

# Separation and identification of ethylene–propylene block copolymer

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In this paper, a commercial impact-resistant polypropylene alloy sample was fractionated with preparative temperature rising elution fractionation (t.r.e.f.) technique and a series of ethylene–propylene block copolymer fractions with different ethylene contents were obtained. Combined with fractionation results, the block structure of them was identified with  $^{13}\text{C}$  nuclear magnetic resonance (n.m.r.) spectroscopy and differential scanning calorimetry (d.s.c.). There are some transition segments between polyethylene and polypropylene segment in the block copolymer. It was found that the number and kind of transition segments decreased with elution temperature, the length and melting temperature of polyethylene segment in block copolymer fractions showed a similar tendency. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Because of its unique practical properties and theoretical value, ethylene–propylene block copolymer has been the subject of considerable research<sup>1,2</sup>. Ethylene–propylene block copolymer is one of the main components in impact-resistant polypropylene for its low brittle temperature and high tensile impact strength<sup>3</sup>. The possibility of synthesis ethylene–propylene block copolymer is related to the lifetime of active site in Ziegler–Natta catalysts<sup>4,5</sup>.

Ethylene–propylene block copolymer is usually synthesized by sequential coordination copolymerization. Due to the complex character of coordination polymerization, the product obtained is inevitably a mixture of propylene homopolymer, ethylene–propylene block copolymer and ethylene–propylene random copolymer. The random copolymer can be readily removed by extraction with *n*-heptane<sup>6</sup>. However, block copolymer and propylene homopolymer cannot be separated with this method. In many previous studies, they were not separated, and so-called ‘block’ copolymer were still mixtures<sup>7,8</sup>. Additionally, the structural similarity between block copolymer and the PE/PP blend made it difficult to distinguish them and the judgement of block copolymer is still controversial<sup>9–12</sup>. The poor purity of block copolymer may also be partly responsible for this. Moreover, it is well known that there exist plural active sites in heterogeneous catalysts, which lead to the compositional heterogeneity of polymer<sup>13,14</sup>. The relative length of two segments in block copolymers may vary with different active sites. Therefore it is necessary to

obtain relatively pure and compositionally homogeneous block copolymer for a better understanding of ethylene–propylene block copolymer. The fractionation of ethylene–propylene block copolymer was conducted by Besomers and Ito through extraction with different solvents or solvent/nonsolvent pair<sup>3,15</sup>, but the emphasis was placed on the thermal behaviour of the fractions, and the block structure was not well characterized.

Recently, the temperature rising elution fractionation (t.r.e.f.) technique was developed for the fractionation of LLDPE and PP based on crystallinity<sup>16,17</sup>. However reports on the fractionation of blends with this method are rare. We believe that the crystallinity of various components in blends should be different and they could be separated with this technique. In the present work, a commercial impact-resistant PP alloy was fractionated and ethylene–propylene block copolymer was obtained. The block structure of the fractions was identified by combining fractionation results with  $^{13}\text{C}$  n.m.r. and d.s.c.

## EXPERIMENTAL

### Materials

An impact-resistant polypropylene alloy sample was obtained commercially. It was produced according to the following steps: Propylene was firstly homopolymerized in bulk, then propylene was evaporated and polymer particles was transported into a gas tank. In this step, ethylene was introduced. To obtain products with good quality, propylene was not removed completely and a small amount of propylene was left in the second step. Some characteristics of this sample are listed in Table 1.

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**Table 1** Characteristics of impact-resistant polypropylene sample

Content of ethylene (mol%)	$\overline{M}_w (\times 10^{-4})$	$\overline{M}_w/\overline{M}_n$	Melt flow index (g/10 min)
11.24	23.6	10.15	27.3

*Preparative t.r.e.f.*

Preparative t.r.e.f. apparatus was used to collect large fractions of fractionated polymers. The polymers were dissolved in xylene at a concentration of  $0.005 \text{ g ml}^{-1}$  at  $130^\circ\text{C}$ . This solution was deposited on a steel column packed with an inert support, sea sand. The column was cooled to room temperature at  $1.5^\circ\text{C h}^{-1}$ . The cooled polymer was heated in incremental steps of temperature and eluted with xylene. The polymer was recovered by evaporating the xylene solvent and drying in a vacuum oven. Because a small amount of antioxidant was added, the recovery of polymer was 105% or so.

