	F7	F8	F10	F11	F12
$S_{\alpha\alpha}$	46.5	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
$S_{\alpha\gamma}$	37.9	207.3	148.8	123.8	97.3	85	68.4	59.5	44.2	42.2	35.7
$S_{\alpha\delta}$	37.5	23.5	12.0	5.9	3.4	1.1					
$S_{\beta\delta}$	27.2	23.5	12.0	5.9	3.4	1.1					
$S_{\gamma\delta}$	30.4	2.4	0.9								
$S_{\delta\delta}$	30.0	0.4									
$T_{\beta\beta}$	28.98	918.7	931.8	958.3	957.7	978.7	988.2	988.1	992.6	995.5	1010.6
$T_{\beta\delta}$	30.99	217.8	164.2	136.4	102.1	90.6	72.3	61.1	45.3	44.0	37.2
$T_{\delta\delta}$	33.27	11.4	4.5								

Table V. Sequence distributions of the fraction polymers

	F2	F3	F4	F5	F6	F7	F8	F10	F11	F12
PPP	71.91	78.49	82.43	86.14	88.03	90.27	91.58	93.64	93.86	94.83
PPE	17.05	13.83	11.73	9.18	8.15	6.60	5.66	4.27	4.15	3.49
EPE	0.89	0.38	0	0	0	0	0	0	0	0
PEP	8.11	6.27	5.32	4.38	3.82	3.12	2.76	2.08	1.99	1.68
EEP	1.84	1.03	0.51	0.31	0	0	0	0	0	0
EEE	0.19	0	0	0	0	0	0	0	0	0
PP	80.48	85.70	88.29	90.71	92.17	93.60	94.35	95.77	95.95	96.55
PE	18.57	13.78	11.45	9.14	7.83	6.40	5.65	4.23	4.05	3.45
EE	0.95	0.51	0.26	0.15	0	0	0	0	0	0
P	89.76	92.59	94.01	95.28	96.08	96.80	97.17	97.88	97.98	98.28
E	10.23	7.41	5.99	4.72	3.92	3.20	2.83	2.12	2.02	1.72

^{13}C NMR

Figure 3 is the ^{13}C NMR spectra of fraction polymers. Here each spectrum relates to the fraction polymer with certain ethylene content, and they are positioned from F2–F12 according to ethylene content. The peaks of ^{13}C NMR spectra are assigned according to the methods of Carman & Wilkes,[25] Randall[26, 27] and Cheng,[28] and Table IV lists the assignment of the important peaks, chemical shifts and intensity of each carbon atom in the ^{13}C NMR spectra of the fraction polymers. In ^{13}C NMR spectrum, $S_{\alpha\gamma}$ (37.9 ppm), $S_{\alpha\delta}$ (37.5 ppm), and $S_{\gamma\delta}$ (30.4 ppm) are thought to relate to the following sequence structure, (1) only an ethylene monomer, PEP; (2) more than two-linked ethylene monomers, P(E)nP, $n \geqq 2$; (3) more than three ethylene monomers, P(E)mP, $m \geqq 3$, respectively. The results show that with elution temperature increasing, peaks of $S_{\alpha\gamma}$, $S_{\alpha\delta}$ and $S_{\gamma\delta}$ decreases, implying the ethylene content decreases. As elution temperature increases beyond 75°C and 90°C, the $S_{\gamma\delta}$ and $S_{\alpha\delta}$ peak vanish one by one, suggesting that the sequence structure of P(E)nP, $n \geqq 2$ begin not to exist in the macromolecular chains at higher elution temperature. In addition, as seen from the experiment, $S_{\alpha\delta}$ is much more than and $S_{\gamma\delta}$, suggesting PEEP is majority in P(E)nP. The dyad sequence distribution of the copolymers is determined from the methylene peaks by using the following relationships:[26, 27]

$$PP = S_{\alpha\alpha} \qquad (1)$$
$$EP = S_{\alpha\gamma} + S_{\alpha\delta} \qquad (2)$$
$$EE = (S_{\alpha\delta} + S_{\delta\delta})/2 + S_{\gamma\delta}/4 \qquad (3)$$

The triad sequence distribution will be analyzed from both methine and methylene absorptions peaks, using:

$$PPP = T_{\beta\beta} \qquad (4)$$
$$PPE = T_{\beta\delta} \qquad (5)$$
$$EPE = T_{\delta\delta} \qquad (6)$$
$$PEP = S_{\beta\beta} = S_{\alpha\gamma}/2 \qquad (7)$$
$$EEP = S_{\alpha\delta} = S_{\beta\delta} \qquad (8)$$
$$EEE = S_{\delta\delta}/2 + S_{\gamma\delta}/4 \qquad (9)$$

