Structural Characterization of Reactor Blends of Polypropylene and Ethylene-Propylene Rubber

Márcia Pires,[1,2] Raquel S. Mauler,[1] Susana A. Liberman[2]

[1]*Instituto de Química, Universidade Federal do Rio Grande do Sul, Av Bento Gonçalves 9500, Porto Alegre, 91501–970, Brazil*
[2]*Braskem S/A, III Pólo Petroquímico, Via Oeste Lote, 5 Passo Raso, Triunfo, Brazil*

ABSTRACT: Blends of isotactic polypropylene (PP), ethylene-propylene rubber copolymer (EPR), and ethylene-propylene crystalline copolymer (EPC) can be produced through *in situ* polymerization processes directly in the reactor and blends with different structure and composition can be obtained. In this work we studied the structure of five reactor-made blends of PP, EPR, and EPC produced by a Ziegler-Natta catalyst system. The composition of EPR was related to the ratio between ethylene and propylene used in the copolymerization step. The ethylene content in the EPR was in the range of 50–70 mol %. The crystallization behavior of PP and EPC in the blends was influenced by the presence of the rubber, and some specific interactions between the components could be established. By preparative temperature rising elution fractionation (P-TREF) analysis, the isolation and characterization of crystalline EPC fractions were made. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2155–2162, 2004

Key words: polypropylene; polyolefin blend; elastomer particulate; reactor blend; ethylene-propylene rubber

INTRODUCTION

Polypropylene (PP) is a semicrystalline thermoplastic polymer widely used in packaging, textile, and automobile industries because of its good processability and properties. Nevertheless, for applications as an engineering plastic, polypropylene shows limited toughness, especially at room and low temperatures.[1,2] Impact resistance is a very important property in many applications and the understanding of the relationship between structure, morphology, and deformation phenomena is necessary to develop polymeric systems with good mechanical properties. To improve toughness of polymeric materials, various modifier particles with different physical properties can be added to the matrix.[3,4] Also, chemical modification or blending with elastomeric materials or other polymers can be made.[5] Several studies about blends of isotactic polypropylene (*i*-PP) with ethylene-propylene random copolymer (EPR) have been made in the past two decades.[6]

The versatility of polymerization processes made possible the production of blends *in situ* directly in the reactor. In this way blends with high ethylene-propylene rubber content can be obtained.[7] Through this process, a polypropylene matix is produced first and then, in a second step, the ethylene-propylene copolymer (EPR). During the formation of the rubber, some crystalline polyethylene is formed, due the high reactivity of ethylene in the reaction medium. With this process it is possible to get materials with distinctive, well-dispersed morphologies, in which the polyethylene particles are generally enveloped in the EPR phase.[8,9]

These thermoplastic polyolefins (TPO) have been widely used for automobile parts, appliances, and other industrial uses because of their properties, good processability, and improved mechanical properties compared with polypropylene homopolymer.[10] The impact properties of these blends are considerably improved by the presence of dispersed rubber particles in the polypropylene matrix.[11] Several studies show that similar blends, produced by a sequential process, with the formation of some crystalline polyethylene, present specific characteristic particle morphology: the polyethylene seems to form a core surrounded by the rubber, which forms a shell in contact with the PP matrix.[7]

The physical behavior of the EPR, produced by a Ziegler-Natta catalyst system, can be described with three structure parameters: average chemical composition, compositional heterogeneity, and sequence distribution of comonomer units along the chain. Depending on these factors, different kind of copolymers, from amorphous to partially crystalline, can be obtained.

TABLE I
Composition of the Blends and Their EPR Fractions

| Sample | Ethylene-propylene ratio in the feed | Crystalline phase | | Amorphous phase | | Oligomers[a] |
| | | PP | EPC | EPR | | |
		% w/w	% w/w	% w/w	Ethylene mol %	% w/w
C-41	0.30	59.9	6.8	31.9	50.9	1.7
C-50	0.55	61.1	11.0	26.5	60.1	1.4
C-54	0.44	46.6	15.9	36.4	64.0	1.2
C-60	0.58	50.4	19.2	29.4	69.7	1.0
C-66	0.67	45.5	29.8	23.6	75.4	1.2

[a] Calculated through xylene fractionation.