 *$^{13}\text{C}$  n.m.r. analysis*

22.5 MHz proton decoupled (NOE)  $^{13}\text{C}$  n.m.r. spectra were recorded on a JEOL FX-90Q NMR spectrometer at  $120^\circ\text{C}$  in pulsed Fourier Transform model with hexamethyldisiloxane (HMDS) as internal standard. The solutions were prepared in *o*-dichlorobenzene- $d_4$  at a concentration of  $0.10 \text{ g cm}^{-3}$ . Typical conditions were: 10000 scans, 5 s relaxation time,  $90^\circ$  pulse, 32 K data points. 100 MHz  $^{13}\text{C}$  n.m.r. spectrum was recorded on a Bruker AMX-400 spectrometer. Analytical conditions were the same as those in spectra measured at 22.5 MHz.

*Thermal analysis*

D.s.c. scans were recorded on a Perkin-Elmer DSC-7 thermal analyser under  $\text{N}_2$  atmosphere. Samples of 5–6 mg were sealed in aluminium sample pans. The samples were heated to  $200^\circ\text{C}$  and maintained for 5 min to eliminate thermal history effects. Then the melting temperature ( $T_m$ ) and crystallizing temperature ( $T_c$ ) were determined. Both cooling and heating rates were programmed at  $10^\circ\text{C min}^{-1}$ .

## RESULTS AND DISCUSSION

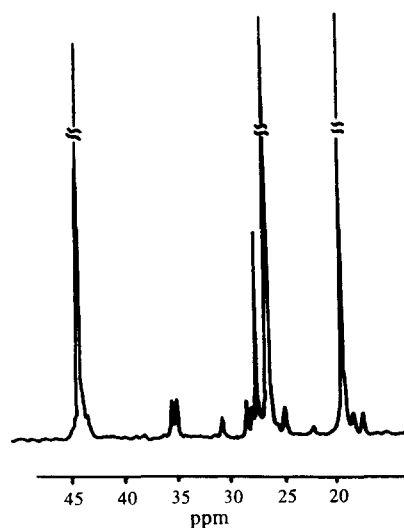
*Fractionation of the original sample*

The overall  $^{13}\text{C}$  n.m.r. spectrum of PP alloy sample is given in *Figure 1*. The assignments of the resonances are listed in *Table 2*. The nomenclature of carbon nuclei such as  $\alpha\alpha, \beta\beta, \dots$  follows the system proposed by Carman and Wilkes<sup>18</sup>. From *Figure 1*, one can see that this sample seems to be a copolymer of propylene with a small amount of ethylene. There is no evidence of the presence for blend or block copolymer.

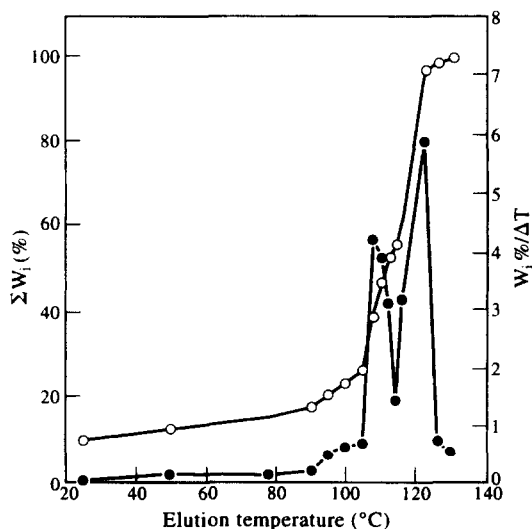
*Figure 2* shows the t.r.e.f. curves of PP alloy and the data of fractionation are listed in *Table 3*. The  $W_i\%/\Delta T \sim T$  curve in *Figure 2* approximates the differential curve of the cumulative weight curve. An obvious point of inflection is found in the cumulative weight curve, as well as a considerable part of polymer (12.37%) eluted at room temperature. Also two peaks appear in the  $W_i\%/\Delta T \sim T$  curve. These results suggest that three main components exist in the polymer alloy.