From the dyad sequence distributions, the ethylene content can be calculated as follows:

$$P = PP + PE/2 \qquad (10)$$
$$E = EE + PE/2 \qquad (11)$$

Table V summarizes sequence distribution of the fraction polymers. As can be seen from Table V, in macromolecular chains, PPP holds the majority of the sequence units, varying from 71.9 to 94.8 mol%. The number average sequence length of the fraction polymers is derived from the following relationship:[26, 27]

**Table VI.** Number average sequence length of the fraction polymers

	F2	F3	F4	F5	F6	F7	F8	F10	F11	F12
$\bar{n}_P$	9.7	13.4	16.4	20.8	24.6	30.3	34.7	46.3	48.4	57.0
$\bar{n}_E$	1.10	1.07	1.04	1.03	1	1	1	1	1	1

$$\bar{n}_P = \frac{[PP] + \frac{1}{2}[PE]}{\frac{1}{2}[PE]} \qquad (12)$$

$$\bar{n}_E = \frac{[EE] + \frac{1}{2}[PE]}{\frac{1}{2}[PE]} \qquad (13)$$

where $\bar{n}_P$ and $\bar{n}_E$ are the number average sequence lengths of monomer P and E, respectively. The number average sequences length, $\bar{n}_P$ and $\bar{n}_E$, are tabulated in Table VI. As shown in Figure 3, Table V, and Table VI, during TREF process, with elution temperature increasing from 52°C to 110°C, ethylene content in fraction polymers is gradually reduced, and number average sequence length of propylene, $\bar{n}_P$, becomes longer and longer, however that of ethylene, $\bar{n}_E$, decreases. When elution temperature in the range from 52°C to 85°C, the ethylene content are more than 4.72 mol%, the n_E is more than 1 and the small peak of $S_{\alpha\delta}$ can appear at 37.5 ppm, implying that a very small amount of more than one ethylene units, like EE, exist in macromolecular chains (F2, F3, F4, and F5). For example, when elution temperature is as low as 52°C, i.e., ethylene content (F2) in about 10.23 mol%, number average sequence length of propylene polymer, $\bar{n}_P$, is only 9.7, however that of ethylene, $\bar{n}_E$, is 1.1, in addition, the intensity of the $S_{\delta\delta}$ peak at 30.0 ppm is 0.4, implying that in F2 fraction polymers there exists a very small amount of three or more ethylene monomerslinked units, like short block ethylene units EEE. The weight of the partial fractions from F2 to F5 is as low as less than 25 wt%. As elution temperature increases from 90°C to 110°C, i.e., ethylene content decreases from 3.92 to 1.72 mol%, $\bar{n}_P$ becomes longer and longer, but $\bar{n}_E$ is close to 1, suggesting that it becomes almost improbable that two ethylene comonomers are successively inserted into a macromolecular chain simultaneously, namely, there is only single E in a macromolecular chain, not EE and EEE sequence. For example, $\bar{n}_P$ and $\bar{n}_E$ of F12 are 57 and 1, respectively, and the peak of $S_{\alpha\delta}$ at 37.5 ppm no longer appears. At elution temperature above 110°C, the weight of fraction polymers with ethylene content as low as less than 1.72 mol% is less than 1 wt%. From above-mentioned analysis, a conclusion can be drawn that most (more than 75 wt%) of the random copolymer can been fractionated in a range of ethylene content from 1.72 to 3.92 mol%; and the triad of PPP, PPE, and PEP are predominately preserved.

Since propylene tacticity complicates the molecular microstructure, it is necessary to assign and scrutinize
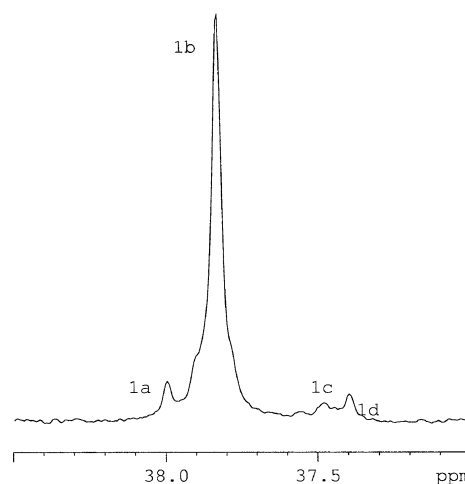
Figure 4. Expanded plots of the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region.

