Impact polypropylene copolymers: fractionation and structural characterization

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Impact polypropylene copolymers may be produced in a two-reactor system to yield a blend of homopolymer with an ethylene–propylene rubber (EPR). The polypropylene homopolymer, which is itself brittle and has low impact strength, is markedly toughened by the presence of the EPR. The rubber-like EPR exists as a phase-segregated discrete particle in a continuous matrix of the hard phase. The molecular structure analysis of the resulting complex mixture is a formidable task.

The purpose of this paper is to describe a preparative and an analytical temperature-rising elution fractionation (t.r.e.f.) technique as the primary tools to separate and characterize a commercial impact copolymer. These techniques permit the isolation and subsequent characterization of the components of the impact copolymer by ancillary techniques, primarily ^{13}C nuclear magnetic resonance and differential scanning calorimetry. These techniques were applied to the structural analysis of a commercial impact-grade polypropylene with a melt flow rate of 6. It was found that this impact copolymer was composed of about 75 wt% of isotactic polypropylene, about 17 wt% of a highly non-crystalline EPR and about 8 wt% of semicrystalline ethylene–propylene copolymers. A major component of the semicrystalline ethylene–propylene copolymers was an ethylene-rich copolymer containing between 0 and 8 wt% of propylene comonomer.

The separate characterization of the components of the impact copolymer gives insight into the chemical synthesis process used to produce these copolymers. Further, it permits one to gain a better understanding of the location and function of each of the components in the complex mixture.

(Keywords: impact polypropylene; copolymers; fractionation; characterization; temperature-rising elution fractionation)

INTRODUCTION

Commercial isotactic polypropylene homopolymer is limited in its applications by its relatively low impact strength and high brittleness temperature. The properties of polypropylene can be greatly extended by blending with a minor fraction of a rubber-like material. This is routinely done commercially by synthesizing reactor blends of isotactic polypropylene and ethylene–propylene rubbers (EPR) *in situ*. These blends of isotactic polypropylene and EPR are widely known as impact polypropylene and dominate a large fraction of the polypropylene market. The EPR acts as a toughener for the brittle, low-impact-strength isotactic polypropylene matrix. It is well known that the addition of a low-T_g, rubber-like material to a high-T_g, hard polymer material may result in dramatic improvement in the toughness of the hard polymer[1]. The rubber-like phase is known to exist as a phase-segregated discrete particle in a continuous matrix of the hard phase[2]. The rubber-like particles are typically added at low concentration and, thus, form a discrete phase in the continuous matrix of the hard phase. An example of a toughened polymer is impact polypropylene[2]. Polypropylene itself has poor impact resistance and is very brittle at low temperatures. However, when about 10–20% of an ethylene–propylene copolymer rubber (EPR) containing about 50% ethylene is added to polypropylene, the impact strength increases dramatically and the brittleness temperature is decreased markedly. The EPR is known to exist as very small, discrete particles in the polypropylene matrix[2]. These particles toughen the matrix against crack propagation by dissipating large amounts of energy in the matrix material around the particle, thereby blunting the crack and inhibiting crack propagation.

Impact polypropylene copolymers may be made either by blending rubbers into polypropylene homopolymer or *in situ* in a two-reactor system[3]. The *in situ* method of producing impact polypropylene is considered to be more advantageous than post-reactor blending, as judged by the superior properties of the resins produced and the commercial success of this method[3]. Polypropylene homopolymer is made in the first reactor and the EPR is made in a second reactor. The polypropylene is blended with the EPR in a sequential process in which the polypropylene is added into the second reactor while the EPR is being polymerized.

This product made in this sequential reactor system, impact polypropylene, is a complex mixture of polypropylene homopolymer and ethylene–propylene copolymers. The complete molecular structure analysis of such a polymer system is a formidable task. The purpose of this paper is to describe the molecular structure analysis of a commercial impact polypropylene using temperature-rising elution fractionation (t.r.e.f.) as the primary technique. The t.r.e.f. technique is primarily employed to separate the complex mixture into discrete

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fractions, which can then be individually characterized, thereby yielding the identification of the individual components of the complex mixture[4]. This knowledge permits one to gain a better understanding of the location and function of each component in the complex mixture.

EXPERIMENTAL

Analytical temperature-rising elution fractionation

Fractionation of the resins was done by temperature-rising elution fractionation (t.r.e.f.)[4]. This technique consists of dissolving the sample in trichlorobenzene (TCB) at a concentration of 0.007 g cm^{-3} at 140°C. This solution is deposited on a steel column (250 mm x 10 mm i.d.) packed with an inert support, Chromosorb P. The column is then capped and cooled to room temperature at 1.5°C h^{-1} over about 3 days. The column is then connected into a system through which TCB is pumped at 2.0 ml min^{-1} while the temperature is increased at 20°C h^{-1}. The species eluting from the column are detected with an i.r. detector set at a detection wavelength of 3.41 μm (C–H stretch). The eluting species can be trapped independently in fractions as a function of elution temperature. Only a very small mass in each fraction can be obtained in this primarily analytical technique.

