Crystallization Elution Fractionation. A New Separation Process for Polyolefin Resins

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Summary: New crystallization procedures have been developed for the analysis of the chemical composition distribution in polyolefins by pumping a small flow of solvent during the crystallization cycle. One of the new techniques, crystallization elution fractionation (CEF) combines the separation power of TREF and CRYSTAF and has been shown to provide very fast analysis of the composition distribution.

Keywords: CCD; CRYSTAF; crystallization; polyethylene; TREF

Introduction

The introduction of single site catalysts and multiple reactor technology allows the design of new polyolefin resins with improved properties for each application, and the chemical composition distribution (CCD) is the most discriminating microstructure parameter in these polymers. The proper analysis of the CCD necessarily requires a fractionation process, and as the incorporation of comonomer will result in the presence of branches or functional groups, and those will influence the crystallinity, it seems obvious that existing techniques like temperature rising elution fractionation and crystallization analysis fractionation were based on a fractionation step according to crystallizability.

Temperature Rising Elution Fractionation

Temperature rising elution fractionation (TREF) has been the most used analytical approach for the analysis of the CCD since its introduction in the industrial practice by Wild et al.[1] to characterize linear low density polyethylene. TREF analysis resembles a liquid chromatography separation where the sample is first dissolved in a proper solvent at high temperature and the solution is then introduced into a column containing an inert support; this is followed by a crystallization step at a slow cooling rate with no flow, during which polymer fractionation occurs by segregation of crystal aggregates of decreasing crystallinity as temperature goes down. Fractionation takes place within this cycle without physical separation of the fractions; all the crystal aggregates, from different crystallinity or branch content are still mixed together and are being deposited *in situ* on the same spot of the column where the initial polymer solution has been loaded.

TREF still requires a second temperature cycle to physically separate or quantify those fractions. This is achieved by pumping new solvent while the temperature is being increased. The eluant dissolves fractions of increasing crystallinity, or decreasing branch content, as temperature rises. These fractions are collected (preparative TREF) or their concentration monitored with an infrared detector (analytical TREF) to generate the CCD curve. The name temperature rising elution fractionation derives from this second temperature cycle.

Although analytical conditions are performed far from thermodynamic equilibrium, it has been shown that the elution temperature still follows a linear relation with the molar fraction of comonomer incorporated (m_c) as predicted from Flory equation for copolymers,[2] that after proper simplification can be reduced to

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Equation (1):

$$T_m \cong T_m^0 - \frac{R(T_m^0)^2}{\Delta H_u} \cdot mc \tag{1}$$

where T_m is the equilibrium melting temperature of the polymer-diluent mixture, T_m^0 the melting temperature of the pure polymer, and ΔH_u the heat of fusion per polymer repeating unit. Equation (1) assumes that ΔH_u is constant in the crystallization temperature range and that the presence of solvent, when crystallizing in solution, plays as an additional temperature shift factor.

Analysis of the CCD by TREF is today a common practice in the polyolefin industry and the long analysis time of the first homemade instruments[1,3] (three or four days per sample) has been reduced significantly down to a few hours; still, there is an interest in further reducing TREF analysis time. Reviews of the TREF technique have been done by Wild,[4] Glöckner,[5] Fonseca and Harrison,[6] Soares and Hamielec,[7] Anantawaraskul, Soares and Wodd-Adams,[8] and Monrabal.[9]

Crystallization Analysis Fractionation

Crystallization analysis fractionation (CRYSTAF) was developed by Monrabal[10,11] in 1991 as a process to speed up the analysis of the CCD, and it shares with TREF the same fundamentals on separation according to crystallizability, but the whole fractionation process is carried out during crystallization.

