Crystallization Analysis Fractionation: A New Technique for the Analysis of Branching Distribution in Polyolefins

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SYNOPSIS

A new technique to analyze the short-chain branching distribution (SCBD) in linear low-density polyethylene has been developed. The technique referred as crystallization analysis fractionation is based on a stepwise precipitation approach. By monitoring the polymer solution concentration during crystallization, the cumulative and differential SCBD can be obtained without the need of physical separation of fractions. The new technique has been shown to provide similar results to temperature rising elution fractionation but in a shorter time and with a simplified apparatus. It allows the simultaneous analysis of various samples and could also be used for analysis of polypropylene and other semicrystalline polymers that can be fractionated on the basis of crystallizability. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The short-chain branching distribution (SCBD) in a linear low-density polyethylene (LLDPE) resin is a fundamental structural parameter, which, together with the molecular weight distribution, defines the potential performance of an LLDPE material. Considerable effort has been made to understand the bimodal nature in the SCBD of LLDPE resins in terms of catalyst active sites,[1] how to modify the SCBD, and how it affects the end product properties.[2-7]

The analysis of the SCBD in an LLDPE resin, however, is not a simple task, and to achieve proper resolution, fractionation of the polymer is required. The most common technique used is temperature rising elution fractionation (TREF), which was first described by Desreux and Spiegels[8] in 1950, but it has also been the work of Wild and Ryle[2,9,10] in the late 1970s with the development of analytical TREF, which established the technique in the polyolefins industry.

In this report, a new technique is described: crystallization analysis fractionation, which performs the SCBD analysis in a simple manner and with shorter analysis time.

THEORETICAL

The principles of polymer fractionation by solubility or crystallization in solution have been extensively reviewed[11-17] on the basis of Flory–Huggins statistical thermodynamic treatment that accounts for melting-point depression by the presence of solvents, which is expressed as follows:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(\nu_1 - \chi_1\nu_1^2) \qquad (1)$$

where T_m^0 is the melting temperature of the pure polymer; T_m, the equilibrium melting temperature of the polymer–diluent mixtures; ΔH_u, the heat of fusion per polymer repeating unit; V_u and V_1, the molar volumes of the polymer repeating unit and diluent, respectively; ν_1, the volume fraction of the diluent; and χ_1, the Flory–Huggins thermodynamic interaction parameter.

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Although most effort has been devoted to fractionation of homopolymers in terms of molecular weight, a few reviews exist in the field of copolymer fractionation.[18-20] For random copolymers, the classical Flory eq. (21) applies:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln(p) \qquad (2)$$

where T_m^0 is the melting temperature of the pure homopolymer; ΔH_u, the heat of fusion of the homopolymer repeating unit, and p, the molar fraction of the crystallizing unit. Flory[12] showed that eq. (1) reduces to the same form as eq. (2) at very small concentrations of solvent. Thus, noncrystallizing comonomer units, diluents, and polymer end groups all have an equivalent effect on melting-point depression when the concentration of each is low and do not enter into the crystal lattice.

Equation (2) can be simplified by replacing $p = (1 - N_2)$, where N_2 is the molar fraction of comonomer incorporated (noncrystallizing unit), and for low values of N_2, the following holds: $\ln(1 - N_2) \simeq -N_2$; hence:

$$\frac{1}{T_m} - \frac{1}{T_m^0} \simeq \frac{R}{\Delta H_u} N_2 \qquad (3)$$

The validity of eqs. (1) and (2) has been widely debated[11,13,20,22] and new thermodynamic models have been described[17,23-26] for semicrystalline random copolymers and for copolymerized units capable of entering into the crystal lattice.[25,26] However, since the liquid–crystal phase transition is strongly governed by kinetic factors, the fractionation results are influenced mainly by the experimental procedure,[17,27] which has deserved the most attention of researchers devoted to improve the fractionation techniques.[8,9,27] A broad review on crystallization kinetics has been recently published by Fatou.[28]

Fractionation of polyethylene according to composition was described by Desreux and Spiegels[8] using an extraction technique with a single solvent at increasing temperatures. This technique was used with success by Hawkins and Smith[29] and Shirayama et al.,[30] who named the technique "temperature rising elution fractionation."

