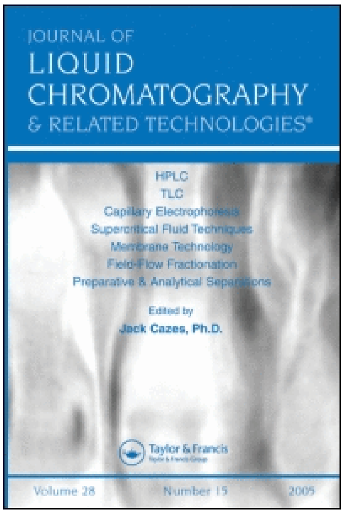

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TEMPERATURE RISING ELUTION FRACTIONATION (TREF) CHARACTERIZATION OF POLYPROPYLENE COPOLYMERS

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ABSTRACT

The fractionation by temperature rising elution fractionation (TREF) of poly(propylene–ethylene) copolymers containing a minor fraction of ethylene was described. A method was developed to determine the ethylene concentration distribution in these copolymers. A poly(propylene–ethylene) copolymer containing 29% wt. ethylene was fractionated by preparative TREF. The fractions were analyzed by analytical TREF, and by ^{13}C NMR spectroscopy to determine the average ethylene concentration in each fraction. A calibration curve relating analytical TREF elution temperature and ethylene concentration was established. It was shown that the weight–average TREF elution temperature was the appropriate average elution temperature to correlate with the weight percent ethylene determined by ^{13}C NMR spectroscopy. This calibration curve was used to obtain the ethylene concentration distribution for a series of poly(propylene–ethylene) copolymers from their analytical TREF elution temperature chromatograms. The average ethylene concentration was calculated from these ethylene concentration distributions and found to be in good agreement with the ethylene concentration determined by ^{13}C NMR. Extrapolation of the calibration curve to 0% ethylene yielded a predicted analytical TREF elution temperature of 108.7°C, which was in excellent agreement with the experimental elution temperature for isotactic polypropylene of 108.7°C.

INTRODUCTION

The development of polymeric materials has increasingly been in the direction of more complex mixtures of polymers. This has emphasized the need for methods to separate the components of such mixtures, and to fractionate component polymers in order to reveal their structural distribution by subsequent analysis and characterization. For example, a formulation of A, B, C, etc. polymers can be separated into each polymer type in order to gain an understanding of the basic composition of the formulation. Each polymer type can be further fractionated into a sufficient number of narrow fractions based on chemical composition in order to gain an understanding of the copolymer composition distribution, stereochemical distribution, monomer sequence distribution, etc. Separations and fractionations of these types have been accomplished by a variety of techniques. However, the technique which has emerged as that of choice is temperature rising elution fractionation (TREF). This technique has been highly developed for both analytical and preparative fractionations over the last 40 years with the major developments occurring during the last 15 years.[1]

The TREF technique is based on the crystallizability of the polymer for the purpose of achieving a compositional separation of molecular species. It is composed of two basic steps. In the first step a very slow crystallization is done to predispose the molecular species to sequential elution from low to high crystallizability. In the second step the crystallized sample is loaded onto a steel column through which a good solvent is passed, as the temperature is uniformly increased. When each molecular species is subjected to its melting temperature in the presence of the solvent, it melts and rapidly dissolves, and elutes from the column to be detected by a concentration detector. The separation is based on composition, as the major determining parameter of crystalizability, and is little influenced by molecular weight for high polymers. A recent review considers details of the technique.[1]

The TREF technique has been frequently applied to the fractionation of poly(ethylene–α–olefin) copolymers, which are rich in ethylene, in order to determine the short–chain branching distribution (SCBD).[1] The TREF technique was used to elucidate the structure of such ethylene copolymers.[2–4] Other applications have been to the determination of the composition distribution of low density polyethylene, ethylene–vinyl acetate copolymers and polypropylene, as discussed in the review by Wild.[1] The structure of a high impact strength ethylene/propylene copolymer was comprehensively determined with the use of preparative and analytical TREF, as the central techniques for separating and characterizing the components of this complex mixture of copolymers.[5] In that work the components of the impact poly(ethylene–propylene) were separated by preparative TREF and identified as isotactic polypropylene, essentially amorphous ethylene/propylene rubber (EPR), polyethylene with a small fraction of propylene comonomer and a distribution of poly(ethylene–propylene) copolymers with partial crystallinity. Further, analytical and preparative TREF were used to fractionate and subsequently characterize the stereoregularity distribution of the polypropylene homopolymer and the chemical structure distribution of the EPR and semicrystalline poly(ethylene–propylene) copolymers.

The purpose of this work was to develop additional applications of the TREF technique. Specifically, the characterization of ethylene/propylene copolymers was extended to the fractionation of statistical copolymers of ethylene and propylene in order to determine the distribution of ethylene over all copolymer chains.

EXPERIMENTAL

Materials

A series of commercial poly(propylene–ethylene) copolymers with a small fraction of ethylene comonomer and a commercial isotactic polypropylene homopolymer were used in this study. Relevant data are given in Table 1 for these polymers.