Preparative temperature-rising elution fractionation

In order to collect large fractions of the fractionated resins, a preparative t.r.e.f. apparatus was constructed. The construction and operation of a similar version of this apparatus has been described in detail, previously[5]. It is shown in *Figure 1*. The polymer is dissolved in TCB and cooled slowly as in the analytical t.r.e.f. procedure. The cooled polymer and solvent are then introduced into the chamber of the apparatus in *Figure 1* and heated slowly in incremental steps of temperature. Fractions are removed from a valve at the bottom of the apparatus. The polymer is recovered by evaporating the TCB solvent and drying thoroughly in a vacuum oven.

In order to facilitate the preparative-scale fractionation, the soluble polymer, which was primarily the EPR, was removed as a room-temperature-soluble prefraction in a preliminary fractionation step. The preliminary fractionation step was done as follows: The impact copolymer (PP/E-1) was dissolved at a concentration of 5.10 g in 250 ml of spectroscopic-grade 1,2,4-trichlorobenzene (TCB). Dissolution was attained at approximately 160°C with gentle stirring. The solution was allowed to cool to room temperature and the precipitated polymer was recovered by centrifugation and filtration. The soluble polymer remained in TCB solution at room temperature. This procedure was repeated two additional times on the TCB-insoluble polymer to remove exhaustively all soluble polymer. The soluble polymer was recovered by evaporative stripping of the TCB solvent and drying in a vacuum oven. The soluble polymer was 15.3 wt% of the original impact copolymer. Only the insoluble polymer fraction was introduced into the preparative fractionation apparatus in *Figure 1*.

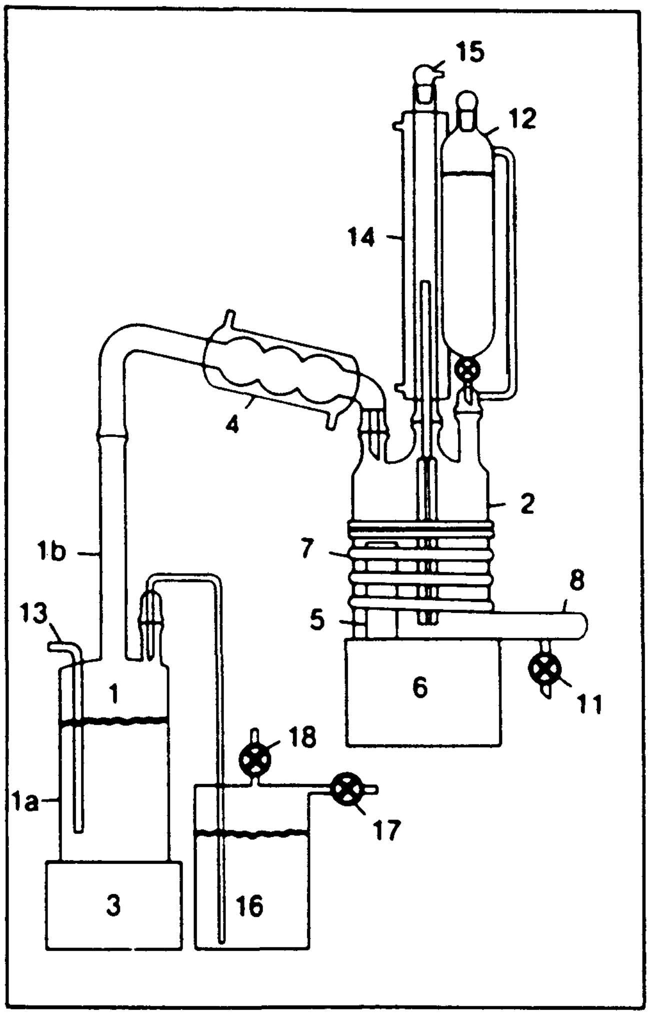

Figure 1 Schematic diagram of the increasing-temperature sequential extraction or preparative t.r.e.f. apparatus. The parts of the apparatus are as follows: (1) distillation chamber consisting of a boiler (1a) and a refluxing column (1b); (2) sample fractionation chamber; (3) hot plate to boil solvent; (4) tap-water-cooled condenser; (5) nickel–chromium wire gauze baskets; (6) hot plate to heat solvent to within 10°C of desired temperature; (7) heat tape to raise temperature to within ±0.2°C of set point; (8) extension tube; (11) PTFE stopcock for aliquot removal; (12) addition funnel for replenishing stock antioxidant solution; (13) nitrogen gas entrance tube; (14) 10°C cooled condenser; (15) nitrogen gas exit fitting to glycerin trap; (16) addition chamber; (17) nitrogen pressure valve; and (18) pressure relief valve

Thermal analysis

The thermal behaviour of the materials studied in this work was determined on a DuPont 990 differential scanning calorimeter. Samples of 5–10 mg were sealed in aluminium sample pans. The temperature was programmed at 10°C min^{-1}. Other parameters used were according to the typical DuPont 990 operating procedure.

