

An Improved Analytical Temperature-Rising Elution Fractionation System for Automated Analysis of Polyethylenes

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The authors describe a system for automated analytical temperature-rising elution fractionation that uses the built-in differential refractometer of a commercial gel-permeation chromatography instrument and a stop-flow method for sample crystallization. They discuss the performance of the system and its ability to fractionate different types of polyethylenes.

Polymers basically are heterogeneous materials, and heterogeneity can be exhibited in various ways such as distribution of chain lengths, differences in chemical composition, stereoregularity, and architecture (tacticity or branching). Branching can be characterized as either long chain or short chain.

Temperature-rising elution fractionation is a technique that allows the analysis of semicrystalline polymers by separating fractions according to their crystallizability. Temperature-rising elution fractionation enables analysts to evaluate structure heterogeneity and to characterize the distribution of short-chain branching. Elution during temperature-rising elution fractionation is governed by the melting of semicrystalline polymers in the presence of a solvent (1).

Preparative temperature-rising elution fractionation can be performed to isolate fractions for additional investigations. During this process, a large quantity of solvent is required for eluting the sample, and a large amount of non-solvent, usually methanol, also is used for precipitating the eluted fractions (2). This technique is quite time-consuming; it typically requires several days to perform a fractionation.

The development of analytical temperature-rising elution fractionation has been an improvement upon preparative temperature-rising elution fractionation. Analytical

temperature-rising elution fractionation overcomes the limitations of preparative temperature-rising elution fractionation by reducing the column and sample sizes considerably and by continuously monitoring the amount of the eluted polymer fractions as a function of column temperature using an on-line detector.

For polyethylenes, the major factor that determines melting in a solution is the degree of short-chain branching (3). Each branching point in a chain is rejected from the growing crystal, thereby limiting crystal thickness and hence reducing the melting temperature. Thus, a direct relationship exists between the melting temperature and the degree of branching, which is reflected in analytical temperature-rising elution fractionation curves. Moreover, Nagano and Goto (3) and Mirabella (4) have reported that a linear relationship exists between the elution temperature and the degree of short-chain branching (number of branches per 1000 carbon atoms). Therefore, analytical temperature-rising elution fractionation curves do in fact describe the short-chain branching distribution (5).

The short-chain branching distribution provides some information about the mechanism of polymerization and the nature of the catalysts. As an example, when chemists use conventional Ziegler-Natta catalysts for the polymerization of ethylene, a broad

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bimodal distribution of polymer chains with different short-chain branching contents is present in the final product because of the multisite nature of these catalysts (6), as compared with metallocene catalysts, which produce a much narrower short-chain branching distribution (7). Short-chain branching distribution and the molecular mass distribution have a marked influence upon the polymer properties. The shapes of these distributions have a profound effect upon the end-use properties of the material, and their determination can generate a more complete understanding of the behavior of polyethylenes in different applications (8).

Several researchers have described systems for analyzing a solution of a crystalline or a semicrystalline polymer sample to determine its short-chain branching distribution (9–11). As a general method, the polymer sample first is precipitated from a solution during a decreasing temperature gradient to produce a precipitated polymer sample. The precipitated polymer sample then is redissolved and eluted during an increasing temperature gradient to produce successive fractions of the polymer sample, which are measured to produce concentration data from which the short-chain branching distribution is calculated. The concentration detector is a built-in differential refractometer (9) or a separate infrared (IR) or nuclear magnetic resonance (NMR) detector (10). In both cases the polymer solution is introduced into the fractionation column, which is placed in an oil bath, using a complex procedure that requires high quantities of solvent and polymer sample.