Separation according to degree of tacticity was achieved by Allen et al.[31] on poly(propylene oxide) and by Kamath and Wild[32] on polypropylene. The authors used a step precipitation procedure from solution at decreasing temperatures. In all the above cases, the separation was practically independent of molecular weight and this has been further supported by the theoretical studies of Huggins and Okamoto[11] and Casassa.[17] In the case of polyethylene, fractionation by crystallization is independent of molecular weight at M_w above 15,000, especially in solution crystallization.[28] Experiments in TREF[2] show that when considering the end groups as noncrystallizing defects fractionation is independent of molecular weight down to M_w 1000. On the other hand, when fractionation is performed at temperatures above the polymer melting point, separation unambiguously occurs on the basis of molecular weight.[33]

CRYSTALLIZATION ANALYSIS FRACTIONATION OF LLDPE

In LLDPE, the incorporation of comonomer into the linear polyethylene chains results in irregularities (side-chain branches) that modify the crystallizability of the polymer. Disregarding the minor influence of molecular weight as discussed above, the solution crystallization of LLDPE will, under proper conditions, segregate crystals according to comonomer-branch content.

Crystallization analysis fractionation uses a unique approach to monitor the solution crystallization of LLDPE that will allow the calculation of the overall SCBD. The analysis is carried out by monitoring the polymer solution concentration during crystallization by temperature reduction. Aliquots of the solution are filtered and analyzed by a concentration detector. In fact, the whole process is similar to a classical stepwise fractionation by precipitation, with the exception that in this new approach no attention is paid to the polymer precipitated but to the polymer that remains in solution.

The first data points, taken at temperatures above any crystallization, provide a constant concentration equal to the initial polymer solution concentration (zone 1 in Fig. 1); as temperature goes down, the most crystalline fractions, composed of molecules with zero or very few branches, will precipitate first, resulting in a steep decrease in the solution concentration (zone 2 in Fig. 1). This is followed by precipitation of fractions of increasing branch content as temperature continues to decrease (zone 3 in Fig. 1). The last data point, corresponding to the lowest temperature of the crystallization cycle, represents the fraction that has not crystallized (mainly highly branched material) and remains soluble.

The top curve in Figure 1 corresponds to the cumulative SCBD when the temperature scale is calibrated and transformed to number of branches/1000 carbons. The first derivative of this curve can