^{13}C nuclear magnetic resonance

^{13}C nuclear magnetic resonance was done on a JEOL FX-90Q n.m.r. spectrometer. Typical conditions were: 300 scans, 90° pulse angle, 10 s pulse delay (ca. 1 h scan accumulation) and 10 mm tubes were used for relatively small sample mass (ca. 25–50 mg). Samples were swelled with a minimum volume (ca. 1 ml) of TCB. Data were handled according to standard techniques[6].

Materials

The impact copolymer characterized in this work was a commercial impact polypropylene copolymer with a melt flow rate $MFR = 6$ and designated PP/E-1.

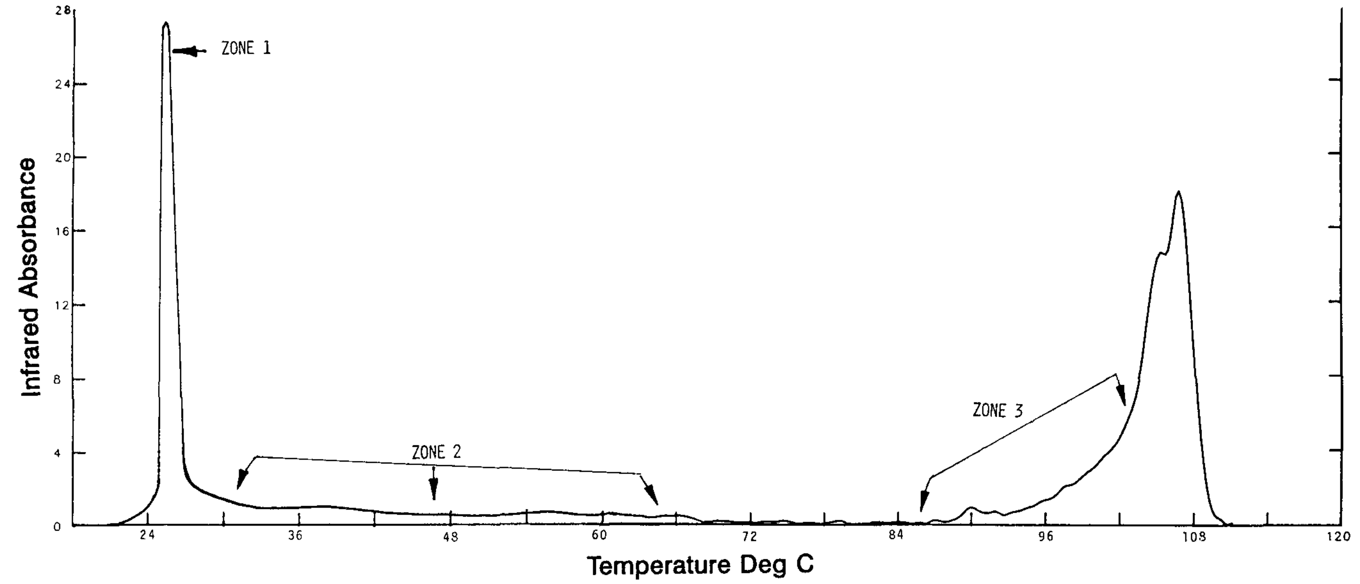

Figure 2 Analytical t.r.e.f. of the whole commercial impact grade polypropylene copolymer (PP/E-1). Elution temperature range designations are defined later in the text and in *Figure 9*

RESULTS

The molecular structure of commercial impact polypropylenes, which are typically produced in multi-reactor systems, has been rarely reported in the literature. The primary reason for this scarcity of microstructural data on commercial impact polypropylene resins is the difficulty of separating the many different components of these complex mixtures. Identification and characterization of the components in the unfractionated whole polymer is presently not possible, if a definitive analysis is required. One of the few studies in the literature reported on the fractionation of impact polypropylene copolymers into two fractions, a xylene-soluble fraction and a xylene-insoluble fraction[7]. The xylene-soluble fraction was found to contain ethylene–propylene copolymer. The xylene-insoluble fraction was found to contain isotactic polypropylene homopolymer and a small amount of polyethylene. No evidence was seen for ethylene-to-propylene linkages due to block or graft ethylene-to-propylene sequences. Analysis was done by d.s.c. and ^{13}C n.m.r.