Several studies have been done to establish the influence of rubber characteristics on the mechanical properties and in the crystallization process of the matrix.[12]

In this work we study ternary reactor-made blends of polypropylene homopolymer (PP), EPR, and ethylene-propylene crystalline copolymer (EPC), produced by a Ziegler-Natta catalyst system. The composition of the blends will be evaluated by fractionation techniques and the structural and thermal characterization of fractions will be discussed.

EXPERIMENTAL

Materials

Five reactor-made blends of PP, EPR, and EPC of different compositions were used. These blends were supplied by Braskem S/A and prepared with a Ziegler-Natta catalytic system.

Xylene fractionation

The samples were dissolved in xylene at 135°C with reflux for 1 h. After this step the solution was control

cooled to room temperature. The insoluble fraction at 25°C was separated by filtration and identified as crystalline polymer. The soluble phase at 25°C was precipitated from the solution in an acetone-methanol mixture and the amorphous polymer was separated (prefraction). Oligomers remained soluble in the solvent mixture.

Preparative temperature rising elution fractionation (P-TREF)

The samples were fractionated by P-TREF. The insoluble polymer, previously separated through xylene fractionation, was dissolved in xylene (1 wt %) stabilized with 0.025% w/v of 2,6-di-*tert*-butyl-4-methylphenol (BHT), at 125°C with reflux for 1 h. The solution was introduced on a silica column maintained at 135°C. The temperature was decreased to room temperature at 2°C/min. During controlled slow cooling of the solution, the sample crystallized on the solid silica, promoting selective crystallization. After an equilibrium delay of 9 h at 25°C, the temperature then was raised with a linear gradient (15°C/min). The first fraction was eluted at 70°C with xylene and the sub-
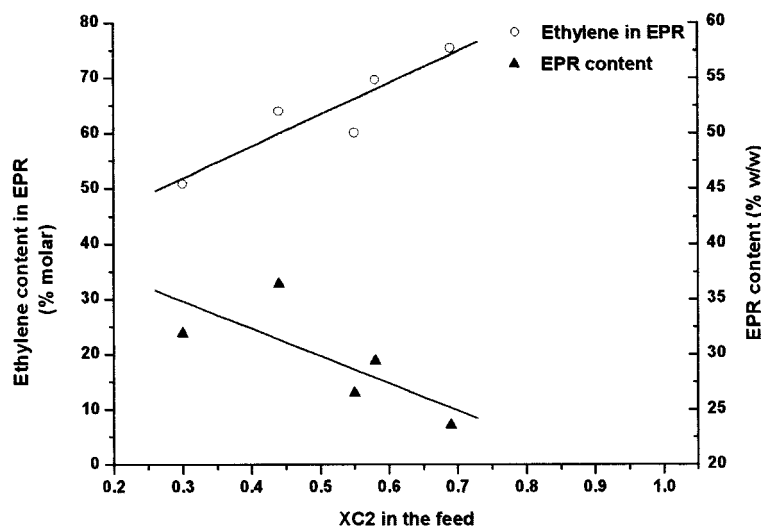

Figure 1 Relationship between the ethylene in the feed (X_{C_2}) and the composition of EPR and the EPR content in the blend.
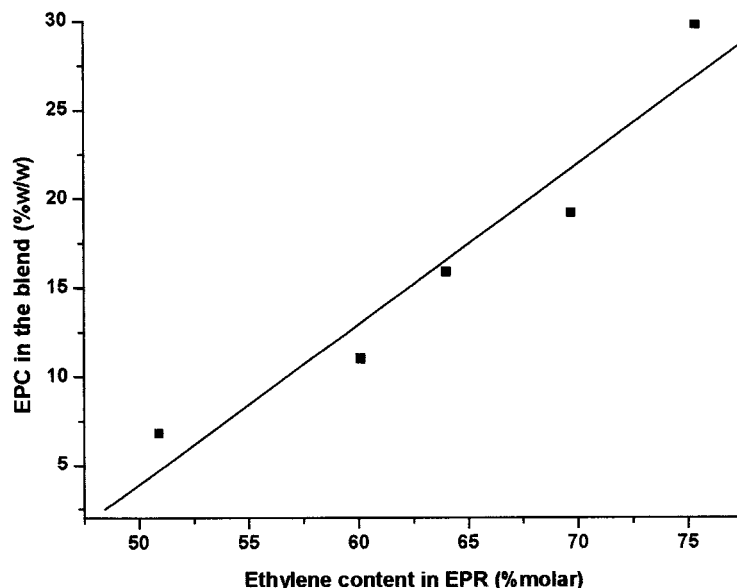
Figure 2 Relationship between composition of the EPR and EPC content.