Preparative TREF

Large fractions of the resin sample E/P–A were obtained by preparative TREF. The apparatus and procedure have been described elsewhere.[5] Specifics of

TABLE 1

Properties of Random Polypropylene Copolymers and Polypropylene Homopolymer.

	Ethylene* % wt	$\bar{M}_n$ x 10^{-4}	$\bar{M}_w$ x 10^{-4}	Calculated** Ethylene %
E/P–A	2.9	5.6	40.0	2.8
E/P–B	2.3	4.9	40.9	1.9
E/P–C	3.0	3.0	20.5	3.1
E/P–D	3.2	4.7	27.9	2.9
PP	0	–	–	–

*^{13}C NMR, precision is ± 0.2% wt.
** From equation 6, using Te (w)

the procedure used in this work were as follows. The resin was dissolved at a concentration of 4.0 g in 600 ml p–xylene and solution achieved at 130°C with gentle stirring. The solution was cooled in a programmable oil bath at –5°C/hr from 120°C to room temperature. This precipitate suspended in the p–xylene was poured into 100 ml of cold acetone to complete the precipitation of all polymers. The precipitate was slurried with about 35 g of diatomaceous earth, filtered and dried to recover a free flowing solid. This was introduced into the preparative TREF unit as shown schematically in Figure 1. P–xylene solvent was introduced, also. Fractions were taken by incrementally raising the temperature of the p–xylene while gently stirring the solvent in order to dissolve all polymers which melt and dissolve at the specified fraction temperature. A period of 1.5 hours was employed for complete dissolution. Temperature was very carefully controlled to ± 0.5°C of the specified temperature. The fractions were then removed at the specified temperature through a valve at the bottom of the apparatus. The polymer fractions dissolved in xylene were then poured into 1500 ml of cold acetone, the precipitate was filtered and dried to constant weight. The fractionation temperatures and fraction weights of the E/P–A resin are given in Table 2. The recovery was 93% by weight.

Analytical TREF

Polymer samples were dissolved at a concentration of 2 to 5 mg in 10 ml of p–xylene and solution achieved at 130°C with gentle stirring. The solutions were

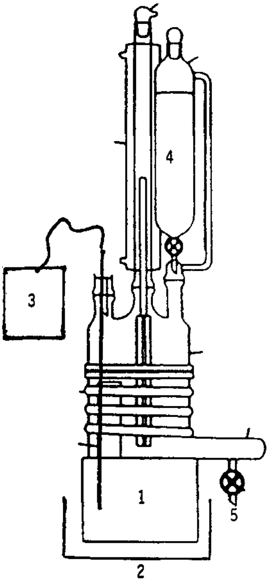

Figure 1 – Preparative temperature rising elution fractionation apparatus: 1. sample chamber, 2. heating mantle, 3. temperature sensor, 4. solvent reservoir, and 5. take–off valve.

TABLE 2

Characterization Data on the Preparative TREF Fractions of the Random Polypropylene Resin E/P–A

Fraction Number	Maximum Preparative TREF Temperature	Fraction Weight Percent	Weight Percent Ethylene ^{13}C NMR E	Molecular Weight x 10^{-4}		Weight Average Analytical Elution Temperature Te(w)°C	Calculated Weight Percent Ethylene From Equation 6
				$\overline{M}n$	$\overline{M}w$		
1	86	35.7	4.9	2.8	17.4	83.6	5.2
2	90	9.4	4.6	2.2	4.8	90.0	3.8
3	94	8.5	3.0	3.2	9.6	92.8	3.3
4	98	15.5	2.0	6.7	22.1	97.7	2.3
5	104	24.0	1.7	10.8	46.2	101.0	1.6
Whole Polymer	–	–	2.9	5.6	40.0	95.3	2.8

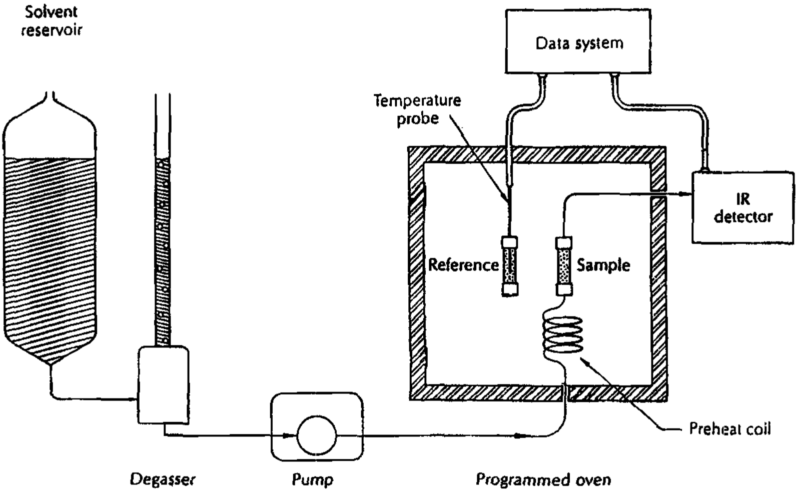

Figure 2 - Analytical temperature rising elution fractionation apparatus.