The analytical t.r.e.f. elution pattern for the impact polypropylene copolymer studied in this work is shown in *Figure 2*. This impact copolymer (PP/E-1) was fractionated in a preliminary step to remove the EPR component. The remainder of the polymer was analysed by analytical t.r.e.f. and this is shown in *Figure 3*. It can be seen that *Figure 3* is similar to *Figure 2*, except that the low-temperature-eluting EPR component is absent from *Figure 3*. The polymer in *Figure 3* was fractionated by preparative t.r.e.f. and separated into 12 fractions. The analytical t.r.e.f. chromatograms of each of these 12 fractions are shown in *Figures 4–7*. It can be observed in *Figures 4–7* that the approximate peak elution temperatures increase as fraction number increases. The increase in peak elution temperature indicates an increase in the level of crystallinity. However, the analytical t.r.e.f. curves are rather broad and complex, and display significant overlap between fractions. This is indicative of the complexity of the mixture of components in the

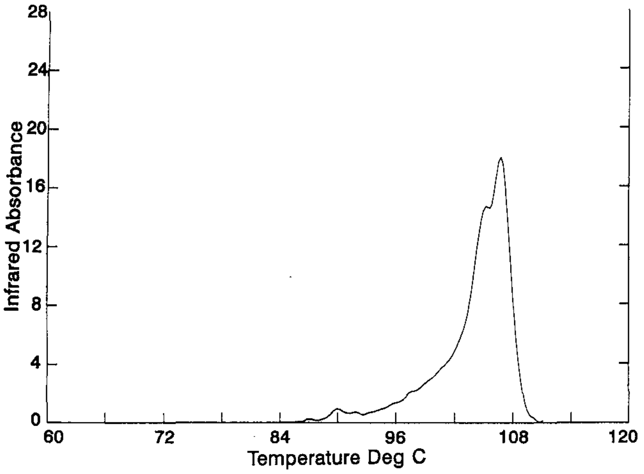

Figure 3 Analytical t.r.e.f. of the TCB fraction, insoluble at room temperature, of the impact-grade polypropylene copolymer

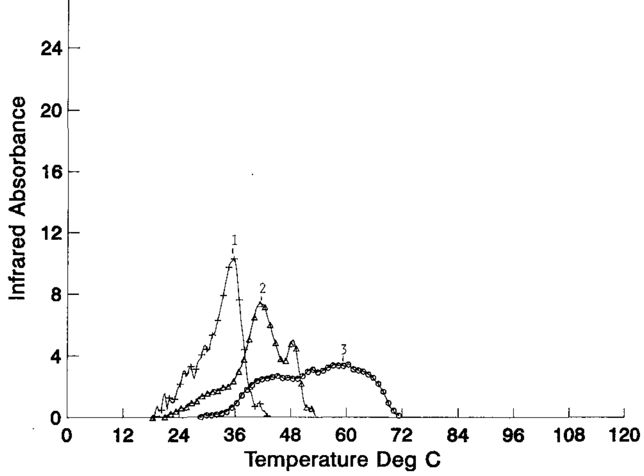

Figure 4 Analytical t.r.e.f.s of preparative t.r.e.f. fractions 1–3

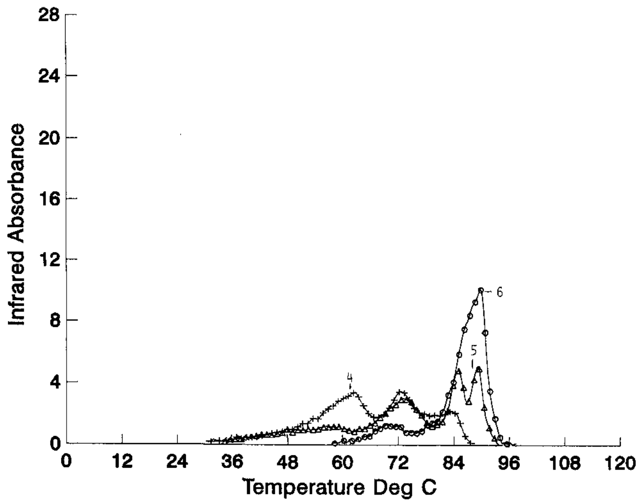

Figure 5 Analytical t.r.e.f.s of preparative t.r.e.f. fractions 4–6

polymer, and also the limited separation efficiency of the preparative t.r.e.f.

The elution temperature ranges of the room-temperature prefraction and the succeeding 12 preparative t.r.e.f. fractions are presented in *Table 1*. These fractions were characterized by differential scanning calorimetry (d.s.c.) and ^{13}C nuclear magnetic resonance spectroscopy (n.m.r.). Copolymer compositions, monomer sequence distributions and stereoregularity of propylene units were determined by ^{13}C n.m.r. by established techniques[6]. Melting endotherms from d.s.c. analysis were used to determine copolymer compositions by comparison with d.s.c. data of copolymers with known composition. These d.s.c. and ^{13}C n.m.r. data were used to determine the chemical composition and stereoregularity of the components of each fraction. *Table 1* shows the major and minor chemical components and stereoregularity of these 13 fractions.