sequent fractions were collected by stepwise increases in temperature to 125°C. The eluted polymer fractions were precipitated in a mixture of methanol and acetone at room temperature, filtered, and dried in a vacuum oven.[9,13–15]

Intrinsic viscosity (IV)

The intrinsic viscosity of the samples and its fractions were determined in a CINEVISCO model Sofica capillary viscometer. The analysis was performed in decalin at 135°C.[16]

Infrared spectrometry-Fourier transform (FT-IR)

FT-IR analyses were performed in a Nicolet 710 spectrometer using films prepared by hot pressing. All the spectra were measured in the transmission mode. The quantitative analysis of ethylene and propylene content was performed using specific calibration curves that took into account the composition of each sample. In each case the calibration curve was obtained by

considering the area of absorbance of some specific band as a function of the comonomer content measured by ^{13}C-NMR. In crystalline samples, the ethylene content was determined by the ratio between the band areas at 720 cm^{-1}, attributed to the absorption of methylene sequences,[17] and at 4,482–3,950 cm^{-1}, there is a large band that depends on the thickness of the film due to the combined absorption of methyl and methylene groups.[18] In the rubber, the ethylene content was determined using the ratio between the bands at 720 cm^{-1} and 1,156 cm^{-1} due to PP.[19] In samples rich in ethylene, the propylene content was determined by the ratio between the absorbance at 1,378 cm^{-1}, attributed to methyl groups,[18] and the area at 4,482–3,950 cm^{-1}.[17–19]

Differential scanning calorimetry (DSC)

DSC experiments were carried out in a TA Instruments MDSC-2920. The samples were heated to 200°C and held at this temperature for 2 min, to eliminate the thermal history. The sample then was cooled to 40°C

TABLE II
Thermal Properties of the Blends and Their Fractions

| Sample | Blend | | | | Crystalline fraction (PP + EPC) | | | |
| | EPC | | PP | | EPC | | PP | |
	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)
C-41	98	117	117	163	—	122	120	164
C-50	103	121	118	163	107	122	121	164
C-54	104	121	116	161	107	122	120	163
C-60	106	122	116	162	107	122	120	163
C-66	107	123	114	161	108	123	119	163
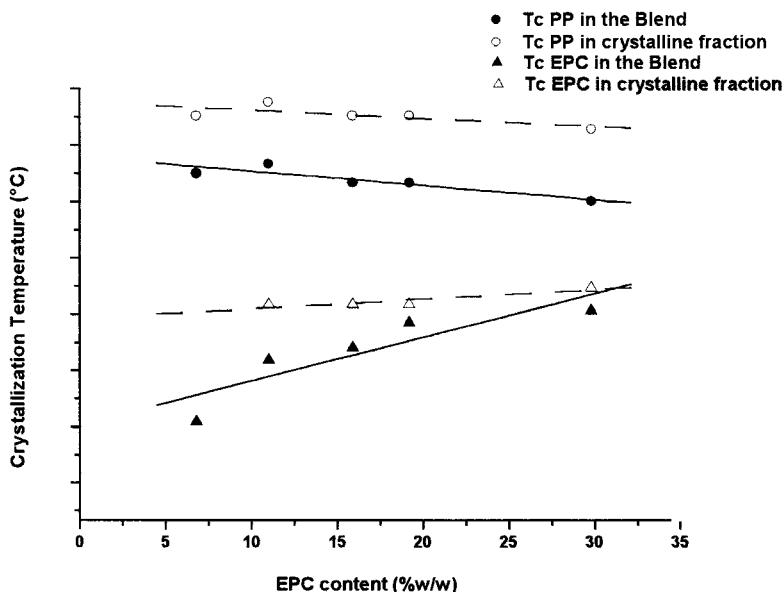
Figure 3   Relationship between EPC content and T_c of EPC and PP in the blend.

RESULTS AND DISCUSSION

at 10°/min. The crystallization temperature (T_c) was determined in this step. The melting temperatures (T_m) were obtained in a second heating run from 40 to 200°C at 10°/min. The melting enthalpies of 100% crystalline materials were 190 and 236 J/g for polypropylene and polyethylene, respectively.