cooled in a programmable oil bath at –5°C/hr from 120°C to room temperature. Then 10 ml of cold acetone was added to the precipitated polymer in p–xylene and shaken gently. About 1 g of diatomaceous earth was added to the slurry and the entire contents were quantitatively loaded onto a steel column (250 mm x 10 mm i.d.). The column was connected into a system as shown schematically in Figure 2. Orthodichlorobenzene was pumped through the column at a rate of 3.0 ml/min while the temperature was increased at 4°C/min. The species eluting from the column were detected with an infrared detector set at a detection wavelength of 3.41μm (C–H stretch). The temperature inside a reference column with no sample but packed identically to the sample column was monitored with a temperature probe. This temperature was taken as that in the sample column. This procedure was expected to account for any temperature lag between the oven temperature and that inside the sample column and to give an accurate indication of the temperature inside the sample column. The detector response and elution temperature were digitized and stored in a computer. Subsequent computations were performed on digitized data.

^{13}C Nuclear Magnetic Resonance

^{13}C nuclear magnetic resonance was done on a Varian Gemini 200 super–conducting NMR system. Typical conditions were: 300 scans, 90° pulse angle, 10 sec. pulse delay (ca. 1 h scan accumulation); 10 mm tubes were used for relatively small sample mass (ca. 400 mg). Samples were swelled with a minimum volume (ca. 2 ml) of TCB. Data were handled according to standard techniques.[6]

Gel Permeation Chromatography

Molecular weight distributions were determined on a Waters 150C GPC at 140°C in trichlorobenzene.

RESULTS AND DISCUSSION

Modern polymer formulations routinely produced by the plastics industry have tended to become more complex in the number of chemically different polymer components and the structural distributions of each of the polymer components. The TREF technique is ideally suited to the compositional separation of the components and to fractionate the individual components to reveal their structural distribution. The TREF technique is effectively insensitive to molecular weight variations for polymer species with $>10^4$ molecular weight.[1]

Polypropylene and its copolymers represent such a complex array of formulations. In previous work it was shown that polypropylene homopolymer and copolymers were readily separable by TREF.[5] The analytical TREF technique was used to separate the components and to tentatively identify each component by developing a list of elution temperature ranges for a set of known polymer types. Preparative TREF was then used to obtain large fractions of polymer from a series of elution temperature ranges. The fractions were then characterized to confirm the identity of the components and the structural distributions within each component, as previously indicated by the analytical TREF.

Currently, the only calibration of analytical TREF is for the determination of the comonomer distribution [i.e. the short–chain branching distribution (SCBD)] in poly(ethylene–α–olefin) copolymers which are rich in ethylene.[1] Other common copolymers related to these are so–called random polypropylenes, as they are known in the industry, which contain a minor amount (ca. 1–5% weight) of ethylene comonomer and are known to be statistical copolymers. These random polypropylenes are used in a variety of applications, including film, sheet, bottles, etc. The distribution of ethylene over all copolymer chains is an important variable in the determination of the polymers performance in such properties, such as stiffness, impact, hardness, hot–tack, etc. The TREF technique may be used to determine the ethylene distribution over all copolymer chains, if a calibration of ethylene concentration as a function of TREF elution temperature were available.

The analytical TREF elution temperature chromatogram for random polypropylene resin E/P–A is shown in Figure 3. The elution temperature range is from approximately 75°C to 105°C. This broad range of elution temperature implies a rather broad distribution of ethylene concentration over all copolymer chains. The E/P–A resin was fractionated in the preparative TREF into five fractions with the upper fractionation temperature for each fraction as given in Table 2. The fractions were analyzed by ^{13}C NMR and GPC to determine the average weight percent of ethylene and molecular weight for each fraction, and these data are given in Table 2, also.

Each fraction was run in the analytical TREF and the elution temperature chromatograms are presented in Figures 4 and 5. The analytical TREF chromatograms reveal that the preparative TREF fractions tend to be broad and in some cases multimodal. It would be desirable to obtain very narrow fractions, however, a relatively large amount of material (ca. 200–400 mg) is needed for the ^{13}C NMR analysis of each fraction and this would require significantly more preparative fractionation work to be done.

The average weight percent of ethylene in each preparative TREF fraction is known (Table 2). In order to calibrate the analytical TREF it is necessary to