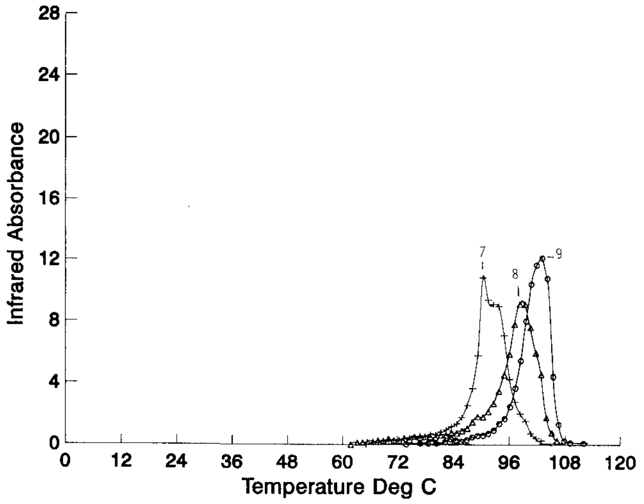

Figure 6 Analytical t.r.e.f.s of preparative t.r.e.f. fractions 7–9

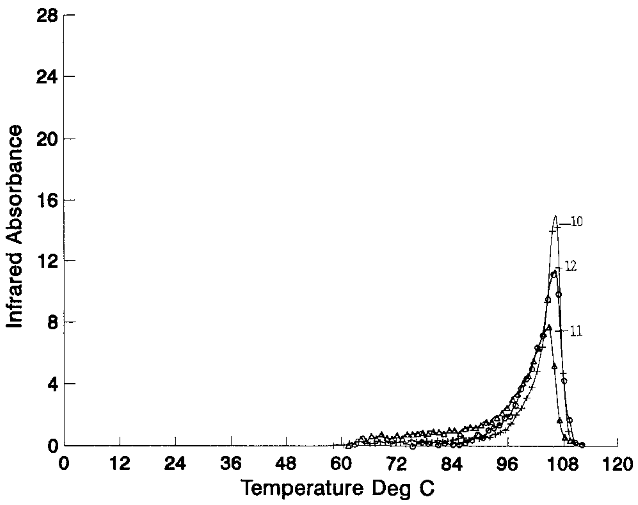

Figure 7 Analytical t.r.e.f.s of preparative t.r.e.f. fractions 10–12

Table 1 Components of fractions from PP/E-1

Elution temperature range (°C)	Fraction number	Fraction wt%	Component Major	 Minor	 Trace
RT	prefraction	15.3	EPR 50/50 C_2/C_3	Atactic polypropylene	
RT	1	0.4	E/P copolymers (negligible crystallinity)		
RT–40	2	1.4	E/P copolymers (negligible crystallinity)	PP[b]	
40–60	3	2.2	E/P copolymers (low crystallinity)	PP[b]	
60–85	4	3.5	LLDPE[c] + PP[b] (crystalline)	PP[b]	
89–90	5	2.1	LLDPE[c] + PP[b] (crystalline)	PP[b]	
90–95	6	1.4	PP[a] + LLDPE[c]	PP[b]	
95–100	7	1.6	PP[a]	PE (linear)[d]	PP[b]
100–105	8	6.1	PP[a]	PE (linear)[d]	
105–110	9	10.8	PP[a]	PE (linear)[d]	
110–115	10	23.1	PP[a]		PE (linear)[d]
115–120	11	13.2	PP[a]		PE (linear)[d]
120–140	12	18.9	PP[a]		PE (linear)[d]

[a] Highly isotactic PP
[b] Low stereoregularity PP
The observation of high- and low-stereoregularity PP may be in different or the same molecular chain(s)
[c] LLDPE refers to PE with a minor amount of propylene comonomer (≤8%)
[d] PE (linear) refers to PE without observable comonomer

In *Table 1*, PP = polypropylene, PE = polyethylene and LLDPE = polyethylene with a small concentration of propylene. The complex structure of impact propylene copolymers can be rationalized on the basis of the sequential polymerization process used to produce these polymers. The weight percentage of each fraction is given in *Table 1*. The polypropylene accounted for about 75 wt%, the EPR about 17 wt% and the other copolymers about 8 wt% of the total.

The results of the characterization of this impact copolymer show that impact copolymers are typically blends of polypropylene homopolymer, EPR (with negligible crystallinity), a high-density-like polyethylene component and crystallizable copolymers of ethylene and propylene. The presence of polypropylene homopolymer is obviously explained by the production of such homopolymer in the first reactor where only catalyst, propylene monomer and hydrogen are present. The ethylene–propylene rubber (EPR) is present because of its deliberate production in the second reactor where ethylene, propylene, catalyst and hydrogen are all present in order to form this copolymer.

However, it is unexpected that crystallizable copolymers of ethylene and propylene are also present besides the non-crystallizable EPR. The reason that the presence of these crystallizable ethylene–propylene copolymers is unexpected is because the monomer ratio of ethylene to propylene in the second reactor is such that a copolymer rich in both ethylene and propylene should be produced. This copolymer is expected to be non-crystallizable and rubber-like, which is the copolymer that is desired. The majority of the copolymer produced in the second reactor, i.e. the EPR, fulfils these requirements.