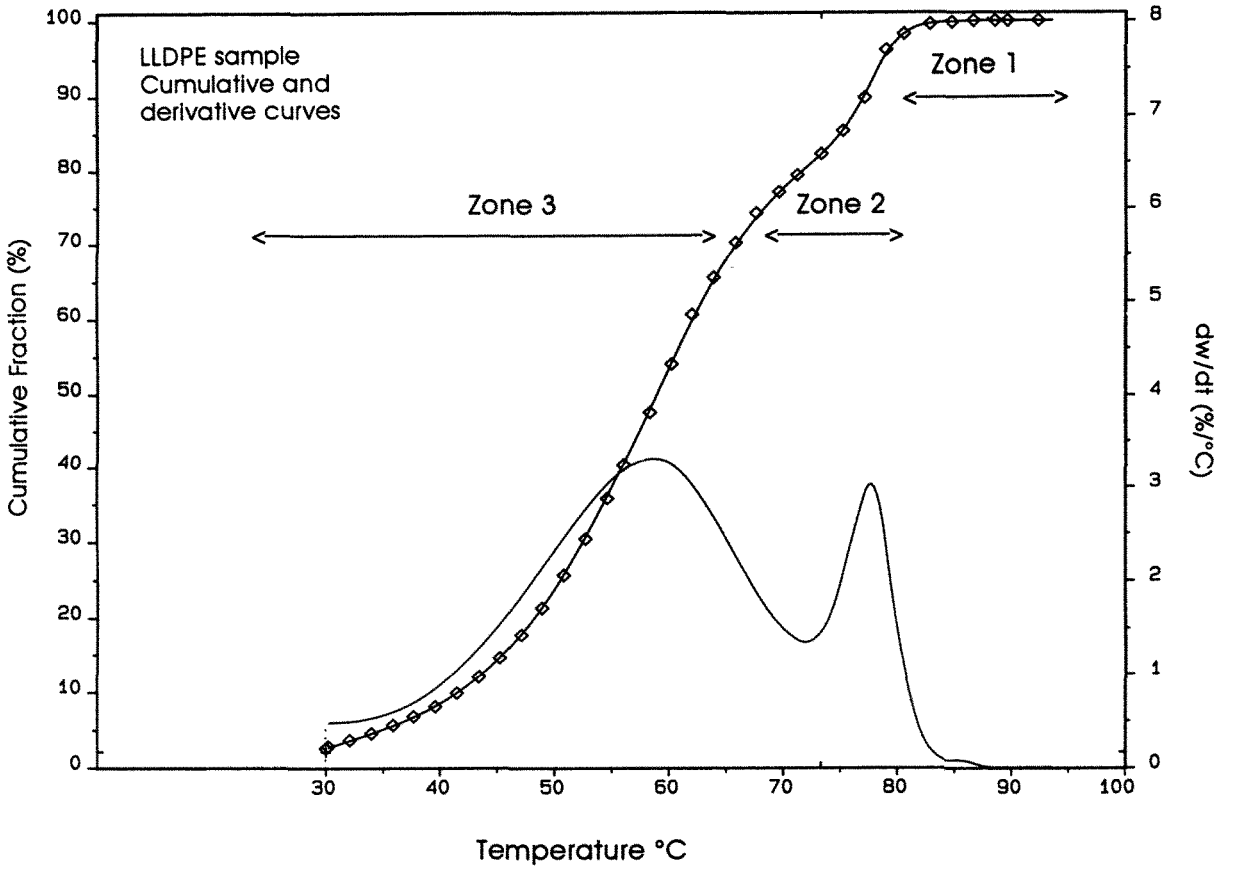

Figure 1 Cumulative and differential SCBD of an LLDPE sample as obtained by crystallization analysis fractionation at 24°C/h crystallization rate.

be associated with the SCBD as shown in Figure 1. With this approach, we are capable of fractionating the polymer and, most important, of analyzing the SCBD in a single crystallization cycle without physical separation of the fractions. The term crystallization analysis fractionation (CRYSTAF) stands for this process.

CRYSTAF AND TREF TECHNIQUE COMPARISON

TREF is a well-established technique for the preparative fractionation of polyolefins and, more specifically, for the analysis of the SCBD in LLDPE. Excellent reviews have been recently published by Wild[34] and Glockner.[35] Both TREF and CRYSTAF fractionate on the basis of crystallizability; TREF, however, does the crystallization on a packing and uses a dissolution (elution) step to perform the final fractionation.

In TREF, the sample is first dissolved in a proper solvent at high temperature and the solution is then introduced into a column containing glass beads; this is followed by a crystallization step at a slow cooling rate during which polymer layers of increasing branch content are deposited on the glass beads. This completes the first temperature cycle, which we can refer to as the *crystallization cycle.* A second temperature cycle is then initiated by increasing the temperature at a slow rate, meanwhile pumping new solvent through the column; the eluent dissolves fractions of decreasing branch content as temperature rises that can be collected (preparative TREF) or the concentration of the solution is continuously monitored to obtain the SCBD (analytical TREF). The term temperature rising elution fractionation derives from this second temperature cycle, referred to here as the *elution cycle.*

At the end of the first temperature cycle (crystallization cycle), crystals have been segregated with information of the whole SCBD. The CRYSTAF technique extracts this information directly during the crystallization process by looking to the solution concentration depression and no column packing is

required; however, no fractions are being obtained with exception of the soluble fraction at the last temperature of crystallization.

EXPERIMENTAL

Crystallization was carried out with the first prototype in stainless-steel columns 2.3 cm i.d. and 15 cm length without any packing material. The columns are held vertically and have a stainless-steel porous frit in the bottom connected to an IR filter-type detector (Wilks 3.5 microns) through a rotary valve. In this experimental setup, the analysis of up to three samples can be carried out simultaneously. The tops of the columns are attached to a nitrogen line with separate on/off valves for each column. A Hewlett-Packard 5890 GC oven is used for temperature control of the columns. An schematic diagram is shown in Figure 2.

The LLDPE samples are first dissolved at 140°C in 50 mL of 1,2,4-trichlorobenzene (typically at 0.2% w/w concentration) in a separate oven. The solutions are then introduced into the various columns and left at 95°C for 1 h to stabilize before crystallization begins. Crystallization is carried out typically from 95 to 30°C at a 12°C/h cooling rate.

During crystallization, sampling is carried out by applying nitrogen pressure (up to 2 bars) to the selected column. This results in the filtration and transfer of an aliquot of the solution to the detector that is maintained at 120°C during the experiment. The flow is discontinued by closing the nitrogen valve when 0.5–0.7 mL has been sampled (dead volume of lines plus detector is less than 0.4 mL) and the detector concentration reading is recorded together with the sampling temperature of the selected column. This is followed by sampling the other columns in a sequential manner; meanwhile, the temperature cooling process continues. The sampling process takes 2 min to complete and is repeated 30–40 times for each column in the overall temperature crystallization range.