On the other hand, Yau and Gillespie (11) describe an analytical temperature-rising elution fractionation system with an automatic injector and an IR detector. This detector was tuned to 3.48 μm , the C–H

bond stretch frequency. IR detection generally is used for analytical temperature-rising elution fractionation because it offers better baseline stability than differential refractive index detection for both large variations of temperature and pressure during the elution process (7,12–16). However, the IR detector has poor sensitivity and consequently requires the use of large amounts of polymer in analysis. For this reason, either the baseline presents a high level of noise (for example, see reference 7's Figure 1 or references 4 and 12's Figure 1) or the peaks contain spikes (for example, see reference 8's Figure 8 or reference 15's Figure 9). To decrease the noise level, analysts sometimes average the chromatogram data points and smooth the curves (see reference 8's Figure 11).

The presence of a high noise level becomes even more important when mathematical transformations are applied to analytical temperature-rising elution fractionation chromatograms to obtain methylene sequence length distributions for polyethylene copolymers (17) or to predict differential scanning calorimetry thermograms (4,16,18). Furthermore, IR detectors are unavailable on commercial equipment and are complicated to install. For this reason, the results obtained using the analytical temperature-rising elution fractionation technique are very difficult to reproduce from one laboratory to another.

In this article, we describe an improved analytical temperature-rising elution fractionation system that uses a commercial instrument for high-temperature gel-permeation chromatography connected with an oil bath. Our goal was to keep the modification to a minimum by using the existing parts of the chromatograph as much as possible: namely, the automatic injector and the differential refractometer, which is more sensitive than an IR detector. This system allowed the use of a lower quantity of injected polymer, which enabled the possibility of completely automating the process by reducing the injected volume of solution to 200–500 μL .

Experimental

Analytical temperature-rising elution fractionation apparatus:

The analytical temperature-rising elution fractionation was performed using a modified Waters GPC 150CV gel-permeation chromatography (GPC) system (Waters Corp., Milford, Massachusetts) using greater than 99% pure 1,2,4-trichlorobenzene (Sigma-Aldrich Co., St. Louis, Missouri) as the solvent. The sol-

vent was stabilized with 2% of antioxidant Irganox 1010 (Ciba Specialty Chemicals, Inc., Basel, Switzerland). We placed a 100 mm \times 10 mm stainless steel column packed with aluminum oxide (70–230 mesh, Merck KGaA, Darmstadt, Germany) in a Julabo F32 HP oil bath (Julabo Labortechnik GmbH, Seelbach, Germany).

In the first step of the analysis program, 400 μL of solution was injected in the column automatically using the built-in injector at a low flow rate of 0.2 mL/min. This low flow rate was used to avoid a pressure-induced leak of the polymer solution through the column after injection. In the second step, the flow was stopped and the column was cooled in the oil bath at -0.5 $^{\circ}\text{C}/\text{min}$ from 135 $^{\circ}\text{C}$ to 35 $^{\circ}\text{C}$. In the third step, the polymer was eluted at a flow rate of 0.8 mL/min, while the temperature was increased at 1 $^{\circ}\text{C}/\text{min}$ from 35 $^{\circ}\text{C}$ to 135 $^{\circ}\text{C}$. The concentration of the eluted species was measured using the instrument's built-in differential refractive index detector. Both the chromatogram and the temperature were recorded using two data channels and stored using Millennium 32 software (Waters). We allowed an additional 40 min for complete cleaning of the column before the next injection. Therefore, the total time for analysis was approximately 6 h, and the system could perform five analytical temperature-rising elution fractionations in an automated mode.

Sample preparation: To check reproducibility and to calibrate the area versus the concentration, we used polyethylene standards from the National Institute of Standards and Technology, denoted polyethylene NBS 1475 (linear polyethylene) and polyethylene NBS 1476 (branched polyethylene). The polymer solutions were prepared at 145 $^{\circ}\text{C}$ in 1,2,4-trichlorobenzene at 1–15 mg/mL concentrations with the instrument's built-in procedure.