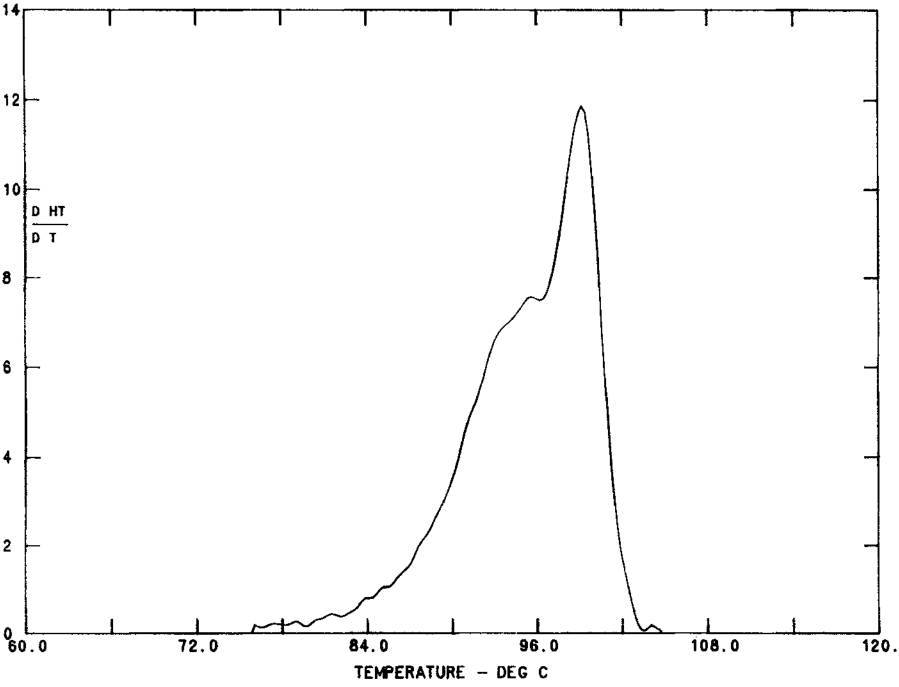

Figure 3 - Analytical TREF temperature chromatogram of random poly(propylene-ethylene) copolymer E/P-A.

determine the correct "average" elution temperature from the analytical TREF curves (Figures 4 and 5). This may be accomplished by making the following two critical assumptions. First, it is assumed that the average weight percent ethylene in the fractions determined by NMR spectroscopy (E) is the summation of the ethylene concentration (E_i) in all concentration "slices" of the distribution (C_i):

$$E = \sum_i C_i E_i \qquad (1)$$

Second, it is assumed that the correlation of analytical TREF elution temperature (T_e) with average weight percent ethylene for the fractions is represented by a straight line equation:

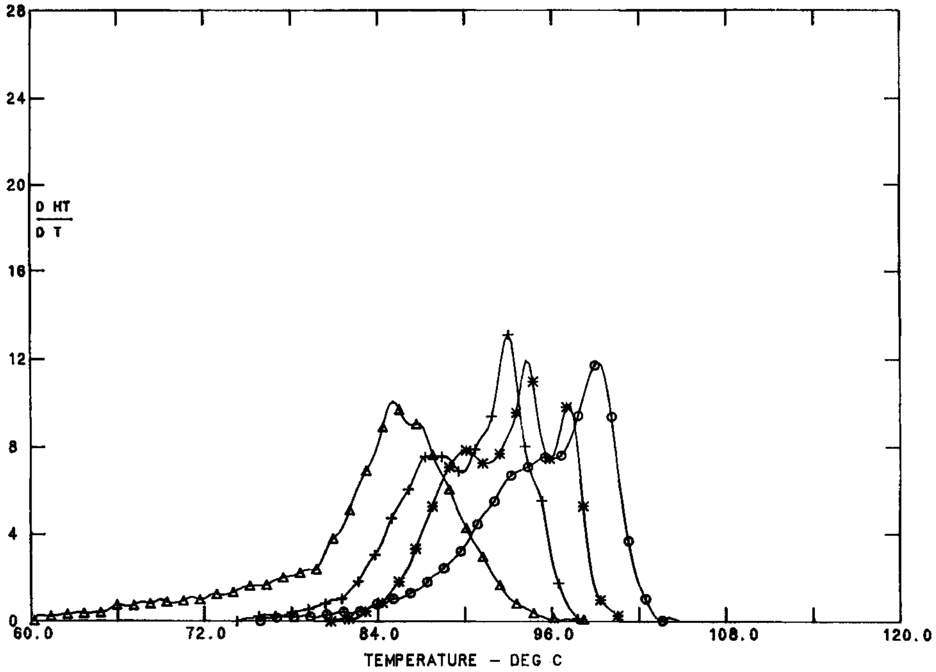

Figure 4 – Analytical TREF temperature chromatograms of preparative TREF fraction 1 Δ, fraction 2 +, fraction 3 ✱, and whole polymer E/P–A O.

$$E = a\,Te + b \qquad (2)$$

where a is the slope and b is the intercept of the straight line. This second assumption limits the calibration curve to a specified range of E values, and it also ignores band–broadening effects in the analytical TREF. If equation 2 is substituted for E_i in equation 1 we obtain:

$$E = \sum_i C_i\,(aTe_i + b) \qquad (3)$$

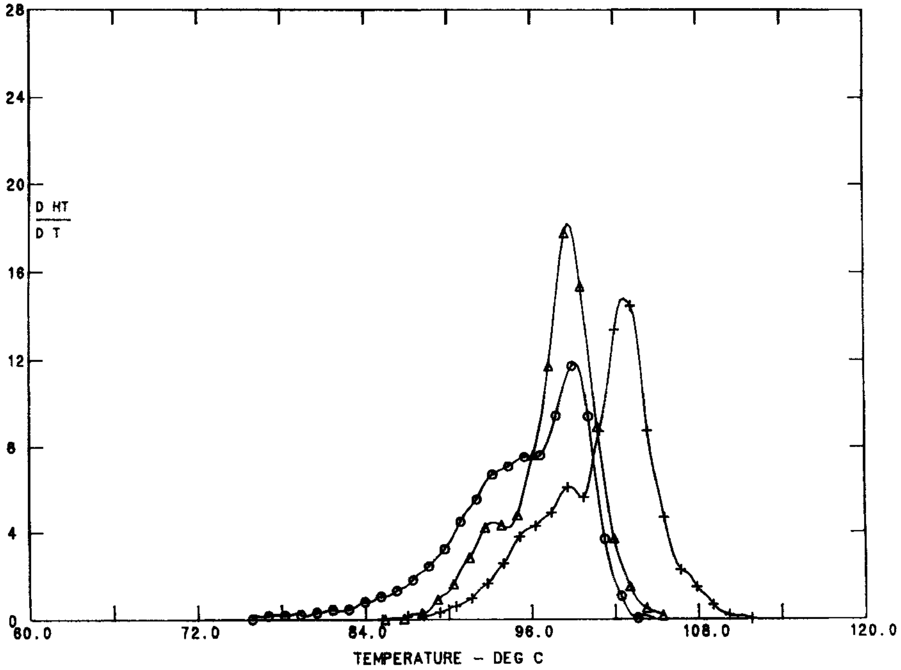

Figure 5 – Analytical TREF temperature chromatograms of preparative TREF fraction 4 Δ, fraction 5 +, and whole polymer E/P–A O.

Expanding equation 3 and dividing by $\sum_i C_i$, which is normalized to unity, yields:

$$E = a \sum_i C_i \, Te_i / \sum_i C_i + b \qquad (4)$$

Equation 4 shows that the average weight percent of ethylene determined by NMR spectroscopy (E) is correlated with the weight–average TREF elution temperature ($T_e(w)$) where $T_e(w) = \sum_i C_i Te_i / \sum_i C_i$. The data obtained from the analytical TREF is in terms of concentration "slices" from the infrared detector (i.e.

heights, H_i, where H_i = absorbance at each point on the elution curve) and an elution temperature (Te_i). Therefore, the weight-average elution temperature is:

$$Te(w) = \sum_i H_i Te_i / \sum_i H_i \qquad (5)$$

The weight-average elution temperature was calculated for each fraction and these are presented in Table 2. The values of average ethylene concentration (E) and weight-average analytical TREF elution temperature ($T_e(w)$) from Table 2 were fitted to a straight line by linear regression in order determine the constants in equation 2 and this resulted in the calibration curve:

$$E = -0.206Te + 22.39 \qquad (6)$$

The correlation coefficient for the linear regression was r = 0.95. The calibration curve is plotted in Figure 6. Equation 6 is the calibration curve for deconvoluting analytical TREF elution temperature chromatograms into ethylene concentration distribution curves. The range of validity of equation 6 is up to about 10% wt. of ethylene. The analytical TREF elution temperature chromatogram of E/P–A in Figure 3 was deconvoluted into the ethylene concentration distribution curve in Figure 7 by the use of equation 6. The weight-average elution temperature (Te (w)) for resin E/P–A was 95.3°C, as given in Table 1. From equation 6 this gives an ethylene weight percent of 2.8% wt. which is in good agreement with that determined by ^{13}C NMR of 2.9% wt. It should be noted that equation 6 implies that at zero weight percent ethylene (polypropylene homopolymer) the elution temperature is Te = 108.7°C. The analytical TREF elution temperature chromatogram for a polypropylene homopolymer (PP) is shown in Figure 8. The peak elution temperature of this narrow peak is 108.7°C in excellent agreement with that calculated from equation 6.

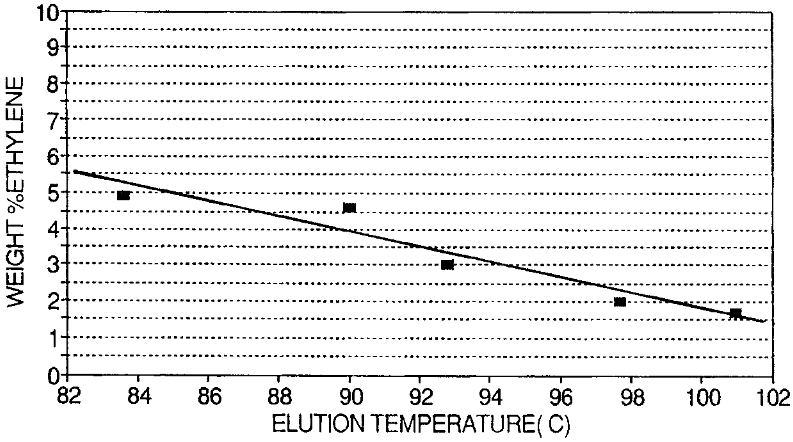

Figure 6 – Calibration curve for analytical TREF relating percent ethylene and TREF weight–average elution temperature.