some peaks that can reflect information on tacticity of propylene segment. Figure 4 indicates fine assignment of some peaks of the fraction polymers, including $S_{\alpha\gamma}$, $S_{\alpha\delta}$. According to Randall and Cheng,[26–28] the $S_{\alpha\gamma}$ reflects sequence structure of the PEP, namely, only an ethylene monomer between two propylene monomers, and the experiment suggests that this kind of sequence structure occupies the majority of the macromolecular chains; $S_{\alpha\delta}$ reflects sequence structure of the P(E)nP, $n \geqq 2$, namely, more than two-linked ethylene monomers between two propylene monomers. Figure 4 shows $S_{\alpha\gamma}$ consists of two main peaks: 1a and 1b, which can be assigned to molecular sequence structure of the PPPEP(m_1r_2) and PPPEP (m_1m_2), respectively. The spectrum reveals that the PPPEP (m_1m_2) occupies most part of the PEP, more than 90 wt%, implying that isotacticity sequence of propylene segment is very high, and the distribution of ethylene comonomer in macromolecular chains is almost uniform too. The 1c and 1d included in $S_{\alpha\delta}$ can be assigned to EPEEP and PPEEP, respectively. The results indicate that PPEEP (m) is most sequence unit. From Figures 3 and 4, we can find that with elution temperature increasing, isotacticity of propylene segment becomes higher and higher, and the distribution of ethylene comonomer in macromolecular chains becomes more and more uniform.

If the ethylene comonomer and racemic structure of propylene sequence are thought to be the attribution to the destruction of tacticity of propylene polymer, the peaks of methyl from 18 to 23 ppm in Figure 5 must be considered. According to Randall and Cheng,[26–28] the peaks of 2a, 2b, 2c, and 2d are assigned
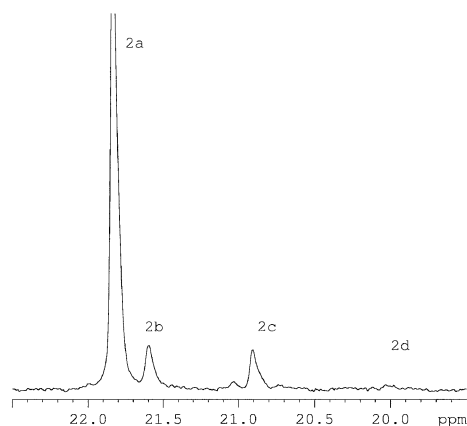
**Figure 5.** Expanded plots of the methyl region.

to PPPPP (mmmm), PPPPE (mmm) + PPPPP (mmmr), PPE (m) + PPP(mr), EPE + PPP(rr), respectively. As seen from Figures 3 and 5, the PPPPP (mmmm) is the most probable sequence unit of fraction polymers, suggesting that the fraction polymer is a copolymer with high isotactic propylene sequence plus a small amount of ethylene comonomer. So we can conclude that with elution temperature increasing, the tacticity of propylene sequence becomes higher and higher.

FT-IR

The above-mentioned conclusion is also supported by FT-IR experiments. According to Rudin and Bucci,[29–31] the absorption peak at $733\,\mathrm{cm}^{-1}$ in Figure 6 can be assigned to the $-(CH_2)_n-$, $n = 3$, but the absorption peak at $722\,\mathrm{cm}^{-1}$, which can reflect the structure of $-(CH_2)_n-$, $n > 3$, do not appear, implying that the amount of the long chain ethylene is too small to be detected distinctly. In other words, the ethylene comonomer incorporated in macromolecular chains is mainly isolated, and there is hardly a group of two or more ethylene monomers in the propylene macromolecular chains. The conclusion from FT-IR is identical to that by NMR. In addition, the experiment also reveals that with eluting temperature increasing from environment temperature to 110°C, the intensity of absorption peak at $733\,\mathrm{cm}^{-1}$ of IR spectra of fraction polymers becomes smaller and narrower, showing that the ethylene content in fraction polymers gradually decreases.

Melting and Crystallization Behavior

For copolymers of propylene with a small amount of ethylene comonomer, the macromolecular chain length and the ethylene content are considered to be the important factors to affect the melting and crystallization behavior of copolymers. The melting temperature of the fraction polymers from solution can be obtained from TREF, $T_{m\,(sol)}$, and the melting temperature of fraction
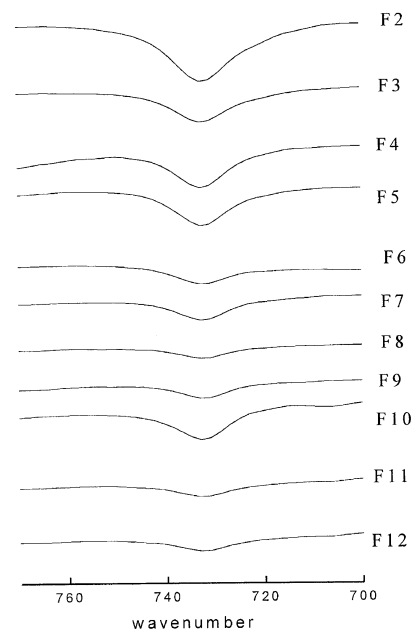