In CRYSTAF the analysis is carried out in stirred crystallization vessels with no support, by monitoring the polymer solution concentration, through the crystallization process, while decreasing temperature. Aliquots of the solution are filtered (through an internal filter inside the vessel) 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 approach, no attention is paid to the precipitate 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; as temperature goes down the most crystalline fractions, composed of molecules with zero or very few branches (highly crystalline) will precipitate first, resulting in a steep decrease in the solution concentration on the cumulative plot. This is followed by precipitation of fractions of increasing branch content (or less crystallinity) as temperature continues to decrease; the last data point, corresponding to the lowest temperature of the crystallization cycle, represents the fraction which has not crystallized (mainly highly branched or amorphous material) and remains in solution at the lowest temperature. The first derivative of this curve corresponds to the CCD, very similar in shape to the one obtained in TREF with the only difference of a temperature shift, as equilibrium is not reached, and CRYSTAF is measured in the crystallization while TREF is measured in the dissolution (melting).

With this approach, the CCD can be analyzed relatively fast in a single crystallization cycle without physical separation of the fractions. The term crystallization analysis fractionation stands for this process. Reviews of the CRYSTAF technique have been done by Soares and Hamielec,[7] Anantawaraskul et al.[8] and Monrabal.[9]

Dynamic Crystallization

In the previous sections, TREF and CRYSTAF methods have been reviewed, and it has been discussed how both techniques share the same principles of fractionation on the basis of crystallizability through a slow cooling of a polymer solution. TREF is carried out in a packed column and demands two full temperature cycles, crystallization and elution, to achieve the analysis of the composition distribution. In CRYSTAF the analysis is performed in a single step, the crystallization cycle.

In Figure 1.a, the analysis of a blend of three different components by TREF is represented in three steps: 1) Sample loading into the column, 2) Crystallization cycle where the components are being crystallized in the same location where

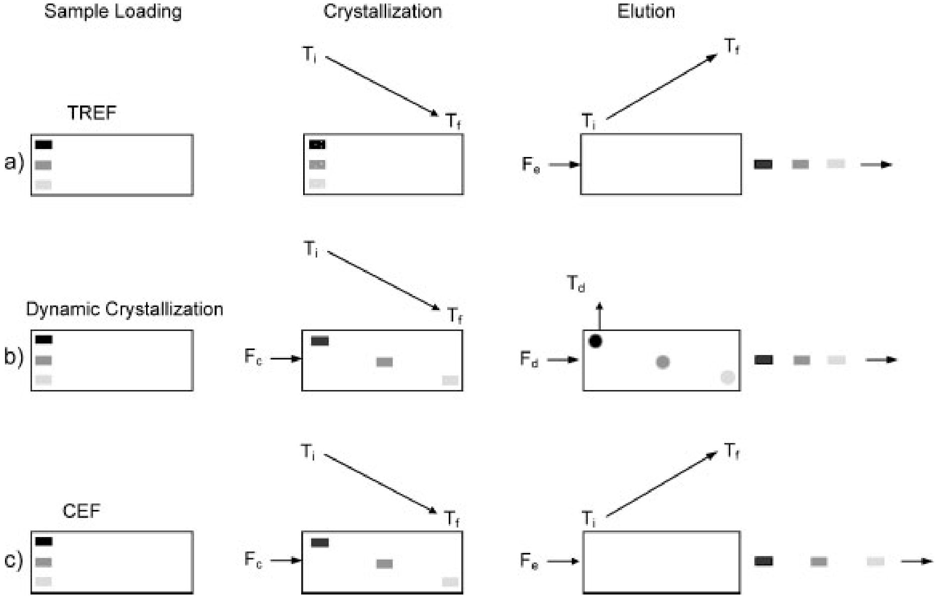

Figure 1.
Separation diagram by crystallizability. a) TREF separation process, b) Dynamic crystallization, c) Crystallization elution fractionation.

sample was loaded, and 3) Elution cycle where a solvent flow, F_e, is passed through the column to elute the fractions being dissolved as the temperature rises. The three components of the blend are physically separated from each other in the last cycle as shown in Figure 1.a.