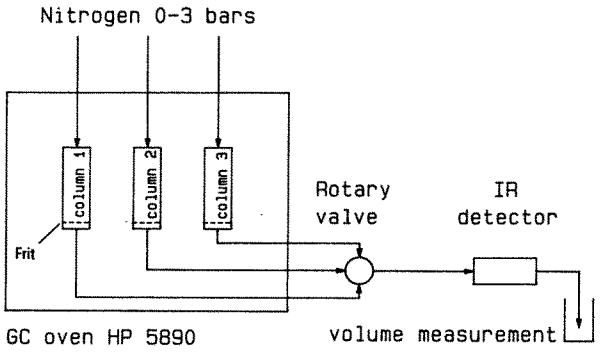

Figure 2 Schematic diagram of first prototype.

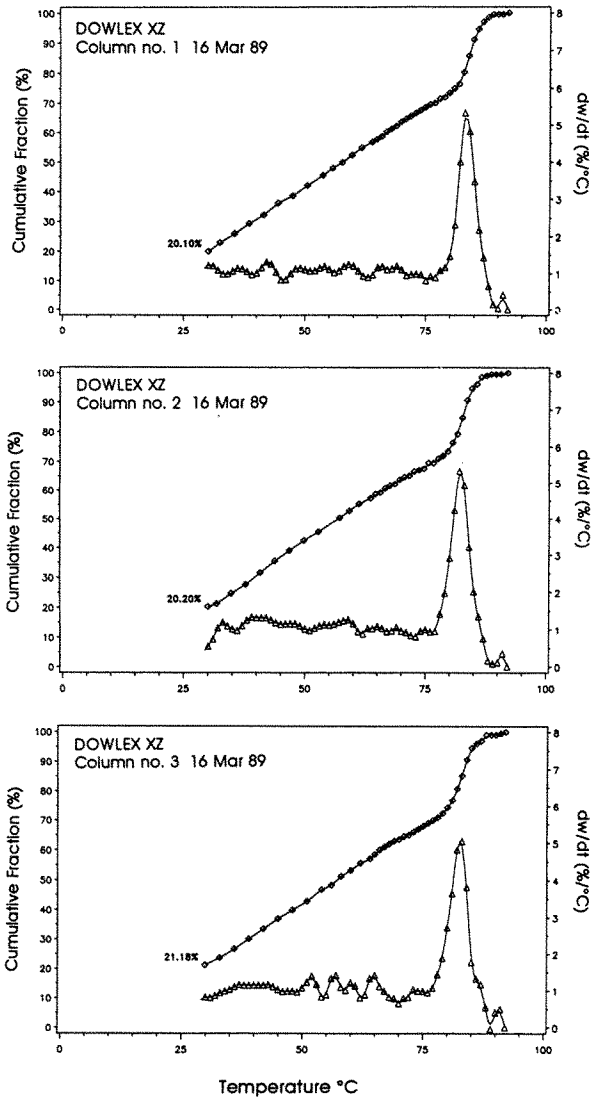

Figure 3 CRYSTAF curves obtained in the simultaneous analysis of three LLDPE resins at 12°C/h crystallization rate.

In about 6 h, the analysis of the three samples (the same LLDPE resin was analyzed in all columns in the shown example) has been completed, providing three sets of temperature-concentration data. The results are plotted in Figure 3 and correspond to the normalized cumulative SCBD expressed in terms of crystallization temperatures (the last point corresponding to the polymer soluble fraction at 30°C). The first derivative of these curves result in the SCBD, which can be expressed in CH_3/1000 C when calibrated with standards of same comonomer type.

Table I Characterization of Narrow LLDPE Fractions Obtained by TREF

Fraction No.	CH_3/1000 C (No.)	M_n (g/mol)	CRYSTAF Peak T (°C)
1	23.3	15,600	40.8
2	21.7	18,500	45.5
3	16.1	27,400	55.0
4	14.9	34,900	57.0
5	13.3	38,500	61.8
6	12.2	39,500	64.8
7	10.1	46,600	69.3
8	4.3	62,100	79.8

At the end of the experiment, the columns contain a remaining amount of solution with a large precipitate. The level of remaining solution has been shown not to affect significantly the CRYSTAF results, but for convenience, the experiment is designed to end with 30–50% of the initial volume.

CALIBRATION

A series of fractions obtained by preparative TREF of an octene LLDPE copolymer has been characterized by IR spectroscopy for the comonomer incorporation (CH_3/1000 C with end-group correction) with the results shown in Table I.