 *$^{13}\text{C}$  n.m.r. analysis of fractions*

Fractions No. 1, No. 5, No. 8, No. 11 and No. 13 were

**Figure 1** 22.5 MHz  $^{13}\text{C}$  n.m.r. spectrum of the impact-resistant PP alloy sample**Table 2** Assignments of the  $^{13}\text{C}$  n.m.r. spectrum of ethylene-propylene copolymer

Peak	Chemical shift (ppm)	Assignments
1	44.5	$S_{\alpha\alpha}$
2	35.8	$S_{\alpha\gamma}$
3	35.4	$S_{\alpha\delta}$
4	31.1	$T_{\delta'\delta'}$
5	29.0	$S_{\gamma\gamma}$
6	28.3	$S_{\gamma\delta'}$
7	27.8	$S_{\delta'\delta'}$
8	26.8	$T_{\beta\beta}$
9	25.3	$S_{\beta\delta}$
10	22.8	$S_{\beta\beta}$
11	19.6	$P_{\beta\beta}$
12	18.6	$P_{\beta\gamma'}$
13	17.8	$P_{\gamma'\gamma'}$

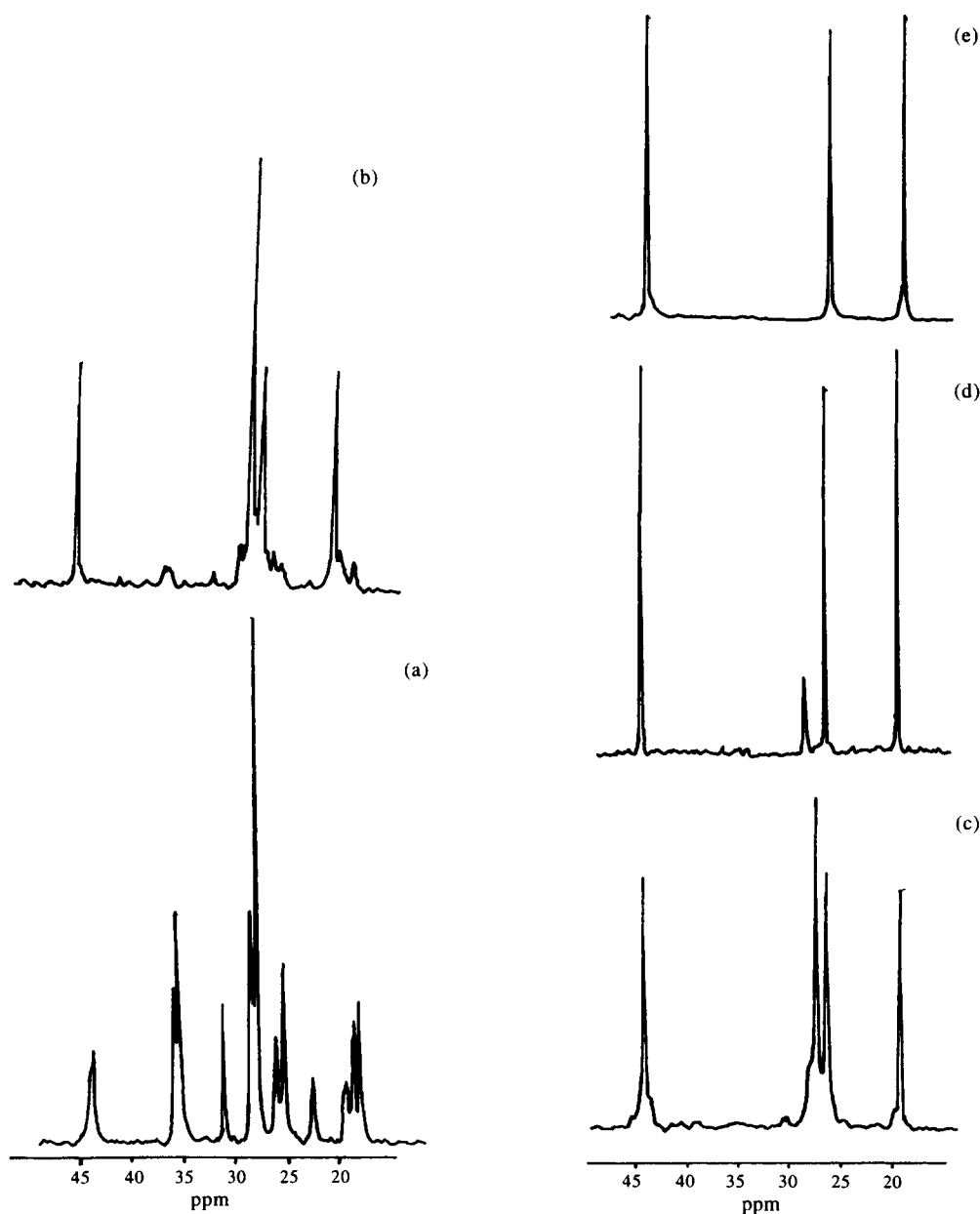
**Figure 2** T.r.e.f. curves of the impact-resistant PP alloy sample