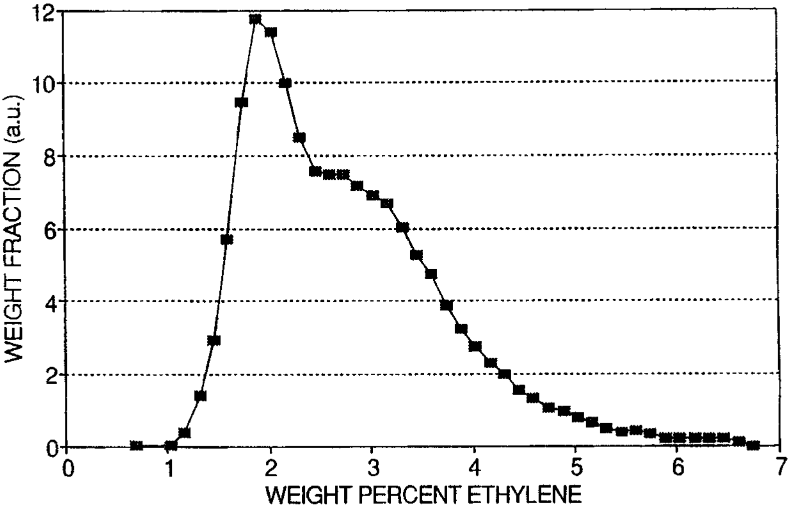

Figure 7 – Ethylene concentration distribution of random copolymer E/P–A.

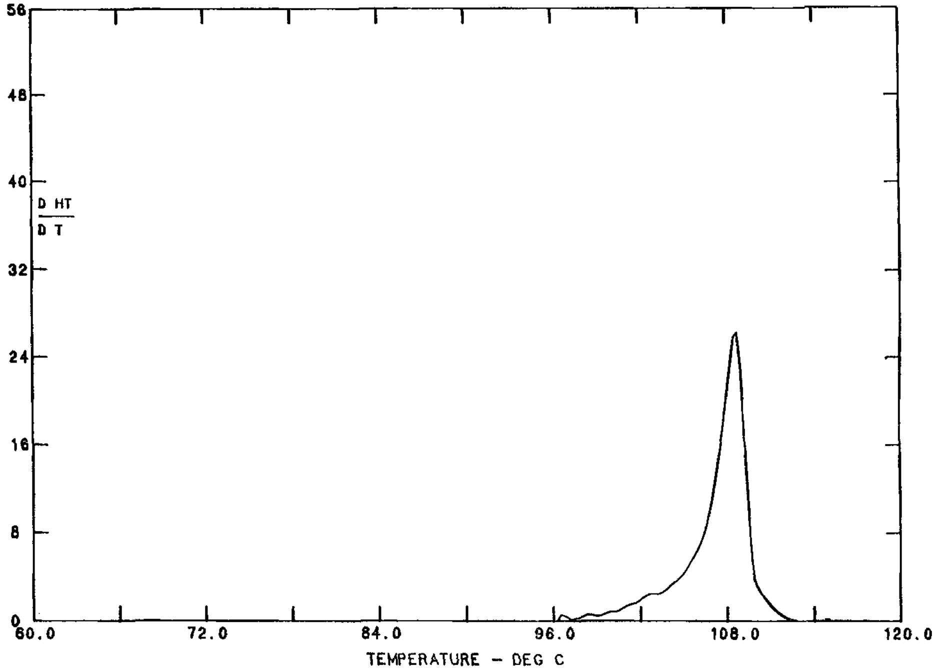

Figure 8 – Analytical TREF temperature chromatogram of isotactic polypropylene.

The analytical TREF elution temperature chromatograms and the ethylene concentration distribution curves, obtained by deconvolution of the chromatograms with equation 6, are shown in Figures 9–11 for random polypropylene resins E/P–B, E/P–C and E/P–D, respectively. It may be observed in Figures 7 and 9–11 that the ethylene concentration distributions of the four random polypropylene resins differ considerably. The weight percent ethylene for random polypropylenes E/P–B, E/P–C and E/P–D were calculated from equation 6 using the weight–average elution temperature, Te(w), obtained from the TREF elution temperature chromatograms, shown in Figures 9–11. These data are presented in Table 1. The agreement between the calculated and experimentally determined NMR values of weight percent ethylene in Table 1 may be seen to be quite good within the precision of the NMR