However, it was initially surprising to find, in addition to the EPR, an apparent spectrum of crystallizable copolymers of ethylene and propylene, which contain small quantities of propylene in an ethylene-rich copolymer and small quantities of ethylene in a propylene-rich copolymer. The purpose of the next section is to give a theoretical basis for the presence of these crystallizable ethylene–propylene copolymers, as well as the EPR.

THEORETICAL DISCUSSION

The theory that describes the expected composition of copolymers is well developed for copolymers made with homogeneous catalyst systems[8]. In the case of copolymers made with heterogeneous catalysts, it is known that these systems often produce heterogeneous copolymers, i.e. copolymers with very broad compositional distributions[9,10].

This behaviour has also been observed in fractionation studies on linear low-density polyethylenes[11]. These LLDPE copolymers are made on similar titanium-based catalyst systems as used in the production of impact copolymers. In these studies, it was shown that the copolymers of ethylene and butene gave not only broad composition distributions, but also multimodal composition distributions. No theory exists for the calculation of the copolymer composition distributions of copolymers made over heterogeneous catalysts. However, the calculation of the theoretical composition distribution function for copolymers made with homogeneous catalyst systems is helpful in understanding the composition of copolymers produced in the secondary reactor in the production of impact copolymers. This copolymer composition distribution function is[8]:

$$W(y)\,dy = \frac{3(\lambda/2a_0b_0k)^{1/2}}{4(1+\lambda y^2/2a_0b_0k)^{5/2}}\,dy \qquad (1)$$

where λ = number-average DP of growing chains, a_0, b_0 = average molar copolymer composition, A, B = molar composition of monomer feed,

$$k = a_0r_2A/B + b_0r_1A/B$$

r_1, r_2 = reactivity ratios, $y = a - a_0 = b_0 - b$ is the composition deviation parameter, and a, b = variable molar copolymer composition.

This function is the composition distribution for all chain lengths and is calculated from some basic polymerization parameters such as feed composition, reactivity ratios, number-average chain length and average copolymer composition. The calculated composition distribution functions for several typical copolymers formed as second reactor products are presented in *Figure 8*. These composition distributions are relatively narrow, but they do exhibit the type of distribution of copolymer species expected for second reactor products. It is anticipated that the actual composition distributions of the second reactor product are much broader than those presented in *Figure 8*. This is because heterogeneous catalysts may contain a spectrum of sites and processes in contrast to

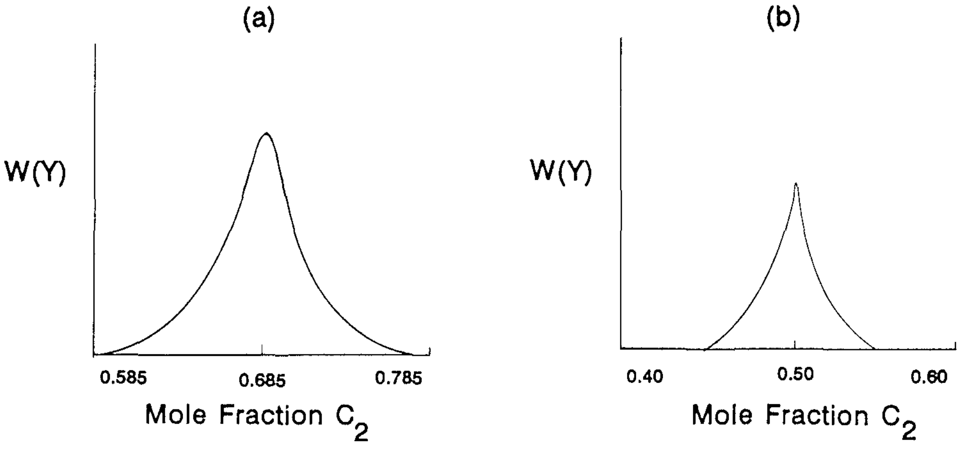

Figure 8 Composition distribution functions (equation (1)) for ethylene–propylene copolymers containing an average mole percentage of ethylene (C_2) of (a) 68.5% and (b) 50%

homogeneous catalysts[10]. However, the distributions presented in *Figure 8* are useful for qualitatively demonstrating the effect of these distributions on the structure of the copolymers produced.

DISCUSSION

Figure 9 shows a qualitative representation of the broad composition distribution that was observed for the second reactor in the production of impact copolymers. The important point to illustrate in *Figure 9* is that the central portion highlighted with cross-hatching represents copolymers that contain a large fraction of ethylene and propylene and, therefore, are expected to be rubber-like and exhibit negligible crystallinity. The extremities of the curve, on the other hand, represent copolymers that are rich in one of the monomers with only a small fraction of the other monomer. These copolymers would be expected to be semicrystalline. *Figure 2* shows the temperature ranges in *Figure 9* in which the various polymers elute in the t.r.e.f. chromatogram of the impact copolymer. It has been observed in these t.r.e.f. chromatograms that the copolymers of ethylene and propylene elute from the chromatograph in two distinct regions. The EPR elutes immediately at room temperature. On the other hand, the crystallizable ethylene–propylene copolymers elute just before the elution of the propylene homopolymer. The order of the elution of these copolymers from the t.r.e.f. is governed by the melting point of the crystals as described by the Flory equation[12].