The analysis of the fractions by CRYSTAF is shown in Figure 4 and Table I. A representation of crystallization temperature vs. comonomer incorporation shows a linear relationship that facilitates the calibration of the technique (Fig. 5). Linear relationships between elution (dissolution) temperature and comonomer incorporation have been found using the TREF technique[1,2,29,36–38] with no significant fractionation by molecular weight. Similar plots have also been reported previously with the melting temperature of pure copolymer fractions.[38–40]

The linear dependence of temperature with comonomer content is predicted from eq. (3) by assimilating $T_m \cdot T_m^0 \simeq (T_m^0)^2$ and assuming ΔH_u to be constant in the crystallization temperature range; hence, eq. (3) is reduced to

$$T_m \simeq T_m^0 - \frac{R(T_m^0)^2}{\Delta H_u} N_2 \qquad (4)$$

where the presence of solvent in CRYSTAF experiments is just an additional shift factor. At the low polymer concentrations of the experiment (equal or less than 0.2% w/w) and with a favorable solvent interaction parameter, the varying solution composition during the crystallization process should not have a significant influence in melt depression over that of the pure solvent. The thermodynamic model of Eby has been shown to reduce to a similar form as well.[25,26,41]

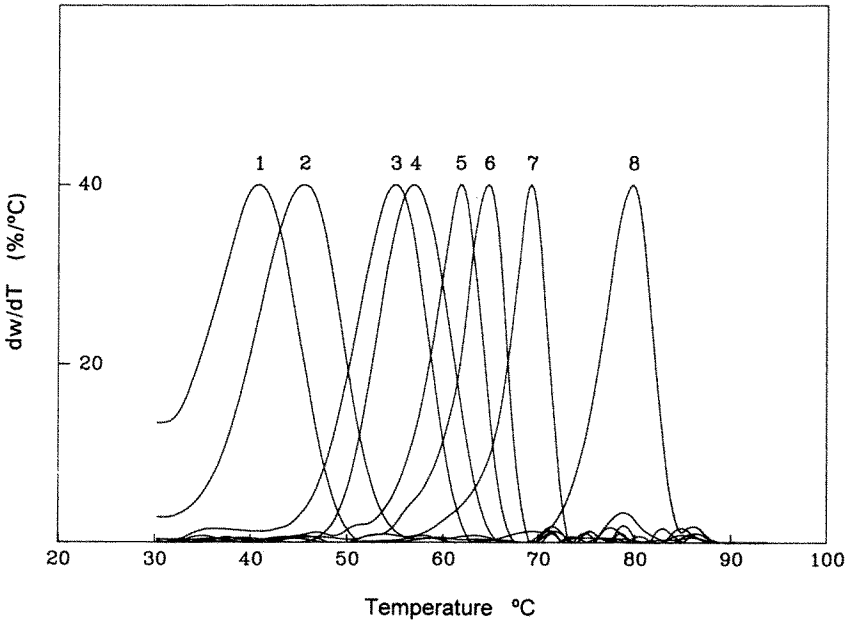

Figure 4 CRYSTAF analysis at 24°C/h crystallization rate of narrow-composition LLDPE fractions.

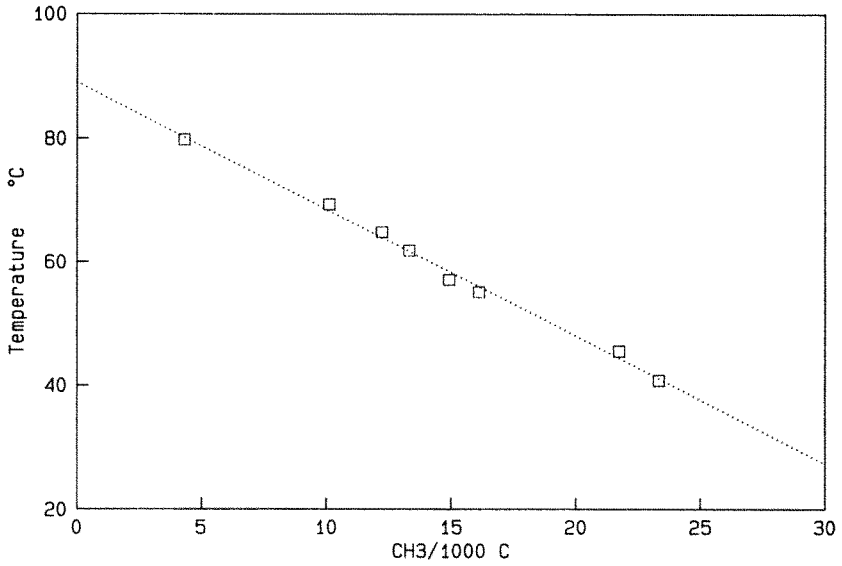

Figure 5 Crystallization temperature dependence on number of hexyl branches in narrow-composition LLDPE fractions.

