

Carbon-13 NMR, GPC, and DSC Study on a Propylene-1-Butene Copolymer Fractionated by Temperature Rising Elution Fractionation

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ABSTRACT: A random copolymer of propylene with small amounts of 1-butene comonomer, synthesized with a Ziegler–Natta catalyst, was fractionated by temperature rising elution fractionation (TREF) to systematically investigate the fraction samples' molecular microstructure, as well as their relationship to the melting and crystallization behavior. First, TREF was employed to fractionate the sample, and then crystallization analysis fractionation (Crystaf) was used to check the effect of the TREF experiment. In the characterization of the molecular microstructure, carbon-13 NMR spectroscopy (^{13}C NMR) and gel permeation chromatography (GPC) experiments gave the following results: the fraction samples have relatively uniform molecular microstructure; with an increase in elution temperature, the 1-butene

content in the fraction samples decreases, but the molecular weight (M_n) and number average sequence length of propylene (\bar{n}_p) increase. In the study on melting and crystallization behavior, differential scanning calorimetry (DSC) experimental results show that the melting temperature increasingly decreases with an increase in 1-butene content; however, dependence of the melting temperature on molecular weight becomes weaker and weaker with an increase in the number average molecular weight in the range of number average molecular weight below 1.82×10^5 g/mol. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 845–851, 2006

Key words: carbon-13 NMR; DSC; GPC; propylene-1-butene copolymer; temperature rising elution fractionation

INTRODUCTION

A random copolymer of propylene with a small amount of 1-butene is a kind of material used in the packaging markets due to its advantages, such as lower process and sealing initiation temperatures, good clarity, and fewer tendencies to crosslink during the process of surface treatment.^{1–3} Undoubtedly, these merits must have an intrinsic relationship to its molecular microstructure and morphological structure. However, to date, study on this kind of copolymer has received much less attention than other propylene copolymers; thus, our knowledge is limited in the field. Abiru et al.⁴ investigated the relationship between molecular microstructure of propylene-1-butene copolymers and their melting and crystallization behavior by the use of some techniques, including TREF, NMR, GPC, and DSC. However, the samples in that report are a set of polymer elastomers with very large amounts of 1-butene. Normally, the propylene-1-butene copolymer available in plastic film has a relatively lower content of 1-butene, so in the present study we are more interested in propylene copolymers with relatively lower 1-butene content. To study thoroughly the relationship

between the melting temperature and the molecular microstructure of propylene-1-butene copolymers with small amounts of 1-butene, a copolymer sample was first synthesized with a Ziegler–Natta catalyst, and then was fractionated by the TREF technique^{5–7} to obtain a set of fraction samples with relatively uniform molecular microstructure, such as molecular weight and 1-butene concentration. In the characterization of the molecular microstructure, the new method recently proposed by Zhang⁸ will be employed to determine the monomer sequence distributions of the set of samples. At the same time, GPC was used to characterize the samples' macromolecular size.

Central to this study is to give a systemic investigation of a sample of a propylene-1-butene copolymer, and to determine some relationships between melting temperature and 1-butene content, as well as number average molecular weight. Therefore, by the use of DSC, the melting and crystallization behavior of some samples will be studied to match the molecular microstructure of the relative samples.

EXPERIMENTAL

Materials

The sample used in the present study was synthesized through a gas-phase polymerization process with an

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isospecific Ziegler–Natta catalyst. The propylene sequences of the copolymer obtained are confirmed by ^{13}C NMR to be essentially high isotactic without head-to-head or tail-to-tail monomeric units. To obtain a set of copolymer samples with relatively uniform molecular microstructure, like molecular weight, and 1-butene content, the TREF technique was used to fractionate the propylene-1-butene copolymer.