Previously, it was unclear why there should be effectively two regimes of copolymers structure observed in the t.r.e.f. fractionation process. However, now it is clear, by consulting *Figure 9*, that this is to be expected because in the central region of the copolymer distribution are rubber-like copolymers that elute at room temperature in the t.r.e.f. The copolymers represented by the extremities of the curve in *Figure 9* are semicrystalline and, therefore, are expected to elute at a much higher temperature from the t.r.e.f., as observed in *Figure 2*.

This behaviour was substantiated by fractionating an EPR synthesized under conditions typical of the second reactor but without any propylene homopolymer present. *Figure 10* shows the t.r.e.f. chromatogram for this EPR. It can be seen that both an EPR eluting at room temperature and a small peak around 85–105°C are observed. This small hump, at higher temperature, would appear as a shoulder on a large polypropylene peak in the t.r.e.f. This can be observed by consulting *Figure 2* where the shoulder is identified as zone 3. The copolymers that elute around 85–105°C are much richer in ethylene than the EPR or much richer in propylene than the EPR, so that these copolymers are semicrystalline.

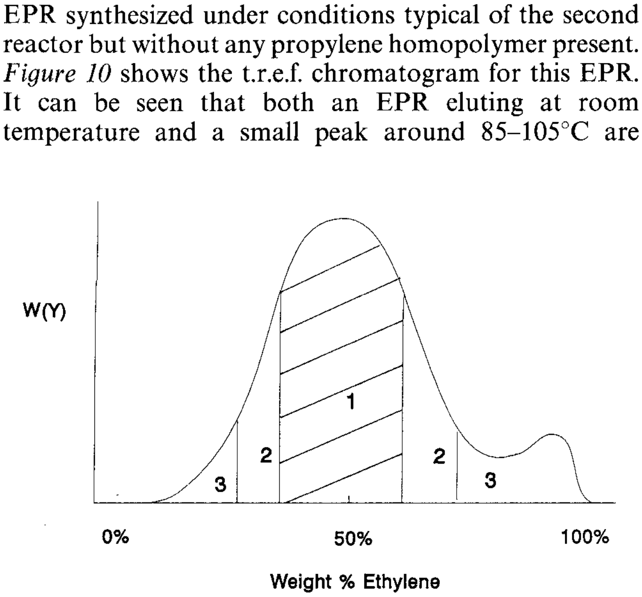

Figure 9 Qualitative representation of the composition distribution function (weight percentage of ethylene) of the second reactor polymer in an impact-grade polypropylene copolymer. Zone designations refer to those indicated in *Figure 2*

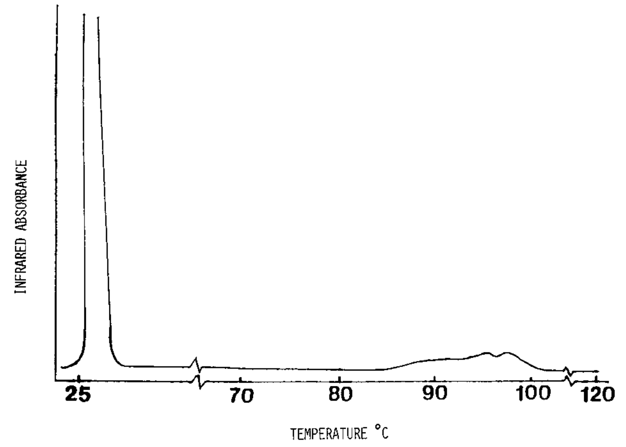

Figure 10 Analytical t.r.e.f. of an EPR made separately under second reactor conditions, i.e. no polypropylene homopolymer present

Table 2 Elution temperature (T_E) ranges for components of impact polypropylene copolymers

	T_E (°C)
Ethylene–propylene rubber (~30–70% ethylene)	25–60
High-density polyethylene	93–95
Isotactic polypropylene	107–109
Atactic polypropylene	25–60

The identity of the major peaks in the t.r.e.f. of the impact copolymer can be determined qualitatively according to the elution temperature of each major species. *Table 2* presents the elution temperatures for species present in impact polypropylene copolymers. The polymers eluting around 93°C were shown by ^{13}C n.m.r. and d.s.c. data to be due to polyethylene containing between 0 and 8 wt% of propylene comonomer. This polymer is due to the ethylene-rich extremity of the broad copolymer distribution shown in *Figure 9*. It is close to the large polypropylene peak, which elutes later, and the mixing of these two species is shown in *Table 1*. As shown in *Figure 2*, copolymers rich in propylene and containing small concentrations of ethylene would elute towards the higher-temperature side of the 85–105°C range. However, a copolymer of propylene with a minor amount of ethylene was not observed, as shown in *Table 1*. A t.r.e.f. of such a copolymer containing 96.1 wt% propylene and 3.9 wt% ethylene was analysed by analytical t.r.e.f. and this is shown in *Figure 11*. It, in fact, does elute at a peak temperature of about 100°C, as predicted. However, copolymers richer in propylene than the EPR were not observed in fraction numbers 2–7 (*Table 1*). These copolymers are represented on the left (low-ethylene) side of the curve in *Figure 9*.