A new separation approach is presented here based on the same principles of crystallizability and using a packed column like in TREF, but performing the physical segregation of fractions in the crystallization step as in CRYSTAF. The new separation process is known as dynamic crystallization because the cooling is performed while a small flow of solvent is passed through the column.

Dynamic crystallization is also a three-step procedure as represented in Figure 1.b, but physical separation of the components takes place within the column itself in the crystallization cycle. In dynamic crystallization, a small solvent flow, F_c, is passed through the column during crystallization, in such a way that when a component reaches its crystallization temperature it is segregated and anchored on the support while the other components, still in solution, move along the column until they reach their own crystallization temperature. At the end of the crystallization cycle, the three components are separated inside the column according to crystallizability.

The flow rate in during crystallization, F_c, plays an important role as it has to be adapted to the crystallization rate, C_r, crystallization temperature range, ΔT_c, of the components to be separated, and column volume, V_c, in order to crystallize all the components within the column length; F_c is calculated as follows from Equation (2):

$$F_c = \frac{V_c}{\Delta T_c} \times C_r \qquad (2)$$

Once the crystallization cycle is completed, the flow is interrupted and the column is heated for a few minutes at a temperature where all components are dissolved. After that, the elution cycle begins by adding a proper elution flow to the column. The separation order of the components will be according to CRYSTAF rather than TREF elution temperatures, as separation occurred in the crystallization and not in the dissolution process.

Proper analysis by this technique demands that the temperature range of the polymer components to be separated, ΔT_p is within the crystallization temperature range ΔT_c, and the full power of the dynamic crystallization analysis will be obtained when ΔT_p is equal to the ΔT_c used, resulting in the components crystallizing along the whole length of the column. When the range of ΔT_p is narrower and within the range of ΔT_c, only a fraction of the separation power, equivalent to the ratio of the two temperature ranges, will be obtained.

Crystallization Elution Fractionation

Once dynamic crystallization was developed as a new separation process, it was easy to realize the possibility to combine this crystallization step with a final elution cycle as in TREF to obtain a new *extended* separation. This is represented in Figure 1.c where the dynamic crystallization cycle, at a crystallization solvent flow of F_c, is followed by the temperature rising elution cycle, with a solvent flow F_e as in TREF. The new process is known as crystallization elution fractionation (CEF), as it combines the separation obtained in the crystallization step with the one obtained in the elution cycle; this is schematically represented in Figure 1.c by the extended separation of the three components at the exit of the column in CEF analysis as compared to the TREF approach.

It is quite interesting that the separation power of CRYSTAF (obtained by dynamic crystallization) and TREF are combined in CEF when both systems are based on the same crystallizability principles, and when TREF requires both cycles *per se*. On the other hand, one could expect that analysis of particular blends where differences in supercooling result in separation of the components during crystallization in an opposite direction to the one obtained by elution-melting would result in poor CEF separation.