RESULTS AND DISCUSSION

The blends were obtained *in situ* in a sequential process with the production of PP followed by simultaneous production of EPR and EPC.[8,9]

Through xylene fractionation at 25°C the amorphous phase (EPR) was quantified and separated from the crystalline phase of the blends, composed of a mixture of PP and EPC. The composition of all blends is shown in Table I. The compositions of EPR and the total amount of EPC were different in each blend because of different ethylene/propylene ratios used in the copolymerization step.

By increasing the molar fraction of ethylene in the feed (X_{C2}), rubber with a higher incorporation of ethylene was obtained. At the same time, the EPR amount decreased because EPC started to form due to the high
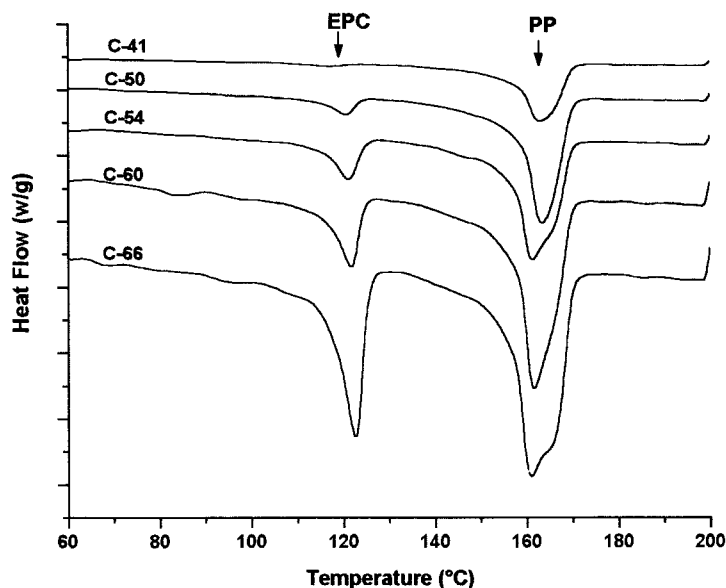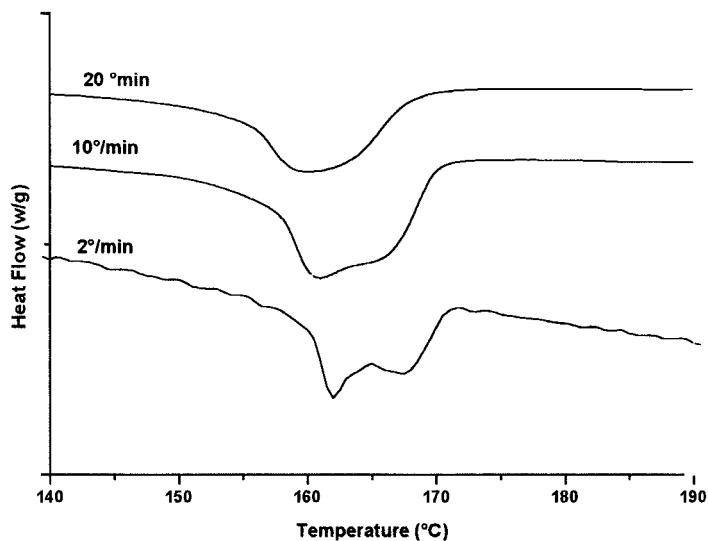

Figure 4   Melting thermograms of the blends.

Figure 5 Melting curves of sample C-66 obtained at 2, 10, and 20°C/min.

reactivity of ethylene in the reaction medium (Fig. 1). The amount of EPC was correlated with the ethylene incorporated in the EPR (Fig. 2).

Thermal properties of the blends and their crystalline phases are summarized in Table II. In the crystalline fraction, which was formed by a mixture of PP and EPC, no changes could be observed in the T_m and T_c of the components. This behavior is associated with immiscibility of PP and EPC.[20]

In the blends both PP and EPC showed some variation in their T_m and T_c, indicating that the presence of EPR was affecting the crystallization of PP and EPC.