Preparative TREF

About 15g sample, stabilized with antioxidant 2,6-ditertbutylpresol, was used in the fractionation experiment. To make macromolecular chains deposit around glass beads in layers step by step in accordance to their crystallizability, it took at least 80 h to cool the column for fractionation from 140 to 25°C. The macromolecular chains with higher crystallizability prefer to precipitate around the glass beads in the innermost layers, whereas those with lower crystallizability always precipitate around the outermost layer. As the column was again heated gradually from 25 to 140°C, polymer fractions with various crystallizability were eluted continuously from the outermost layer to the innermost layer by use of the solvent, 1,2,4-trimethylbenzene, and collected in batches. Finally, the fraction samples obtained were precipitated into excess acetone at room temperature, filtered, and dried in vacuum to constant weight.

Crystaf

A commercial Crystaf Apparatus, Model 200, manufactured by Polymer Char S.A., was used for crystal fractionation to obtain such parameters as σ (variance), R ($T_w / T_n - 1$), T_w , and T_m , which can define the crystallization temperature distribution of polymers, so as to check the effect of the TREF experiment.^{9,10} In this experiment, a sample solution with concentration of 0.1% (w/v) was first prepared (30 mg samples in 30 mL 1,2,4-trichlorobenzene), and then an infrared detector with fixed wavelength of 3.5 μm was used to check *in situ* the change in concentrations of the samples by monitoring the intensity of C-H stretching frequencies of methylene and the methyl group in the macromolecular chain of the propylene-1-butene copolymer.

Carbon-13 NMR

The composition of some fraction samples was determined by analysis of ^{13}C NMR spectra, which were measured on a BRUKER 400 MHz NMR spectrometer operating at 100 MHz in polymer solutions (approximately 10 wt %) with *o*-dichlorobenzene- d_4 as solvent at 125°C, with its highest single peak at 132.99ppm as the standard reference, according to a polyethylene

sample (30.00 ppm). Considering that spin-lattice delay time, T_1 , of methylene carbons and methine carbons in each location was shorter than 2s,¹¹ a pulse program with flip angle of 90° was used, matching with 2s acquisition time and 12s relaxation delay in the sweep width. To eliminate NOE, an inverse-gate decoupling pulse program was selected, and meanwhile, in measurements of the carbon-13 NMR spectrum, proton broad-band noise decoupling was achieved to remove ^{13}C - ^1H coupling. Nomenclature and assignments of various carbon atoms along the molecular chain for absorption bands in the NMR spectra were determined on the basis of previous studies.^{8,12–14}

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.

DSC

Calorimetric measurements were performed in a differential scanning calorimeter (Perkin–Elmer DSC-7) under nitrogen flow. Temperature calibration was carried out with indium as a standard. To ensure identical thermal history, the samples were first heated from room temperature to 200°C at a rate of 10°C/min, held 10 min at the temperature, and subsequently cooled from 200°C to room temperature at a rate of 10°C/min. Then they were once again heated to 200°C at the same heating rate of 10°C/min. In the nonisothermal crystallization process, the maximum point of the exothermic curves was defined as crystallization temperature, T_c ; however, only the main endothermic peak of the second heating cycle was taken as the melting temperature, T_m .

RESULTS AND DISCUSSION

Fractionation and molecular microstructural characterization

By the above-mentioned method, a random copolymer of propylene with a low amount of 1-butene was fractionated by preparative TREF. At least 7 fraction samples were collected from 90 to 140°C. The step-size between two consecutive elution temperatures was kept at 5°C. Figure 1 gives the TREF experimental result: at least 80 wt % of the sample was eluted at 115°C; and at temperatures lower than 95°C or higher than 120°C, only residual elastic polymers with lower

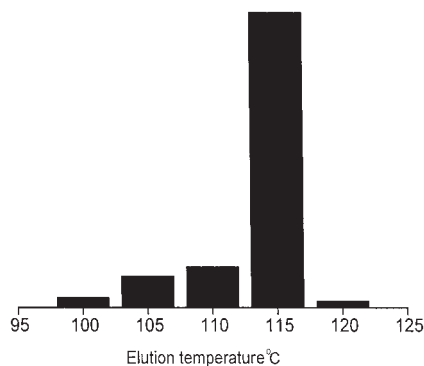


Figure 1 Relative weight distribution of some fraction samples of a propylene-1-butene copolymer by TREF (temperature rising elution fractionation) at various elution temperatures.

melting temperatures, or small amounts of polymers with high melting temperatures, were fractionated, respectively, suggesting that the virgin copolymer sample has comparably uniform molecular microstructure, with a melting range of approximately 25°C in the solvent of 1,2,4-trimethylbenzene.