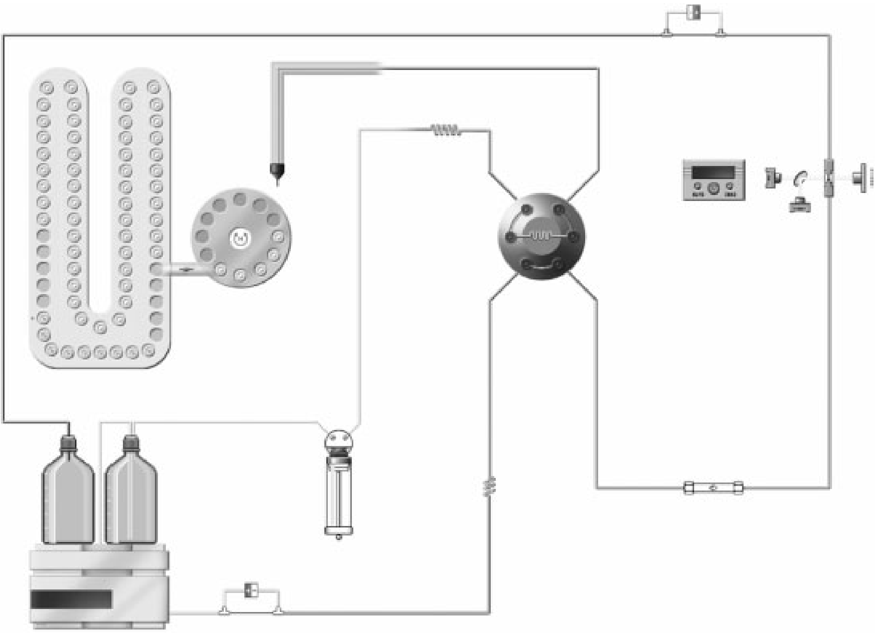

Figure 2.
Schematic diagram of the combined CEF, dynamic crystallization and TREF instrument.

Experimental Part

Dynamic crystallization and CEF experiments were performed in a specially developed apparatus constructed around a simplified Polymer ChAR TREF instrument. As the interest of CEF technology in these initial stages was focused on high throughput analysis, the instrument built incorporated an autosampler for 70 vials of 10 ml.

The CEF instrument diagram is quite simple as shown in Figure 2. The autosampler dissolves the sample in o-dichlorobenzene and it is loaded into the injection valve loop through the syringe dispenser. The sample is injected with the pump flow into the column head and the dynamic crystallization process begins at a given cooling rate and crystallization flow. As the crystallization ends, the oven starts the heating program and flow is adapted to the elution flow (usually higher than crystallization flow) passing through the column to a dual wavelength infrared detector, so concentration and composition can be measured at once. A dual capillary viscometer, as shown in the diagram, was added to the system to measure the composition – molar mass dependence.

The same instrument can be programmed to run TREF, dynamic crystallization, or CEF analysis as described squematically in Figure 1.

Results

Dynamic Crystallization

A blend of two metallocene resins of densities 0.902 and 0.937 g/ml was used to test the separation power of dynamic

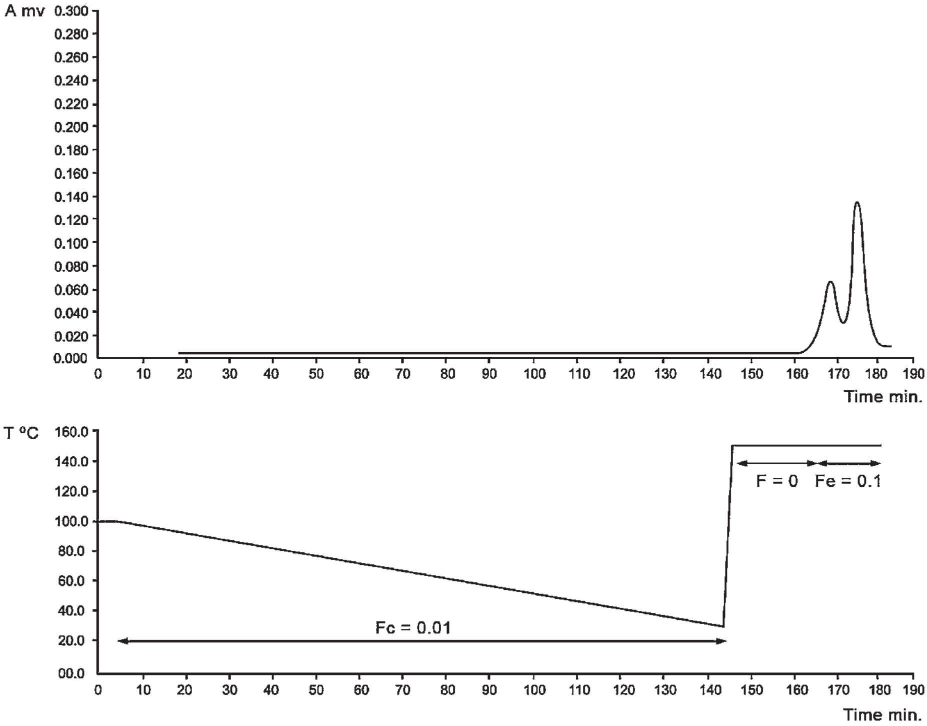

Figure 3.