The polypropylene homopolymer, itself, exhibits a distribution of elution temperatures over the temperature-rising elution fractogram. In fact, the polypropylene elutes over the entire fractogram. This is due to the tacticity distribution of this polymer. The tacticity

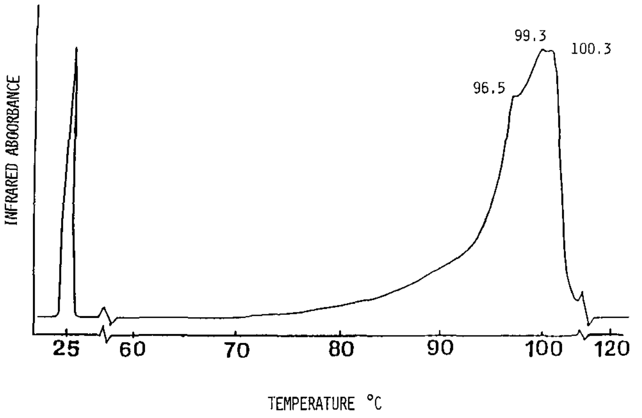

Figure 11 Analytical t.r.e.f. of an ethylene–propylene copolymer containing 3.9 wt% ethylene

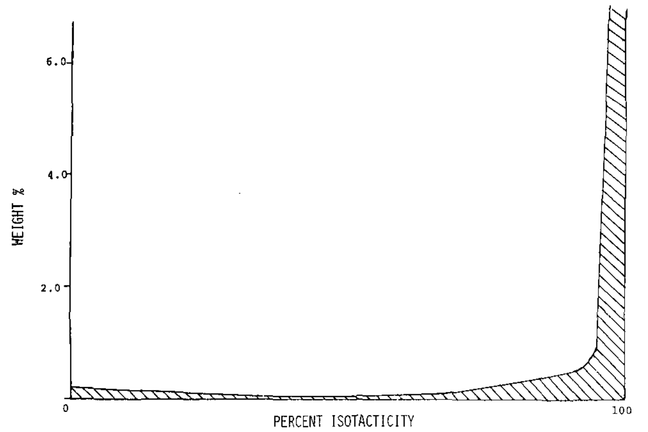

Figure 12 Weight percentage *versus* percentage isotacticity as determined by ^{13}C n.m.r. for polypropylene homopolymer in the impact-grade polypropylene copolymer

distribution of the polypropylene homopolymer component is given in *Figure 12*. The tacticity of the polypropylene was determined according to the well known ^{13}C n.m.r. technique[6,13]. The tacticity distribution for a polypropylene homopolymer made independently of an impact copolymer is essentially identical to that shown in *Figure 12*.

The elution temperatures from the t.r.e.f. of the various components of a PP impact copolymer are related to the chemical structure of these components in a rather complex manner. The superposition of the elution temperature ranges for the EPR, the semicrystalline E/P copolymers and the tacticity-variable polypropylene homopolymer (atactic to highly isotactic) yields the complex temperature-rising elution fractogram shown in *Figure 2*. The identification of the various components was made possible by the previous preparative fractionation followed by fraction characterization. These fractionations further showed that the major species, viz. the EPR, the highly ethylene-rich polymer and the highly isotactic polypropylene copolymer, could be separated into discrete fractions. This proved that these species were not linked together as blocky copolymers. This was in agreement with the results of the study of Vernon[7].

CONCLUSIONS

It was shown that the impact polypropylene copolymer PP/E-1 was composed of about 75 wt% of a highly isotactic polypropylene, which forms the continuous matrix. An ethylene–propylene rubber (EPR) comprised about 17 wt%, which has been shown to exist primarily as a discrete phase-segregated particle dispersed in the polypropylene matrix in similar systems[2]. The balance of about 8 wt% was comprised of partially crystalline ethylene–propylene copolymers. A major component of the partially crystalline ethylene–propylene copolymers was an ethylene-rich copolymer containing no observable propylene up to 8 wt% of propylene comonomer.

The t.r.e.f. technique provides a powerful tool to separate complex mixtures of polymers of dissimilar physical (stereoregularity) and chemical structure. The separated components may then be conveniently characterized, thereby providing an understanding of the detailed structure of the complex mixture. Such an understanding is extremely difficult to deduce from the unfractionated mixture.

This study provides a detailed structural characterization of an impact polypropylene copolymer. The function of the components of the mixture may be deduced from this *a priori* structural analysis. The detailed structure of the impact copolymer would be difficult to anticipate based on synthesis conditions alone.

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