COCRYSTALLIZATION

Cocrystallization in polyethylene has been recently reviewed by Alamo et al.[40] and will always be present to a certain degree when crystallizing a polydisperse resin (in composition and molecular weight). For the purpose of this study and to better understand the limitations of the CRYSTAF technique, the extent of cocrystallization was investigated with the following experiments.

A new design of crystallization columns (containers) of 3.6 cm i.d. with the capability of internal stirring were used in all the cocrystallization studies; the relatively fast cooling rates used in CRYSTAF demanded the use of slight stirring during crystallization when using large i.d. columns to minimize

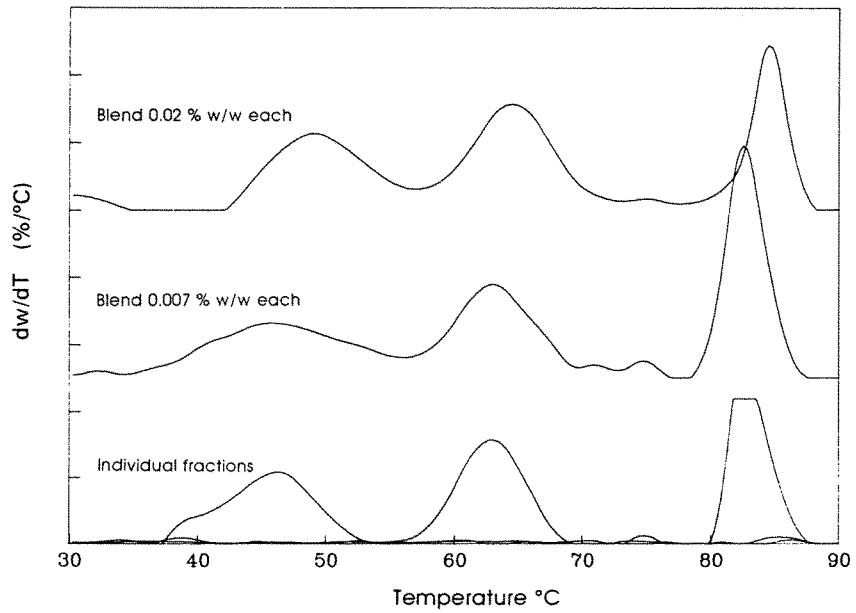

Figure 6 CRYSTAF of narrow-composition LLDPE fractions 2 and 5 and homopolymer standard NBS 1475. Analysis done separately and in a blend at a crystallization rate of 12°C/h.

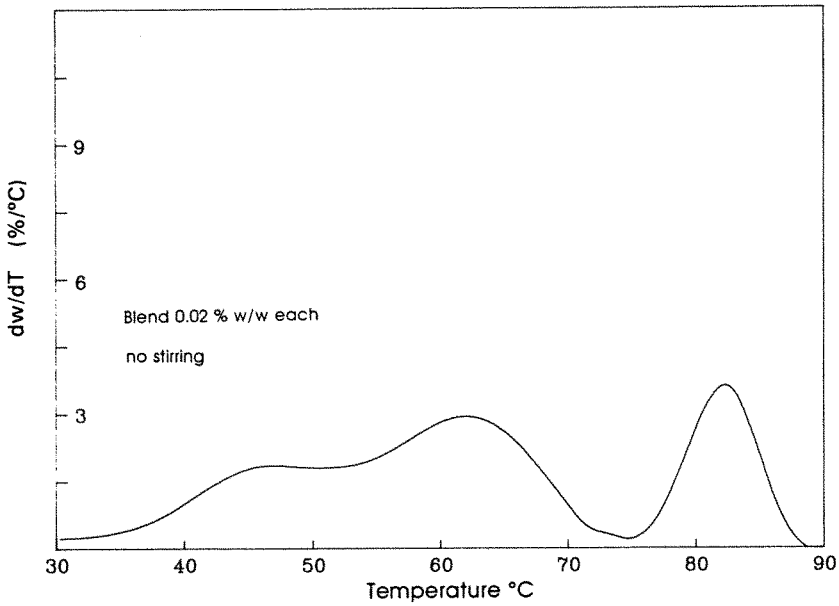

Figure 7 CRYSTAF of blend of fractions 2 and 5 and standard NBS 1475. No stirring during crystallization at 12°C/h.

the temperature gradient inside the column as well as the lag oven–liquid temperature.