Dynamic crystallization analysis of a blend of two metallocene resins. The top diagram is the elution curve showing the separation of the two components. The bottom diagram is the temperature profile with the flow being used at each step.

crystallization analysis. The sample at a concentration of 0.8% w/v was dissolved in a 10 ml vial at the autosampler and 0.1 ml solution was injected into the column. The crystallization rate was 0.5 °C/min. The crystallization flow calculated by Equation (2), according to the column interstitial volume, was 0.01 ml/min. Once the crystallization ends, the flow is stopped and the oven goes in a fast ramp up to 150 °C, staying for ten minutes to ensure full dissolution of the components previously crystallized in the column. After that time, the elution flow begins at 0.1 ml/min to elute the two metallocene resins separated into the column as shown in Figure 3. When the same experiment was repeated without any crystallization flow, only one peak is obtained.

Crystallization Elution Fractionation

Most work done with crystallization elution fractionation so far has been directed to reduce analysis time for applications in high throughput screening of catalyst formulations. The CEF analysis of a complex polyolefin, Elite^{TM} (trademark of the Dow Chemical Company) is shown in Figure 4 with a total analysis time of 23 minutes. The analysis was performed at very fast crystallization and heating rates (10 °C/min), and still the separation of the three components of this resin is reasonably good as shown by the infrared transmission plot in Figure 4 and the final calculated composition distribution in Figure 5.

The capabilities of the CEF technique for high throughput screening were tested analyzing automatically the same sample in 10 different vial preparations every half an hour at a crystallization rate of 5 °C/min and heating rate of 10 °C/min. The samples were previously dissolved at 150 °C for 30 minutes with gentle shaking in the autosampler. The results presented in Figure 6 show the good repeatability of the CEF analysis.