Figure 6. FT-IR spectra of the fraction polymers of the Propylene–ethylene random copolymers.
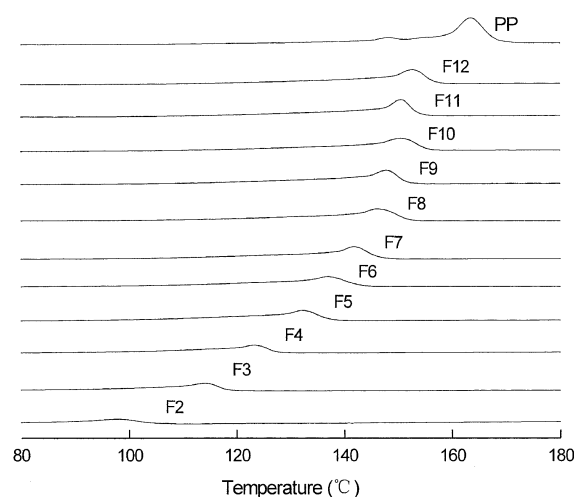
Figure 7. DSC endothermal curves (2nd heating cycle) of the fraction polymers of the propylene–ethylene random copolymer. Heating rate at 10°C min^{-1}.

polymers & the propylene homopolymer from bulk will be recorded from DSC experiments. All DSC endothermic curves are put in Figure 7. Here DSC curves are positioned according to ethylene content. The maximum of the endothermic peak is recorded as the melting temperature, T_m. In order to ensure an identical thermal history of the investigated fraction polymers, only the melting temperatures obtained during a second heating cycle are considered.

On the basis of Flory's theory, in the propylene–ethylene random copolymer, propylene chains is considered as a long crystallizable chain, however ethylene as no crystallizable comonomer, *i.e.*, they will be excluded from the polypropylene crystal lattice as de-
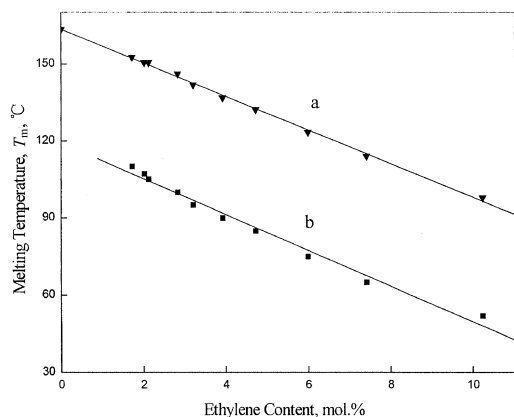
Figure 8. Melting temperature of the propylene–ethylene random copolymer, as a functon of ethylene content (mol%). a: Melting Temperature in bulk (T_m, °C) determined by DSC. b: Melting Temperature in solution ($T_{m\,(sol)}$, °C) determined by TREF.
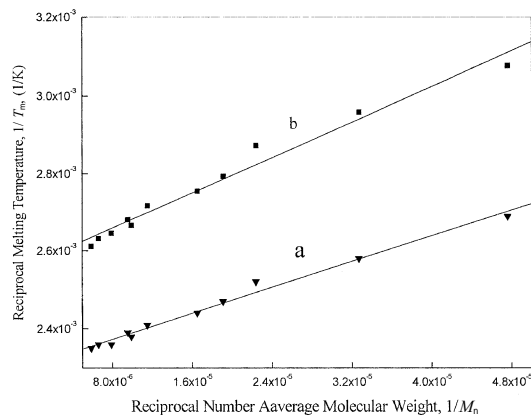

Figure 9. Reciprocal melting temperature, $1/T_m$, (1/K) *vs.* reciprocal number average molecular weight of the fraction polymers ($1/M_n$). a: Melting Temperature in bulk (T_m, K) determined by DSC. b: Melting Temperature in solution ($T_{m\,(sol)}$, K) determined by TREF.