In a first set of experiments, fractions 2 and 5 (Table 1) and a sample of homopolymer standard NBS 1475 were analyzed separately and in a blend at 12°C/h crystallization rate and various concentrations. The results, plotted in Figure 6, show little temperature shift of the fractions in the low concentration blend; however, at higher concentration, there is a small shift toward higher temperatures. When no stirring was used, a significant broadening of the peaks was obtained, as shown in Figure 7.

In a different set of experiments, the analyses of the NBS 1475 and an LDPE resin separately and in a blend (30/70 w/w) were carried out at a fast crystallization rate (24°C/h). The results are plotted in Figure 8 and do not show any significant temperature shift.

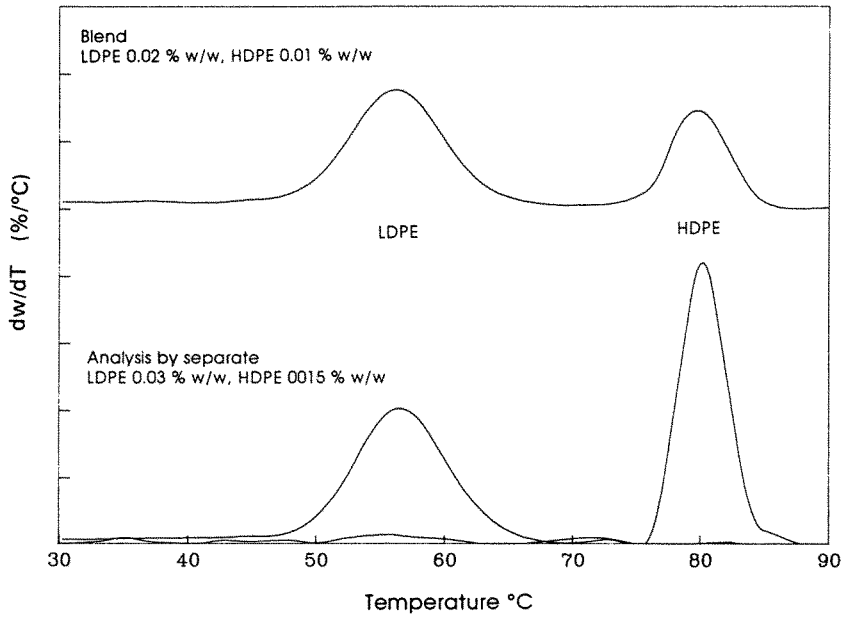

Figure 8 CRYSTAF of HDPE standard NBS 1475 and an LDPE resin separately and in a 30/70 w/w blend. Crystallization at 24°C/h.

From the above results and from comparison of CRYSTAF with TREF data, as will be discussed later, cocrystallization does not significantly influence the practical analysis of the SCBD when proper experimental conditions are used. It is recommended, however, that a cocrystallization study is carried out for any new experimental setup.

CRYSTAF AND TREF RESULTS COMPARISON

The CRYSTAF results shown in Figure 3 were obtained with the first prototype apparatus; a significant improvement is achieved by automation of the technique and better data handling, which will be described in a future publication. A comparison of CRYSTAF, using the automated prototype, and