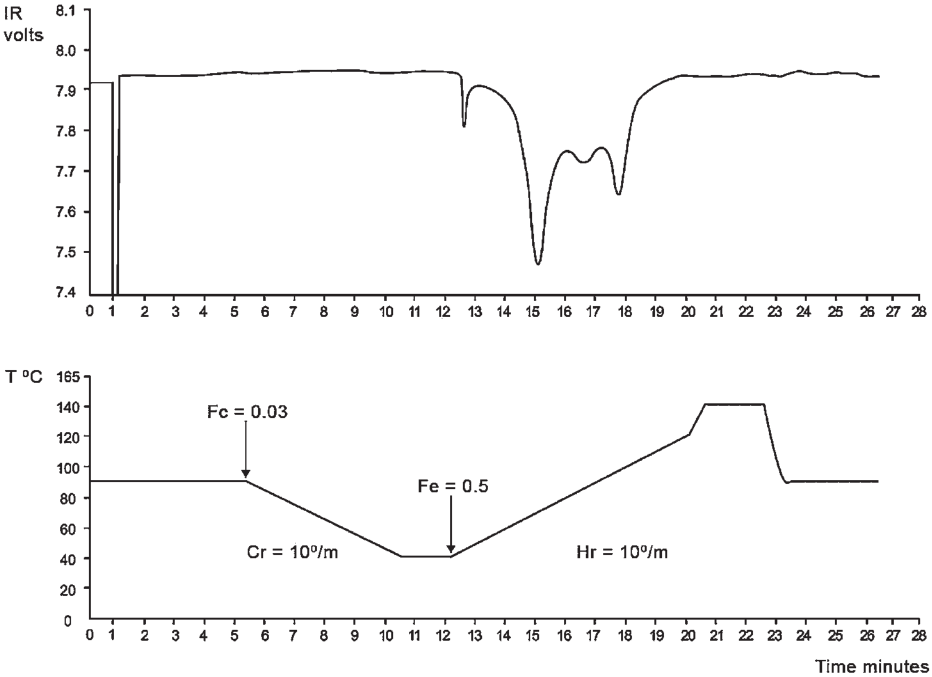

Figure 4.
CEF analysis of an Elite^{TM} resin performed at fast crystallization and heating rates of 10 °C/min. The top diagram shows the elution infrared transmission curve. The bottom diagram is the crystallization and elution temperature profile.

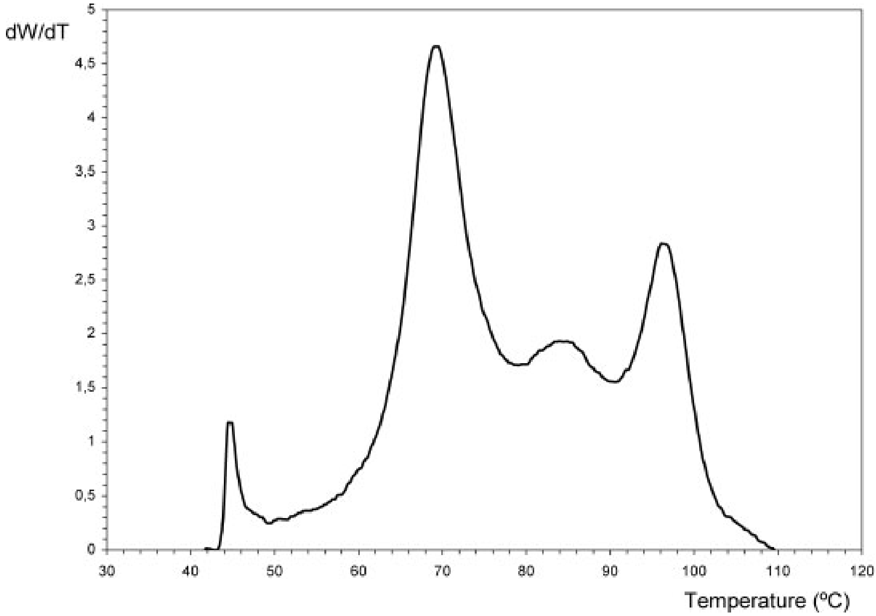

Figure 5.
CEF analysis of an Elite^{TM} resin obtained at crystallization and heating rates of 10 °C/min, injection volume of 20 µl (0.5%w/v) and elution flow rate of 0.5 ml/min.

Comparison of CEF and TREF

A blend of two metallocene resins of densities 0.902 and 0.916 g/ml was used to compare the separation of CEF and TREF under fast analytical conditions with the same column. In both cases the crystallization and heating rates were 2 °C/min and the elution flow rate 0.2 ml/min. The