The T_c of the PP component slightly decreased with the amount of EPC present in the blend (Fig. 3), indicating delayed nucleation.[21] This behavior is probably related to the high viscosity of the medium because of the presence of molten EPC and EPR when PP began to crystallize. The crystallization of PP became affected by the presence of both rubber and EPC molecules, by decreasing the diffusion coefficient, and consequently the mobility of PP chains to form crystals and consequently decrease its T_c. The melting peaks of PP were broad and they seemed to split into two peaks when the EPC content increased (Fig. 4). This effect
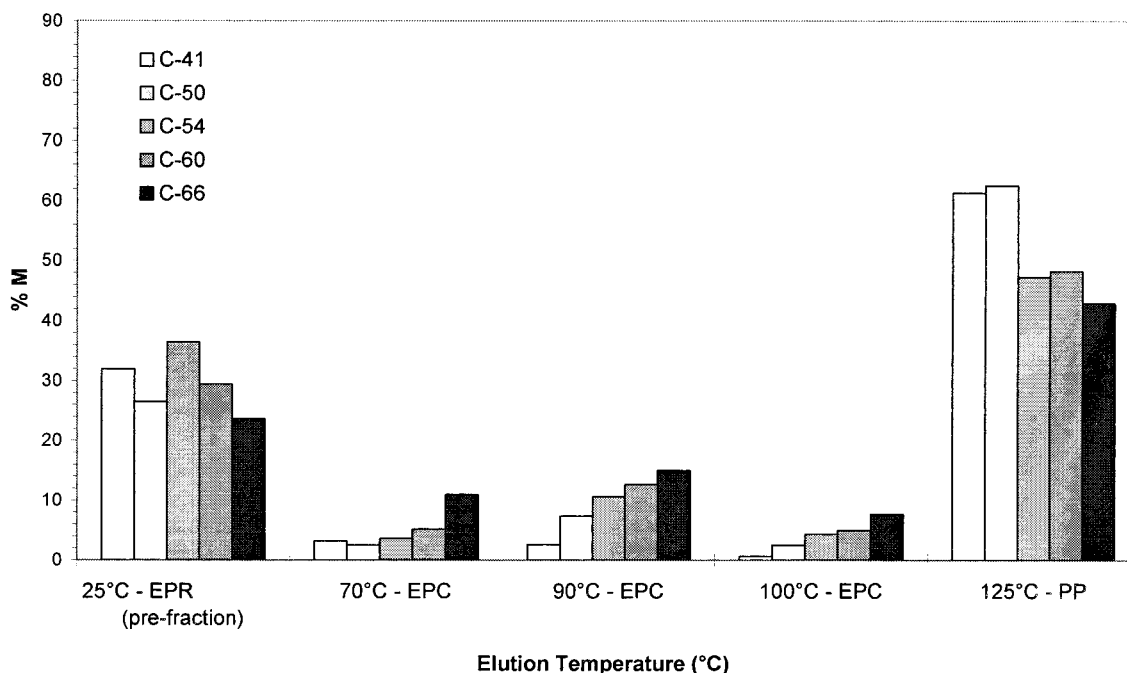

Figure 6 P-TREF profile of the blends.

TABLE III
Properties of P-TREF Fractions

	Fraction 1 - LLDPE					Fraction 2 - LLDPE					Fraction 3 - LLDPE					Fraction 4 - PP				
	C-41	C-50	C-54	C-60	C-66	C-41	C-50	C-54	C-60	C-66	C-41	C-50	C-54	C-60	C-66	C-41	C-50	C-54	C-60	C-66
wi (%w/w)	3.2	2.5	3.6	5.2	10.9	2.6	7.4	10.6	12.7	15	0.6	2.5	2.4	4.9	7.7	61.3	62.5	47.26	48.28	42.9
Intrinsic Viscosity (dl/g)	3	2.4	2.2	2.7	3.2	5.8	4.4	3.7	4.1	3.3	6.5	5.9	4.8	5.3	4.4	1.8	1.7	1.4	1.4	1.4
Ethylene Content (mol %)[a]																0	0	0	0	0
Propylene Content (mol %)[a]	16.7	17.1	17	15.4	13.1	8.3	7.6	7.5	7.3	6.8	NA	4.6	4.4	4	3.6					
T_c (°C)	81	81	77	83	86	104	105	105	106	108	NA	112	112	112	113	118	120	121	119	120
T_m (°C)	99/82	99/82	95/78	102/80	104/87	119	121	121	122	123	NA	126	126	126	129	164	166	165	166	165
X_c (°C)	39.0	36.5	34.5	39.0	44.5	55.6	48.8	49.3	53.0	—	NA	58.1	59.7	63.0	62.0	—	—	—	—	—