Figure 2 shows the results of the Crystaf experiments. In the set of crystallization experiments, each curve spreads in a temperature range of about 20°C, suggesting that the TREF is an effective technique to make samples uniform. As for the fraction samples collected at 100°C, 105°C, 110°C, and 115°C, respectively, their crystallization curves regularly move from left to right with an increase in elution temperature. In other words, fraction samples obtained at higher elution temperatures match higher crystallization temperatures, indicating that the crystallization process of samples in the Crystaf experiment is very consistent with that of the TREF experiment.

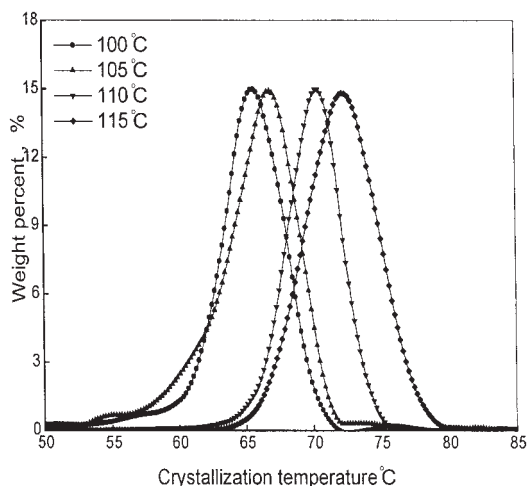


Figure 2 CRYSTAF curves of some fraction samples by TREF eluted at various temperatures (fraction samples from left to right: 100°C, 105°C, 110°C, and 115°C).

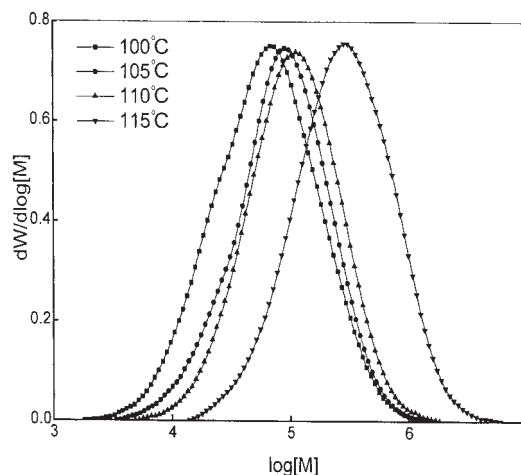


Figure 3 GPC curves of some fraction samples by TREF eluted at various temperatures (fraction samples from left to right: 100°C, 105°C, 110°C, and 115°C).

Figure 3 indicates the GPC experimental results of those fraction samples eluted at 100°C, 105°C, 110°C, and 115°C, respectively. As seen in Figure 3 and Table I, a strange phenomenon, dissimilar to the previous study,^{4,15,16} can be found: Dependence of molecular weight on elution temperature is very strong, that is, the molecular weight of these fraction samples soars, even doubles, with an increase in elution temperature. For example, number average molecular weight of the fraction sample eluted at 115°C is as many as twice that of the fraction sample eluted at 110°C, even though the increase in elution temperature is only 5°C. In other words, significant changes in molecular weight only result in a little increase in melting temperature, that is, the effect of molecular weight on the melting temperature of the sample in solution is very weak. Undoubtedly, the trend of change of molecular weight with elution temperature shows that its melting and crystallization behavior is very different from that of the previous samples,^{4,15,16} and, at the same time, suggests that in this fractionation experiment, the main factor governing the fractionation process is the macromolecular chain structure, not its molecular weight. Furthermore, the molecular weight distribution tends to become narrow with an increase in elution temperature, indicating that molecular weight distribution also has something in common with the elution temperature. Key data of these fraction samples are summarized in Table I, including: elution temperature (T_e); melting temperature (T_m); crystallization temperature (T_c); number average molecular weight (M_n); molecular weight distribution (M_w/M_n); weight average crystallization temperature (T_w); and number average crystallization temperature (T_n); as well as parameters σ (variance) and R ($T_w / T_n - 1$), which can define the crystallization temperature distribution in solution.^{9,10}