selected for  $^{13}\text{C}$  n.m.r. analysis and their spectra measured at 22.5 MHz were illustrated in *Figures 3a–e*. *Figure 3a* is typically a  $^{13}\text{C}$  n.m.r. spectrum of an ethylene-propylene random copolymer. The crystallinity of fraction

**Table 3** Fractionation result of impact-resistant PP alloy sample

No.	$T$ (°C)	Wi%	$\Sigma$ Wi% (%)	Wi%/ $\Delta T$ (%/°C)	$T_m$ (°C)
1	25	9.80	9.80	—	—
2	50	2.66	12.46	0.106	—
3	78	2.83	15.29	0.101	103/120
4	90	2.41	17.70	0.201	105/124
5	95	2.88	20.08	0.576	114/138
6	100	3.04	23.12	0.608	114/138
7	105	3.50	26.67	0.700	124/149
8	108	12.60	39.27	4.200	123/156
9	110	7.69	46.96	3.845	120/156
10	112	6.21	53.17	3.105	113/156
11	114	2.83	56.00	1.415	158
12	116	6.32	62.32	3.160	160
13	122	35.09	97.41	5.848	160
14	126	1.49	98.90	0.373	160
15	130	1.10	100.00	0.275	—

1 is very low and it is eluted at room temperature. Fraction 13 is a propylene homopolymer, because only  $S_{\alpha\alpha}$ ,  $T_{\beta\beta}$ , and  $P_{\beta\beta}$  peaks, which are assigned to continuous propylene units, are present in *Figure 3e*. No splitting in the methyl regions indicates that this fraction is highly isotactic. Therefore, two major components of the PP alloy are ethylene-propylene random copolymer and propylene homopolymer. Our emphasis will concentrate on the third component. *Figure 3b* is very like that reported by Sun<sup>12</sup>. Four strong resonances  $S_{\delta+\delta^+}$ ,  $S_{\alpha\alpha}$ ,  $T_{\beta\beta}$ ,  $P_{\beta\beta}$  exist in it, which result from long and continuous polyethylene segment and polypropylene segment, respectively. In addition, some small peaks, such as  $S_{\alpha\gamma}$ ,  $S_{\alpha\delta^+}$ ,  $T_{\delta+\delta^+}$ ,  $S_{\gamma\delta^+}$ ,  $S_{\beta\delta^+}$ , also appear in *Figure 3b*. This means that various transition segments such as PEP, EPE, PPE and EEP exist between continuous polyethylene and polypropylene segments. Since it is not really a block structure, we call it a blocky copolymer. In *Figure 3c*, the  $S_{\delta+\delta^+}$ ,  $S_{\alpha\alpha}$ ,  $T_{\beta\beta}$ , and  $P_{\beta\beta}$  peaks are very strong and other peaks are