[a] Ethylene and propylene content were analyzed by FT—IR.
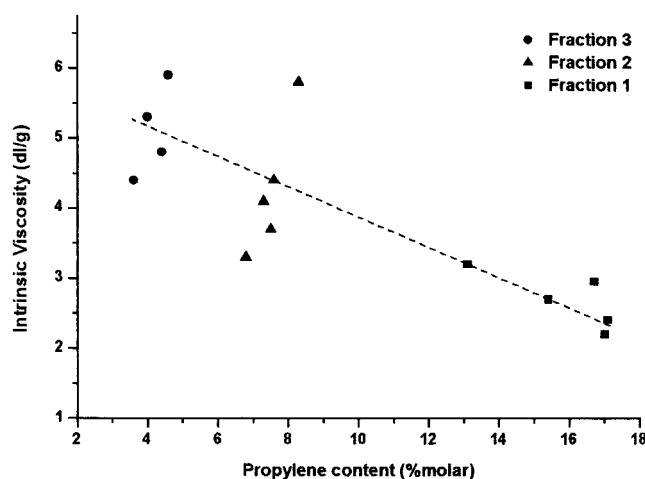[b] NA, not analyzed due to the low quantity of sample.

Figure 7 Relationship between intrinsic viscosity and composition of the P-TREF fractions of EPC.

can be better observed in Figure 5, where melting curves at 2, 10, and 20°C/min are compared. At 2°C/min the split was more pronounced and this could be attributed to a melting-recrystallization process of less perfect crystals.[22] This behavior is supported by the decrease of the area corresponding to the peak at higher temperature at a fast heating rate (Fig. 5).[22]

A decrease of T_c and T_m of EPC was observed when its amount was lower in the blend (Table II and Fig. 4) and that can be related to morphological aspects as well as to some miscibility of EPC and EPR. It is mentioned in several studies that EPR has some compatibility with EPC, and blends of PP/EPR/EPC form a core-shell structure where, in low quantities, the EPC remains inside the rubber particles.[23,24] In this way its crystallization is delayed, decreasing the T_c. For higher EPC content, the EPC is outside the rubber, forming a single well-developed phase, increasing the T_c. These characteristic morphologies have been observed for blends with high amounts of EPC.[25] The EPC melting peak appeared as a weak shoulder in sample C-41 and became sharp and well defined for higher EPC content in the blend. In blends with higher amounts of EPC, the T_m and T_c behaved similar to EPC in the crystalline fraction.

Since these phenomena were not observed in the crystalline fraction formed only by PP and EPC, they can be attributed to the presence of EPR. As a matter of fact, it was verified that the rubber increased the compatibility of the PP and EPC, affecting the crystallization behavior.

The presence of crystallinity in the rubbers with high ethylene content was investigated by DSC. Long ethylene crystallizable sequences can be responsible for the presence of a crystalline phase and, in agreement with the literature, very broad melting peaks can be expected.[12] In our study, the EPR of sample C-66,
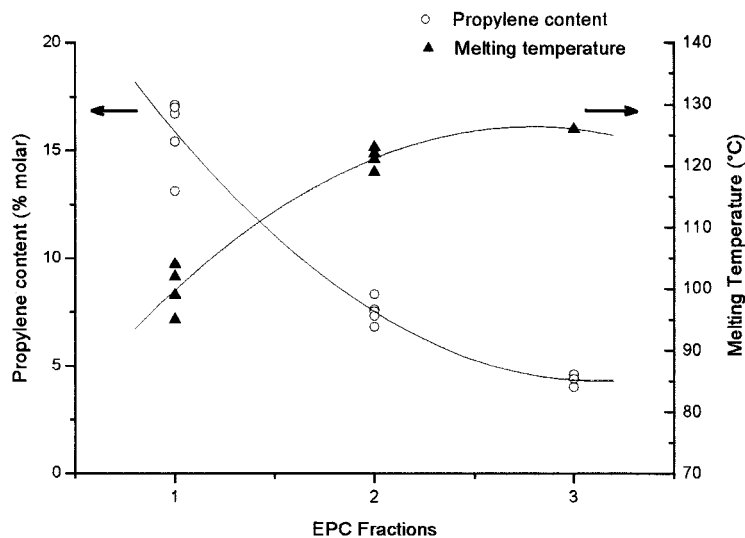
Figure 8 Variation of propylene content and melting temperature for P-TREF fractions of EPC.

with 75 mol % of ethylene, showed a very broad T_m peak around 60°C and, in the sample C-60, no melting was observed.