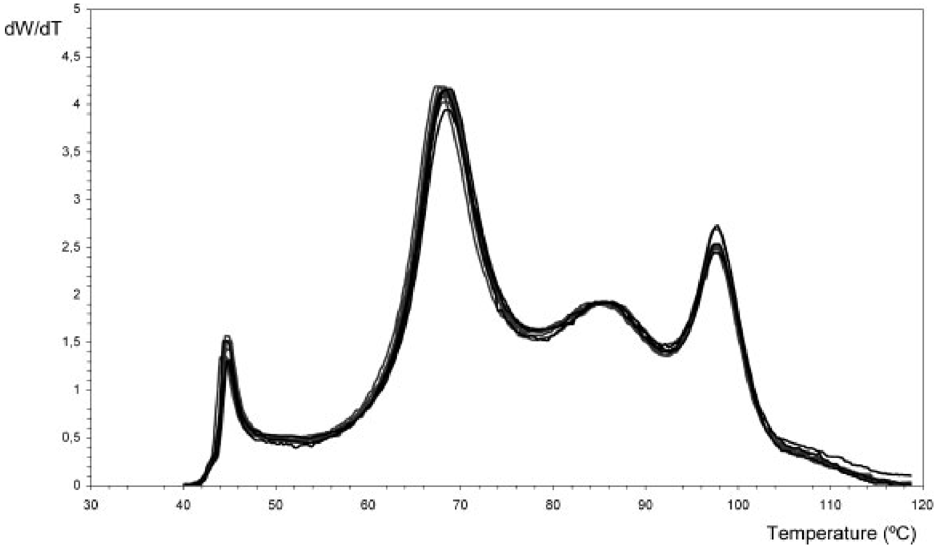

Figure 6.
Multiple CEF analysis (×10) of an Elite^{TM} resin obtained at crystallization rate 5 °C/min and heating rate 10 °C/min, injection volume of 20 µl (0.5%w/v), and elution flow rate of 0.5 ml/min.

only difference between CEF and TREF analysis was the crystallization flow of 0.12 ml/min present in the CEF analysis. The results presented in Figure 7 show the improved resolution of CEF over TREF analysis in the separation of the two components.

Multiple Detectors

The incorporation of other detectors in line to CEF analysis is as easy as with GPC or TREF techniques. In the initial experiments, a dual capillary viscometer and a composition sensor were installed in the CEF instrument to evaluate their potential. The analysis of a linear low density polyethylene is shown in Figure 8. The ratio of CH_3 over CH_2 signals (B/A plot) results in the gray composition line (methyls per 1000 carbon atoms) increasing linearly, as expected, towards lower temperatures. The ratio of viscometer over concentration signals (C/A) results in the intrinsic viscosity black line that increases towards higher temperatures (lower branch content) as expected in a Ziegler-type resin.

Conclusions

A new dynamic crystallization approach has been developed to separate semicrystalline polymers into a packed column according to crystallizability. The physical separation takes place in the crystallization cycle and therefore the results will correlate to CRYSTAF temperature data. Future work is required to better evaluate the interest of this new approach in industrial processes for analytical or preparative fractionation purposes.

Having developed dynamic crystallization, it was obvious to consider this approach to replace the static crystallization cycle being used in TREF before the elution step. The combination of dynamic crystallization and temperature rising elution crystallization results in a new techni-