**Figure 3** 22.5 MHz  $^{13}\text{C}$  n.m.r. spectra of some selected fractions. (a) No. 1, (b) No. 5, (c) No. 8, (d) No. 11, and (e) No. 13

too weak to be observable, which indicates that both continuous propylene and ethylene units are present in this fraction. However, it may be a block copolymer or a PE/PP blend. For the same reason as in fraction 13, it can be seen that the polypropylene in this fraction is also highly isotactic. Nevertheless, isotactic propylene homopolymer was not eluted until 120–128°C. Thus, the clear implication is that the isotactic polypropylene segment is linked with the polyethylene segment and fraction 8 is an ethylene-propylene block copolymer. Due to the presence of the polyethylene segment, which decreases the crystallinity of the polypropylene segment, this fraction was eluted at lower temperature than propylene homopolymer, even though it was also highly isotactic. Since the number of junctions between polyethylene and polypropylene segments was very small, the resonance  $S_{\alpha\delta^+}$  was not observable in the 25.14 MHz spectrum with low sensitivity. Another high resolution spectrum of fraction 8 was measured at 100 MHz as shown in Figure 4. Four additional weak signals,  $S_{\sigma\delta^+}$ ,  $S_{\beta\delta^+}$ ,  $T_{\delta^+\delta^+}$  and  $P_{\gamma^+\gamma^+}$ , which originate from the sequence structure EEPEE and the junctions between the blocks, were clearly observed. This result shows that this fraction still contains a small amount of transition segments in which the isolated propylene units are present in long polyethylene sequences. No observation of the true block copolymer fraction may be related to the preparation process of the original sample. If propylene gas was removed cleanly in the second step, such a structure as EEPEE in fraction 8 may not appear and true block structure may be observed. Compared with fraction 5, the number of transition segments is much less. Moreover, other transition segments such as PEP triad do not appear in Figure 4. Therefore, this fraction is very close to a true block copolymer. Sun obtained a spectrum similar to Figure 3b and concluded that the possibility of forming ethylene-propylene diblock copolymer is questionable<sup>12</sup>. In the present work, we reveal that the whole polymer sample is a mixture of different fractions. Though true block copolymer fraction was not obtained

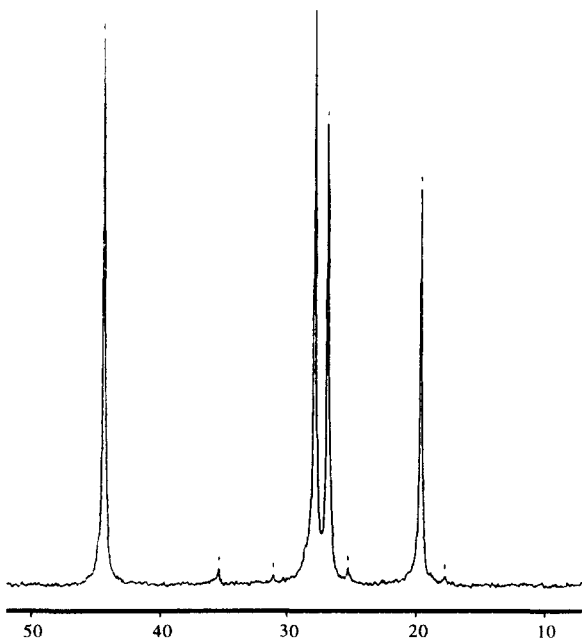


Figure 4 100 MHz <sup>13</sup>C n.m.r. spectrum of fraction 8

by us, from the variation tendency of structure of fractions with elution temperature, we can conclude that it is quite likely we could obtain true block copolymer, if only the polymerization process is improved. Figure 3d is similar to Figure 3c, except that the resonance of the polyethylene segment is weaker. This shows that the ethylene content in block copolymer varies with elution temperature and block copolymer with a different relative length of two segments can be acquired using t.r.e.f. technology.

Thermal analysis

The thermographs of some selected fractions are shown in Figure 5. There is no melting peak for the first two atactic fractions (fractions 1 and 2) and a single peak for propylene homopolymer fractions (fractions 12–14). From fraction 3 to fraction 7, double melting peaks appear and the melting temperature of both peaks increases with the elution temperature. They may correspond to the melting temperature of polyethylene and polypropylene segments, respectively. With the