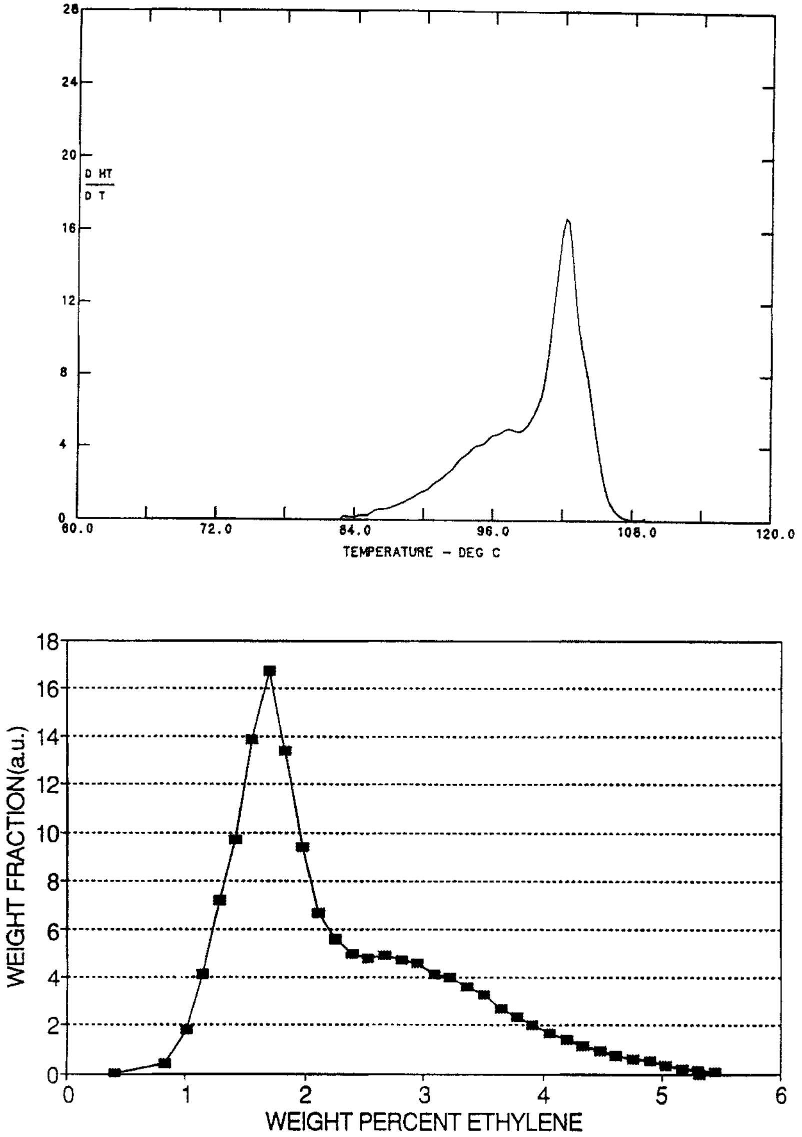

Figure 9 - Analytical TREF temperature chromatogram and ethylene concentration distribution of random copolymer E/P-B.

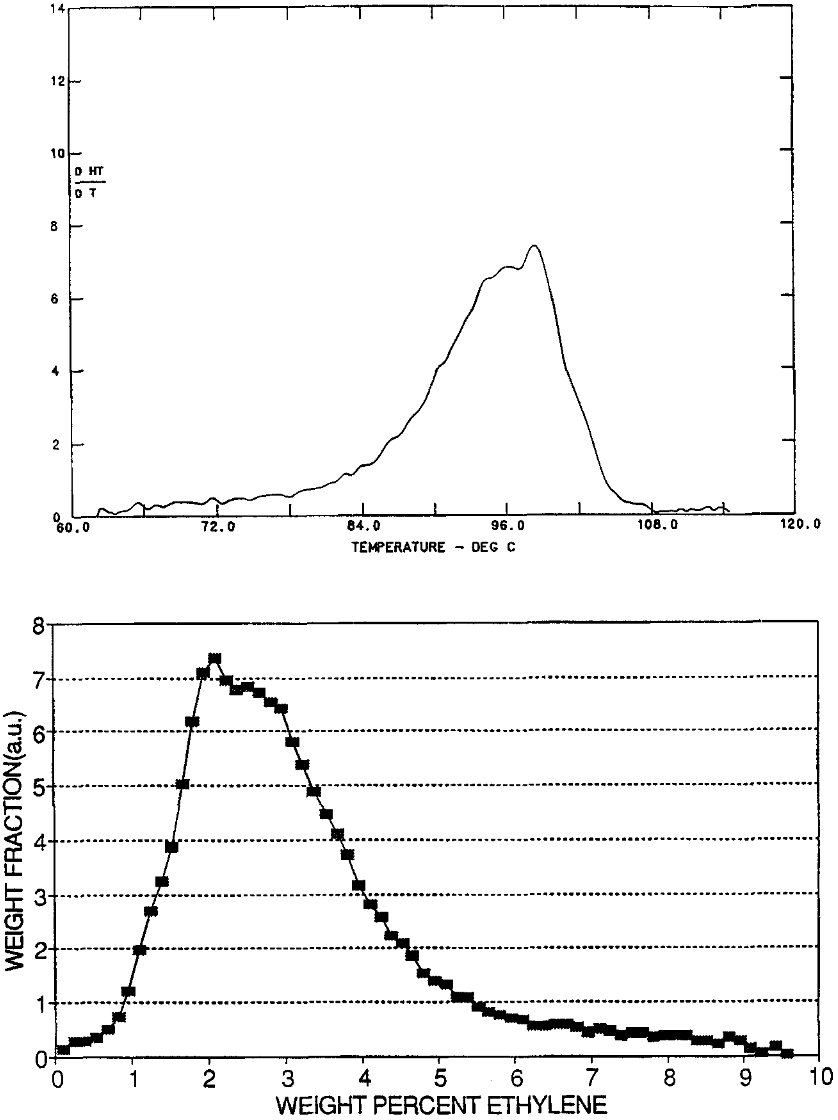

Figure 10 – **Analytical TREF temperature chromatogram and ethylene concentration distribution of random copolymer E/P–C.**