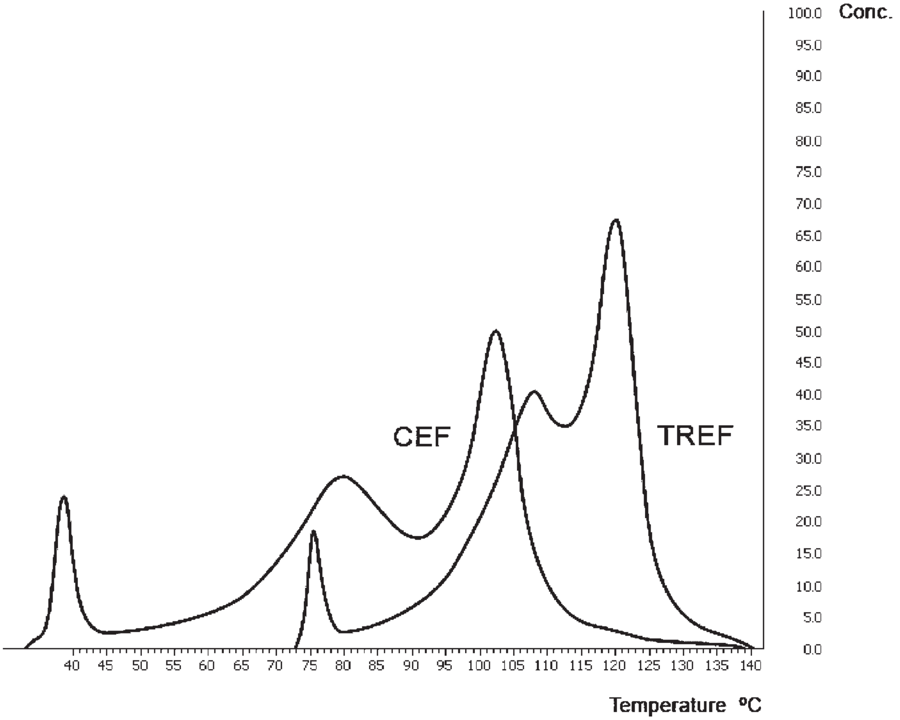

Figure 7.
Analysis of a blend of two metallocene resins by CEF and TREF.

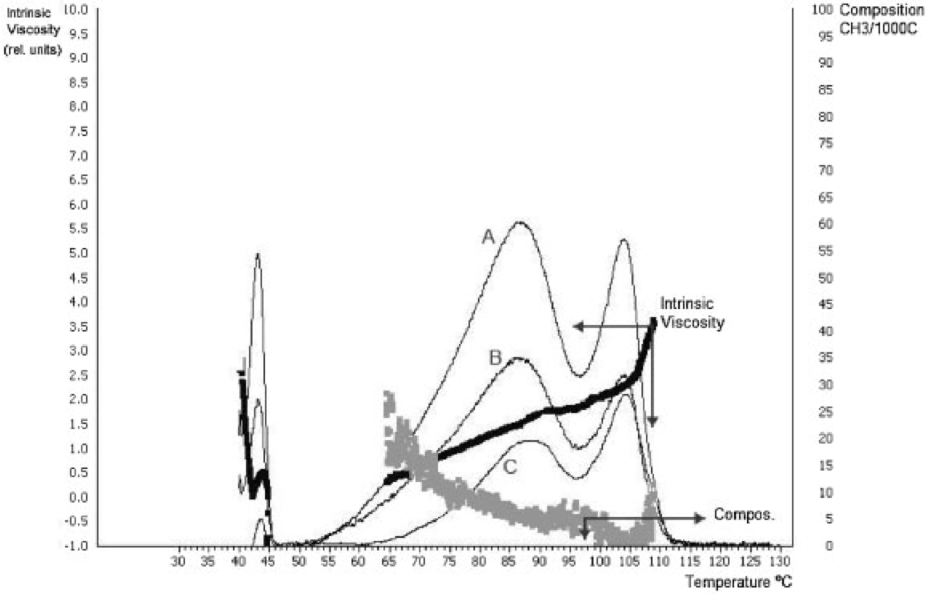

Figure 8.
CEF analysis of a linear low density polyethylene. A - Concentration (CH_2), B - Composition (CH_3) and C - Viscometer output.

que with extended separation. The new technique has been named crystallization elution fractionation, CEF, as it combines the separation power obtained in the crystallization cycle (equivalent to CRYSTAF), with the one obtained in the elution-melting cycle (equivalent to TREF).

CEF is performed in a simplified TREF instrument and can easily adapt viscometry, light scattering, composition, or other detectors to determine molar-mass composition dependence or to obtain further information of polymer microstructure. The same CEF apparatus can perform TREF and dynamic crystallization.

The analysis time of the CCD has been dramatically reduced with improvements in TREF column and hardware design, and with newer techniques becoming available. The analysis by classical TREF of one sample took 100 hours in the eighties (around five samples could be analyzed per week). The development of CRYSTAF in the nineties allowed analyzing five samples in 8 hours (15 samples per day). In the last years, improvements in TREF allowed the analysis of five to ten samples per day. Today, CEF can analyze one sample in less than 30 minutes, enough for the demanded high throughput screening of 50 samples per day.

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