TABLE I
Characteristics of Some Fraction Polymer

Frac No. (T_g , °C)	T_m °C	T_c °C	M_n g/mol	M_w g/mol	M_w/M_n	T_w °C	T_n °C	σ	R
F(100)	144.5	103.1	36,872	101,857	2.76	66.2	67.3	4.2	-1.6
F(105)	147.2	104.0	54,151	126,219	2.33	65.1	65.1	0.9	-0.0
F(110)	151.3	105.3	71,720	156,182	2.18	70.3	70.5	1.7	-0.3
F(115)	155.8	106.0	181,812	427,434	2.35	72.0	71.9	2.0	0.2

Evidently, it would have been crucial to characterize the molecular microstructure of the propylene-1-butene copolymer by use of ^{13}C NMR spectrometry in this study. Figure 4 gives the ^{13}C NMR spectrum of a selected fraction sample, and chemical shift assignments of the only peaks related to monomer sequence distribution determination and some relatively important peaks are summarized in Table II. Based on the spectrum, it can directly be inferred that the macromolecular chain of the sample is composed mainly of PP and PB dyads sequence, in the absence of the BB dyad sequence because of the disappearance of its characteristic peak in the neighborhood of chemical shift 40 ppm. With respect to triad sequences, considering some important characteristic peaks, for example, the peak at chemical shifts of 35.40 ppm for B-CH and the peak at 28.35 ppm for B-Branch- CH_2 , it can be concluded that only a few, in total six, triad sequences

appear in the samples. Therefore, macromolecular chains structure of the copolymer sample can be ascertained as connections of different propylene sequences with isolated 1-butene comonomers.

In the analysis of the quantitative determination of the monomer sequence distribution, to minimize the error, in principle, we prefer using those isolated peaks of methine or methylene in the main chain or the branch, without considering the methyl peaks. Moreover, we do our best to immediately obtain the content of the monomer sequences according to the pattern of the carbon-13 NMR; otherwise, if necessary, we revert to use of some sequence relationship equations. A set of formulae to calculate the triad sequences, dyad sequences, and monomer content (monad sequences), as well as number average sequence length, are summarized in Table III. In addition, the sample used in this study was synthesized in