To better understand the structure of blends components, fractionation by P-TREF was carried out after removing the EPR (prefraction). The crystalline polymer (PP + EPC) was separated into four fractions according to their crystallinities. Each fraction was characterized to determine the composition, intrinsic viscosity, melting, and crystallization temperature.

Figure 6 shows the profile of chemical distribution of the blends obtained by P-TREF analysis, including the EPR prefraction. The amount of each fraction and their characterization results are shown in Table III.

The fractions 1, 2, and 3 were constituted by EPC and the propylene content decreased with increasing

elution temperature. These fractions have been described in the literature as linear low-density polyethylene (LLDPE).[9,26] Fraction 4 was isotactic PP.

With the increase in the amount of propylene incorporated in the EPC fraction, a simultaneous decrease in the molecular weight occurred, as indicated by the intrinsic viscosity values (Fig. 7). This behavior is widely discussed in the literature for Ziegler-Natta catalysts, and it has been explained by the mechanism of ending growth chain by β-elimination.[27,28]

The melting temperatures and composition of all samples, in the same eluted fraction, were very similar (Fig. 8). This is an indication that the composition of the EPC copolymer did not depend on the ethylene-propylene ratio fed in the polymerization step and it was just a consequence of monomer reactivity for the
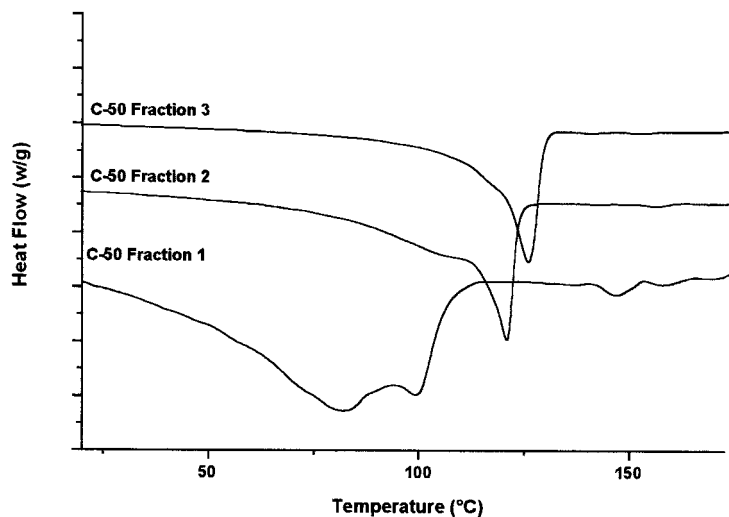

Figure 9 Melting thermograms of P-TREF fractions of sample C-50.

catalytic system and polymerization conditions applied. Also it can be observed that the melting temperature increased with the decrease in the propylene content in the fraction, showing differences in crystallinities of EPC fractions. The crystallinities of fractions 1, 2, and 3 were calculated from the melting entalphies and are shown in Table III.

Figure 9 shows the melting curves of EPC fractions. Fraction 1 presented a very broad melting peak, as a consequence of the presence of molecules with different compositions, considering that this fraction represents the whole compositional range between 25 and 70°C.

The results of IR analysis obtained for fraction 4 in all blends showed the sole presence of isotactic PP.

CONCLUSION

In reactor-made blends of PP, EPR, and EPC, the relative amount of each component depends on the ethylene-propylene ratio used in the copolymerization step. For higher ethylene concentration in the feed, rich ethylene rubber was formed, as well as a higher amount of EPC. The crystallization of PP and EPC in the blends was influenced by the presence of rubber. The crystallization temperature of EPC was delayed when this component was in a lower quantity because of its compatibility with EPR. The P-TREF analysis made the isolation and characterization of EPC possible. Despite different contents of EPC in each blend, the composition of EPC was very similar in all samples.

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