fects.[23] According to Benjamin Monrabal[16] and Robert Brull,[23] the Flory eq 14[32] can be simplified to eq 15, which reveals a relationship between melting temperature and content of comonomer, by assuming that the melting temperature of the copolymer, T_m, is close to that of the propylene homopolymer, T_m^0, hence, $T_m \times T_m^0 \approx (T_m^0)^2$, and also that ΔH_u is constant in the considered crystallization temperature range. A straight-line relationship between T_m and comonomer content is obtained, which is good fit in a range of content of comonomer less than 3.5 mol%.[23] Figure 8 shows the curves of the melting temperature of copolymer as a function of ethylene content according to eq 15. In Figure 5, line a is for the melting temperature from bulk by DSC, and line b is for melting temperature from solution by TREF.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{-R}{\Delta H_u} Lnp \qquad (14)$$

$$T_m \cong T_m^0 - \frac{R(T_m^0)^2}{\Delta H_u} X_E \qquad (15)$$

On the other hand, macromolecular chain length is also an important factor to affect the melting and crystallization behavior of polymer. For copolymer of propylene plus a small amount of ethylene comonomer, when ethylene content is less than 10.23 mol%, the macromolecular chain of the copolymer is considered identical to that of propylene homopolymer. Therefore, another application of Flory's theory is shown as eq 16,[33] which relates to melting temperature, T_m, with number average molecular weight. In eq 16, i is the number average degree of polymerization. When number average degree of polymerization, i, is transformed to number average molecular weight, M_n, the eq 16 will be replaced by eq 17.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{2R}{\Delta H_u} \times \frac{1}{i} \qquad (16)$$

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{2R_m}{\Delta H_u} \times \frac{1}{M_n} \qquad (17)$$

Figure 9 indicates the effect of number average molecular weight on melting temperature. A linear relationship exists between the reciprocal melting temperature ($1000/T$, K^{-1}) and reciprocal number average molecular weight (M_n^{-1}) in a range of number average molecular weight of less than 1.7×10^5, which is in good agreement with the Flory's theory.[33] According to the experiment, with the number average molecular weight (M_n) increasing, the melting temperatures, from both solution, $T_{m\,(sol)}$ and from bulk, T_m, decreases. Within the range of ethylene content less than 10.23 mol%, the melting temperature, T_m, is dependant on the molecular chain length, even though the number average molecular weight is very large nearly to 1.7×10^5. In Figure 9, the line a and line b have same meaning to that in Figure 8.

As seen from Tables III, Figures 8 and 9, when number average molecular weight of the polymers increases, but the ethylene content and the poly-dispersity (M_w/M_n) of molecular weight decreases, the melting temperature increases. In other words, the larger the number average molecular weight, the smaller the ethylene content, and the narrower the poly-dispersity, the higher the melting temperature of polymer is. When polymer has higher ethylene content, the regularization of macromolecular chains is poor, so it is easy to melt at lower temperature (F2, F3, F4, and F5), even though those polymers with higher molecular weight. Therefore, at least two kinds of macromolecular chains have lower melting temperature, that is, the macromolecular chains with low molecular weight and those with high ethylene content. As number average molecular weight of the polymers becomes larger, and ethylene content and poly-dispersity (M_w/M_n) of fraction poly-

mers decreases, regularization of the macromolecular chains becomes higher, so the melting temperature of polymer is higher. Therefore we may conclude that only the macromolecular chains with both high molecular weight and low ethylene content have high melting temperature, that is, the better the regulation of macromolecule, the higher the melting temperature. For example, ethylene content and M_w/M_n of F11 with high melting temperature are only 2 mol% and 2.6, respectively, and its number average molecular weight is also beyond 1.5×10^5. The broadness of crystalline temperature distribution of fraction polymers is also important parameter charactering for crystalline polymers. As shown in Table III, in the range from 85 to 100°C, the fraction polymers has large σ, this is because the crystalline mechanism and morphologies are complicated enough to widen the distribution of crystalline temperature of fraction polymers. With regularization of the macromolecular chain increasing, σ of the fraction polymers decreases, for example, that of F12 is even unexpectedly negative, suggesting that the fraction polymer is uniform very much.

CONCLUSIONS

A set of fraction polymers with uniform molecular weight and ethylene content can be obtained by using a preparative TREF. Each fraction polymer is composed of mainly isotactic propylene sequence plus a small amount of ethylene comonomer. Macromolecular chains with high ethylene content or that of low molecular weight have low melting temperature, however the macromolecular chains with both high molecular weight and low ethylene content have high melting temperature. Distribution of ethylene monomers in a macromolecular chain is uniform, and the propylene sequence had high tacticity. Ethylene content affects linearly the melting temperature in a range of ethylene content as low as less than 10.23 mol%; and there is a linear relationship between the reciprocal melting temperature ($1000/T_m$, K^{-1}) and reciprocal number average molecular weight in a range of number average molecular weight (M_n^{-1}) less than 1.7×10^5.

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