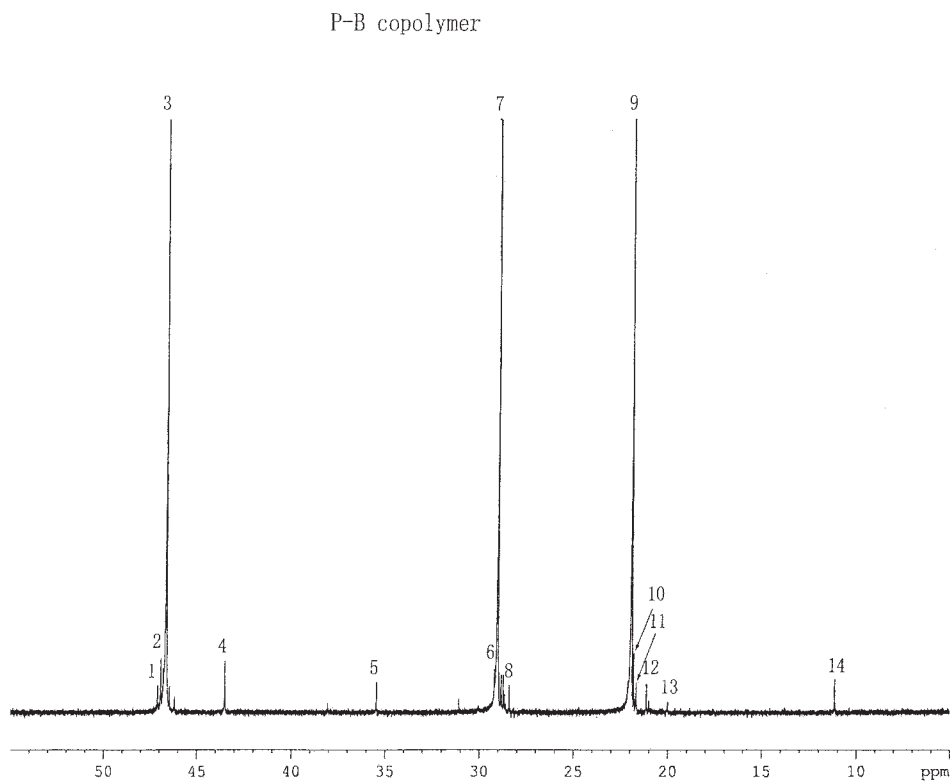


Figure 4 Carbon-13 NMR spectrum of a selected fraction sample eluted at 115°C of propylene-1-butene copolymer.

TABLE II
Chemical Shifts and Sequence Assignments of a Propylene-1-Butene Copolymer Sample (F(115))

Peaks No.	Chem. shift, ppm	Sequences	Carbon
1	47.04	BPPB	—CH ₂
2	46.87	PPPB	—CH ₂
3	46.58	PPPP	—CH ₂
4	43.46	PPBP	—CH ₂
5	35.40	B	B-CH
6	29.14	BPP	P-CH
7	28.98	PPP (mm)	P-CH
	28.79	PPP (mr)	P-CH
	28.67	PPP (rr)	P-CH
8	28.35	PBP	Branch-CH ₂
9	21.88	PPP(mm)	P-CH ₃
10	21.76	PPB	P-CH ₃
11	21.63	BPB	P-CH ₃
12	21.10	PPP (mr)	P-CH ₃
13	20.40	PPP (rr)	P-CH ₃
14	11.00	B	B-CH ₃

similar process conditions to those samples in the reference 8, so we use the same homopolymer of propylene in the reference 8 as the standard sample to calibrate the content of the PP-centered tetrad monomer sequence distributions of the fraction samples, namely, PPPP, PPPB, and BPPB, so as to minimize the effect of configuration of propylene sequence on monomer sequence distributions.

Table IV gives the quantitative result of triad sequences, dyad sequences, and monomer content, as well as number average sequence lengths (\bar{n}_p) of the propylene of some fraction samples. As seen in Table IV, as elution temperature increases, content of propylene monomer, dyad sequence PP, even triad sequence PPP, as well as number average sequence length of propylene (\bar{n}_p), increase; however, content of the dyad sequence PB decreases. It is worth noting that number average sequence length (\bar{n}_B) of the

TABLE III
Formulae for Calculating Triad, Dyad, and Monomer Content, as well as Number Average Sequence Length

	Formula
PPP	PPPP + 1/2PPPB = Peak3 + 1/2Peak2
PPB	PPPB + 2BPPB = Peak2 + 2Peak1
BPB	P - PPP - PPB = Peak7 - 2Peak1 - 3/2Peak2 - Peak3
BBB	0
BBP	0
PBP	Peak8
PP	PPPP + PPPB + BPPB = Peak1 + Peak2 + Peak3
PB	Peak4
BB	0
P	Peak7
B	Peak8
\bar{n}_{rP}	2P/PB
\bar{n}_B	2B/PB

TABLE IV
Sequence Distributions, Monomer Content, and Number Average Sequence Length of Some Fraction Samples