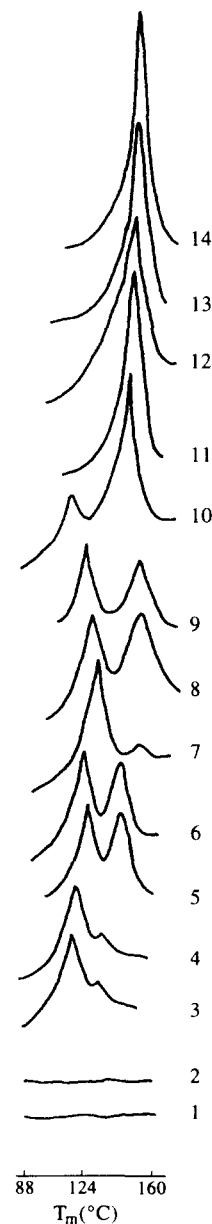


Figure 5 D.s.c. melting curves of some selected fractions

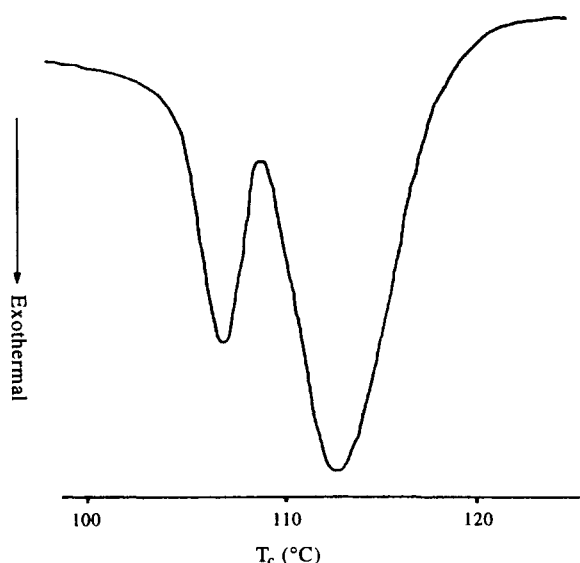


Figure 6 D.s.c. crystallization curve of fraction 8

increase of elution temperature, random copolymers turn gradually to blocky copolymers, which leads to the increase of the melting temperature of both segments. From fraction 8 to fraction 10, the two melting temperatures show different variation tendencies in spite of the appearance of double endothermal peaks. The melting temperatures of polyethylene segments decrease with elution temperature, but that of the polypropylene segment is nearly constant. The variation of melting temperatures of fractions 8–10 also confirms that these fractions are block copolymers. Because the t.r.e.f. method fractionates polymer according to crystallinity, the melting temperature should increase with elution temperature. However, in these fractions, the melting temperatures of polyethylene segment show an opposite tendency. The only reason which can explain it is that the polyethylene segments are present in block copolymer and the length of polyethylene segments is becoming shorter. With regard to the whole fraction, the shorter polyethylene segment has less influence on the polypropylene segment and favours the crystallization of the polypropylene segment, which results in a higher eluted temperature of the fraction. Additionally, the melting temperature of the propylene segment in these fractions is only a few degrees lower than the propylene homopolymer. This is because the covalent bond between blocks restricts the movement of the blocks and affects the crystallization processes in the block copolymer. From Figure 3d we can see that there is a small amount of polyethylene segment in fraction 11. However, the melting peak of the polyethylene segment in this fraction is not observed. This indicates that when the polyethylene segment is short enough, it cannot be crystallizable. In spite of no observation of a melting peak of the polyethylene segment, the existence of it is

evidenced by a lower melting point of the polypropylene segment compared to that of the propylene homopolymer. After fraction 11, the fraction is pure polypropylene and the melting point of propylene homopolymer is observed.

The d.s.c. crystallization curve of ethylene-propylene block copolymer (fraction 8) is shown in Figure 6. Two exothermic peaks appear in it, which correspond to the crystallization temperature of the polyethylene and polypropylene segments, respectively. The presence of two crystallization peaks is one of the characteristics of ethylene-propylene block copolymer<sup>9</sup>.

## CONCLUSIONS

T.r.e.f. provides an effective tool for the separation and purification of ethylene-propylene block copolymer. Also, block copolymers can be further fractionated according to ethylene content and transition region content. The block structure was identified with <sup>13</sup>C n.m.r. and d.s.c. The separated block copolymer with relatively pure structure will further facilitate the characterization of the block copolymer and help in understanding its role. This work will be reported elsewhere.

## ACKNOWLEDGEMENT

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