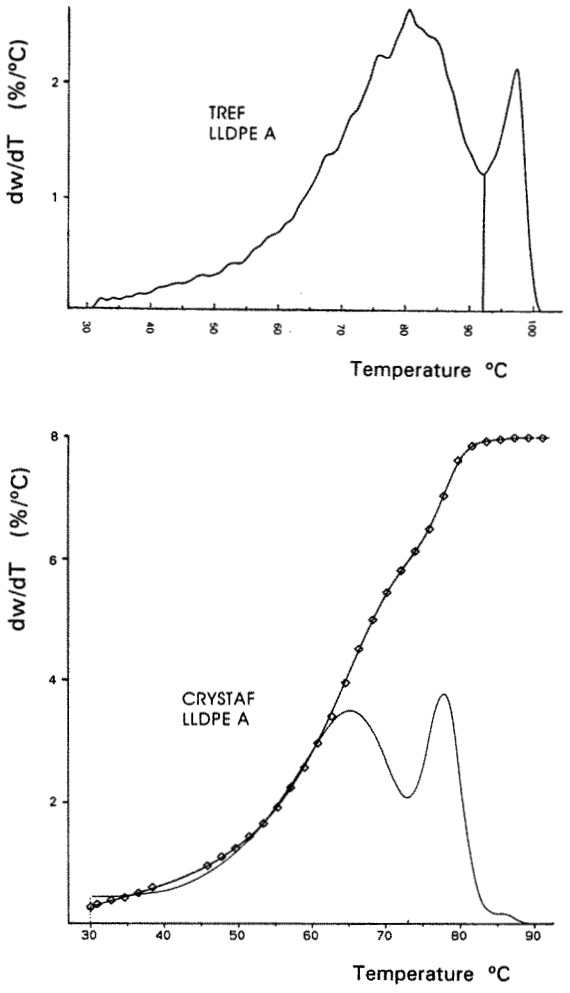

Figure 9 Comparison of CRYSTAF and TREF results for an LLDPE resin with low homopolymer and soluble fractions. CRYSTAF at 24°C/h crystallization rate. TREF at 6°C/h crystallization and 90°C/h dissolution rate.

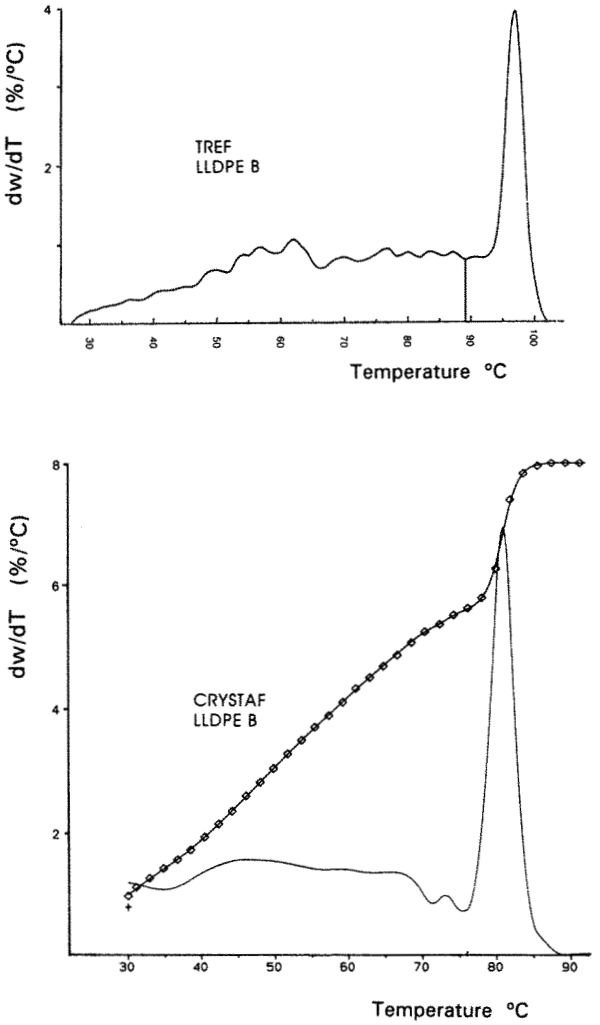

Figure 10 Comparison of CRYSTAF and TREF results for an LLDPE resin with high homopolymer and soluble fractions. CRYSTAF at 24°C/h crystallization rate. TREF at 6°C/h crystallization and 90°C/h dissolution rate.

TREF results is presented in Figures 9 and 10 for two octene-based LLDPE samples. The CRYSTAF results were obtained at 24°C/h crystallization rate and the TREF at 6°C/h crystallization and 90°C/h elution rates. In spite of using such a different operation procedure, TREF and CRYSTAF provide a similar resolution of the highly crystalline peak as well as comparable overall SCBD curves as shown in Figures 9 and 10; an extensive comparison of TREF and CRYSTAF results will be presented in a coming report.

The temperature scale difference is due to the supercooling effect as CRYSTAF is measured during crystallization; meanwhile, TREF is measured during melting; both techniques, however, can be calibrated and results expressed in CH_3/1000 C units

as has been discussed previously and shown in Figure 5.

FINAL CONCLUSIONS

A new technique to analyze the comonomer distribution in polyolefins has been described. The technique, referred as crystallization analysis fractionation (CRYSTAF), has been shown to provide similar results to temperature rising elution fractionation. CRYSTAF, however, requires only one temperature cycle to perform the SCBD analysis, thus simplifying the equipment and reducing significantly the analysis time.

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