	F(100)	F(105)	F(110)	F(115)
PPP, mol%	88.9	91.2	91.8	94.3
PPB, mol%	9.6	7.4	7.2	4.6
BPB, mol%	0.0	0.0	0.0	0.0
BBB, mol%	0.0	0.0	0.0	0.0
PBB, mol%	0.0	0.0	0.0	0.0
PBP, mol%	1.5	1.3	1.0	1.1
PP, mol%	97.0	97.1	97.4	97.9
PB, mol%	3.0	2.9	2.6	2.1
BB, mol%	0.0	0.0	0.0	0.0
P, mol%	98.5	98.6	98.7	99.0
B, mol%	1.5	1.4	1.3	1.0
\bar{n}_P	65.7	68.0	78.5	96.2
\bar{n}_B	1.0	1.0	1.0	1.0

1-butene unit of all these fraction samples characterized was always kept at a constant of 1, consistent with the above-mentioned presumption: 1-butene comonomer spreads in a form of isolate unit in propylene long chain of these fraction samples; dyad sequence BB, as well as corresponding triad sequences, BBB, PBB, even BPB, are absent in these fraction samples, suggesting that it is nearly impossible to link two 1-butene comonomers together in an active site during the reacting process. Additionally, the results also show that the difference in the 1-butene content of the four samples is very small, further testifying that in the TREF experiment, the dependence of melting and crystallization behavior of the propylene-1-butene copolymer on 1-butene comonomer content is significantly strong and sensitive. The possible reason is that the comonomer, 1-butene, has a more voluminous branch than that of propylene, difficult to insert into the crystal lattice of the propylene polymer, significantly affecting its crystal structure, as well as its melting and crystallization behavior.

Melting and crystallization behavior

It is also crucial to investigate the relationship between melting and crystallization behavior and molecular microstructure of propylene-1-butene copolymers. Similar to the previous studies,^{15,16} two important factors, namely, molecular weight and 1-butene comonomer content, were investigated in detail to understand how they would affect the melting temperature of a propylene random copolymer with small amounts of 1-butene. Figure 5 shows DSC endothermic curves of some fraction samples for nonisothermal crystallization arranged on the basis of their fractionation number, and the maximum peak of each endothermic curve is defined as the bulk melting temperature (T_m) of this fraction sample. To ensure an identical thermal

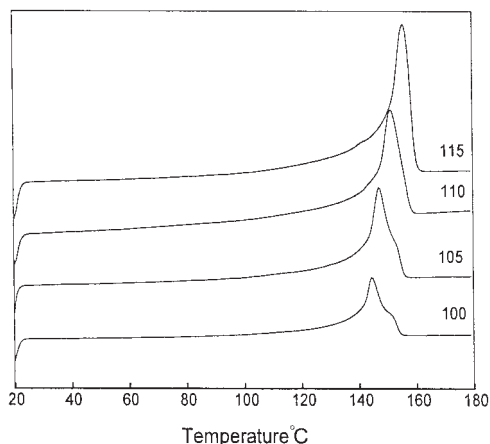


Figure 5 DSC endothermic curves of some fraction samples eluted at various temperatures by TREF (fraction samples from bottom to top: 100°C, 105°C, 110°C, and 115°C).

history, only the melting temperatures during second heating processing were considered. Moreover, as shown in Figure 5, the DSC endothermic curves are not symmetric in the neighborhood of the maximum peaks, and the melting processing starts at a relatively lower temperature with a long melting range. At the beginning, the samples are melted at a small rate, and with the melting process the melting rate becomes increasingly rapid until it reaches the summit; subsequently, the curve drops abruptly after the top. This phenomenon, similar to the previous samples,¹⁶ and the detailed study results will be described in a future article.