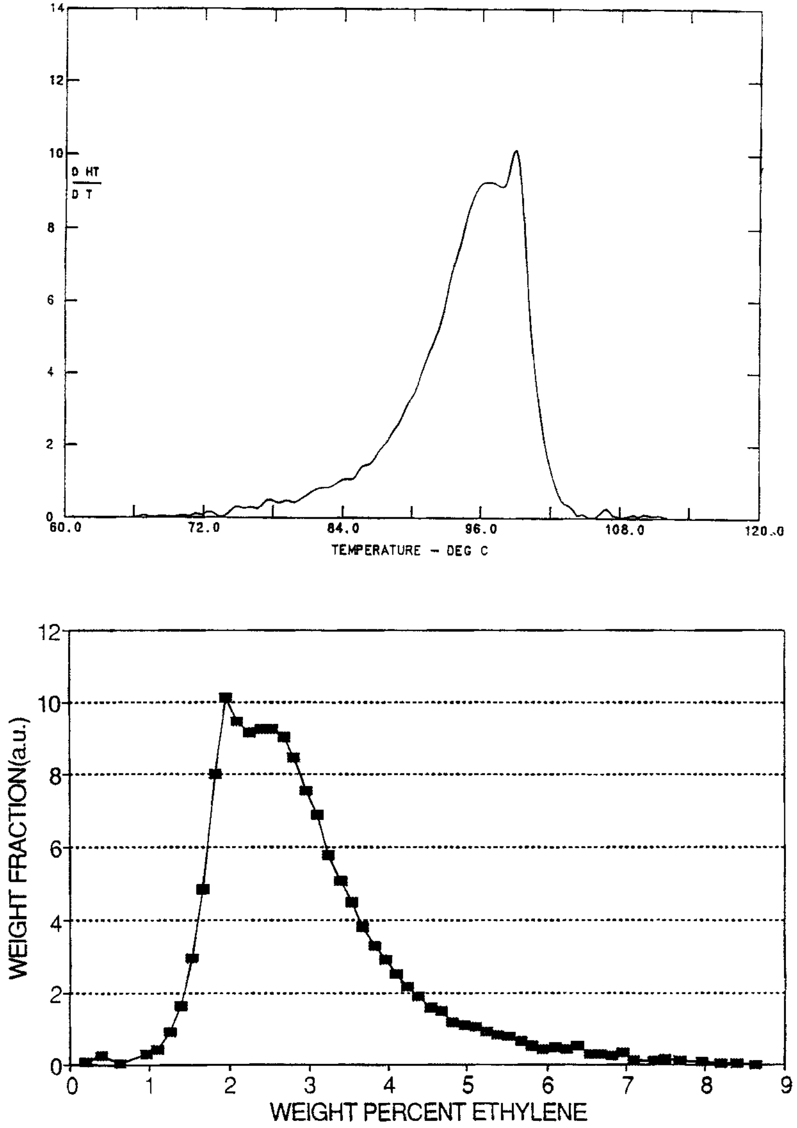

Figure 11 – Analytical TREF temperature chromatogram and ethylene concentration distribution of random copolymer E/P–D.

measurements of ± 0.2% wt. ethylene. The fact that the ethylene content of the random polypropylenes may be recovered from TREF elution temperature chromatograms with the use of equation 6 provides further evidence of the validity of the TREF calibration described herein.

CONCLUSIONS

Application of analytical temperature rising elution fractionation to the composition distribution of polypropylene copolymers was described. In the present work a method was developed to determine the ethylene concentration distribution in poly(propylene–ethylene) copolymers (called random polypropylenes) with a minor fraction of ethylene (ca. 1 to 5 weight percent). A calibration of the analytical TREF was developed correlating elution temperature and ethylene concentration. It was shown that it was the weight–average elution temperature from the analytical TREF chromatogram that correlated with the weight percent ethylene determined by ^{13}C NMR spectroscopy. It should be noted that this also applies to the short–chain branching distribution in poly(ethylene–α–olefin) copolymers; i.e. it is the weight–average TREF elution temperature that correlates with the average short–chain branching in these copolymers. It was also shown that the ethylene concentration distributions of a series of commercial random polypropylene resins were broad and differed in their characteristic shapes. The weight percent ethylene estimated from these distributions was shown to agree with that determined by ^{13}C NMR spectroscopy. The calibration curve was used to predict the TREF elution temperature of polypropylene homopolymer, which agreed well with the experimental value. This indicated that the calibration curve was valid to low levels of ethylene concentration and extrapolation may be used up to about 10% weight of ethylene.

The ethylene concentration distributions of polypropylene containing a minor fraction of ethylene should prove useful in studies of the crystallization behavior of these copolymers in analogy to the use of short–chain branching distributions in crystallization studies of poly(ethylene–α–olefin) copolymers, such as linear low density polyethylene (LLDPE). Such studies of the crystalline morphology of random polypropylene should prove useful for the correlation of the solid–state structure with mechanical properties, such as stiffness, impact, hardness, hot tack, etc.

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