According to previous articles^{15,16} and Flory's theory modified by Monrabal,^{9,10,17} there should be a nearly linear relationship between melting temperature and content of comonomer with small volume, like ethylene, but a nonlinear relationship between melting temperature and content of voluminous comonomer, like 1-butene, which is partly dissimilar to Abiru's conclusion.⁴ When the relationship between melting temperature and 1-butene content of the set of fraction samples was drawn in Figure 6, we found it is a nonlinear curve. Even if only four data are used in this pattern, and meanwhile the molecular weight is various, it is clear enough to show the developing trend of the curve in the defined range of 1-butene content. Like the study on the propylene-ethylene-1-butene terpolymer sample,¹⁶ Flory's theory modified by Monrabal can no longer be directly applied to explain the phenomenon^{9,10,17}; with 1-butene concentration increasing, the curve increasingly bends down, and the melting temperature decreases more and more rapidly.

Molecular weight is also an important microstructural factor governing melting and crystallization behavior of polymers. Figure 7 shows the resultant curve

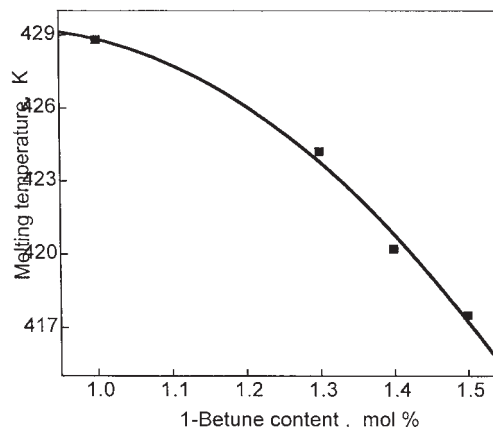


Figure 6 Melting temperature (T_m , K) determined by DSC of some fraction samples of a propylene-1-butene copolymer by TREF as a function of 1-butene content (mol %).

of the melting temperature as a function of the number average molecular weight of the fraction samples. From the pattern it can be found that, with an increase in molecular weight, the increase in melting temperature of the fraction samples gradually tends to slow. In other words, when the polymer sample has relatively lower molecular weight, dependence of its melting temperature on the molecular weight is very strong; however, at a larger molecular weight, the dependence on the molecular weight becomes increasingly weaker. Therefore, in light of the above-mentioned discussion and analysis, it can be concluded that the effect of molecular weight on the melting temperature is significant, even though the number average molecular weight of some fraction samples is close to 1.82×10^5 g/mol, and there is also a small amount of comonomer, 1-butene, in the copolymer. However, a fact must be emphasized: compared to comonomer, the effect of molecular weight on melting temperature

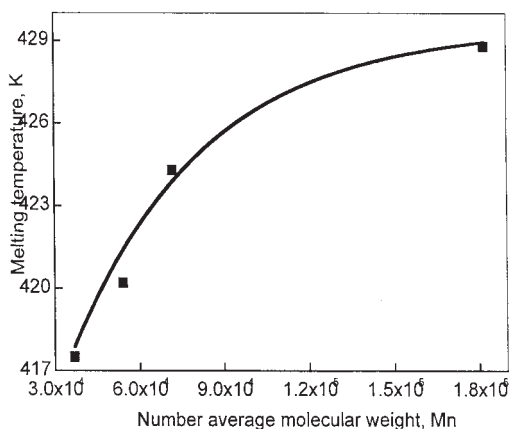


Figure 7 Melting temperature determined by DSC (T_m , K) versus number average molecular weight (M_n) of some fraction samples of a propylene-1-butene copolymer by TREF.

is weak, and meanwhile the effect gradually becomes increasingly weaker with an increase in molecular weight.

CONCLUSIONS

A random copolymer of propylene with a small amount of 1-butene comonomer, synthesized with a Ziegler–Natta catalyst, was systemically investigated to understand its molecular microstructure, as well as the relationship to its melting and crystallization behavior. Fraction samples with correspondingly uniform molecular microstructure by use of the TREF technique, consist of long isotactic propylene sequences and 1-butene comonomer in the form of isolated units. Melting temperature increasingly decreases with an increase in 1-butene content; however, dependence of melting temperature on molecular weight becomes increasing weaker with an increase in number average molecular weight in the range of number average molecular weight below 1.82×10^5 g/mol.

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