Results and Discussion

Chromatogram interpretation: To demonstrate how the variation of column temperature affects the baseline stability, Figure 1 shows two chromatograms of the polyethylene NBS 1475 sample obtained for two concentrations. The baselines overlap outside the elution domain. The baseline drift is caused primarily by the temperature and pressure variations in the column during the heating step. To eliminate the drift, we simply used a linear interpolation of the baseline under the peak.

Optimization of injection time: In previously described methods, the analytical

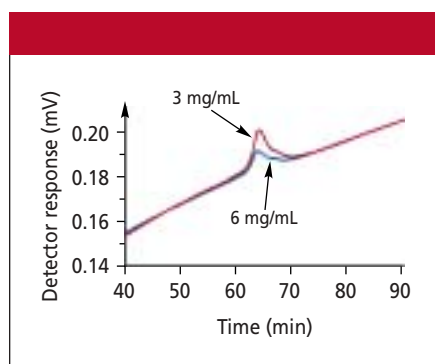


Figure 1: Analytical temperature-rising elution fractionation chromatograms of polyethylene NBS 1475 recorded for two concentrations (3 mg/mL: black line; 6 mg/mL: pink line) showing the continuous drift of the baseline with elution time.

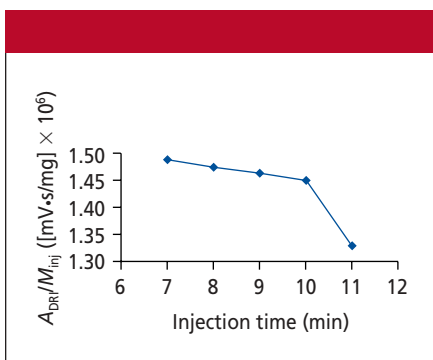


Figure 2: Variation of the ratio between chromatographic area and injected mass versus injection time for polyethylene NBS 1476 at 5 mg/mL.

temperature-rising elution fractionation column was filled with a polymer solution and then closed and cooled with a controlled-temperature program (9–11). After the crystallization step, the column was reintroduced in the solvent stream.

The use of an autoinjector is essential for the possibility of a completely automated process, which implies that the column remains coupled with the high performance liquid chromatography (HPLC) system during both cooling and heating steps. Therefore, the objective of the injection step is to introduce the sample completely into the column and to avoid any spilling of the sample from the column when the solvent flow is stopped. Because of these requirements, it is necessary to measure the optimal injection time in the column.

For highly crystalline samples, shorter or longer injection times will produce the precipitation of the polymer in the inlet or outlet tube, respectively. Because the polyethylene NBS 1476 sample has a lower melting temperature and also presents a broader range of elution temperatures, we selected it for measuring the optimal injection time. These features are essential to prevent obstruction of the capillary tubes when using short or long injection times. Figure 2 illustrates the variation of the ratio between the chromatographic area and the injected mass versus the injection time.

For injection times less than 10 min, we observed a domain of almost constant values. For 11 min, a portion of the injected sample spilled in the outlet tube and was eluted immediately after the flow was restarted. Because this portion was masked by the solvent peak, the analytical temperature-rising elution fractionation peak presented a smaller area than expected. Based upon data

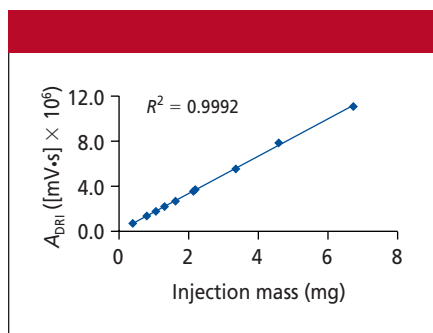


Figure 3: Calibration curve for polyethylene NBS 1475 in 1,2,4-trichlorobenzene with concentrations between 1 mg/mL and 17 mg/mL.

from Figure 2, we selected an injection time of 9 min.

Calibration curve: For quantitative measurements of the eluted fractions, we generated a calibration curve of the detector response versus injected mass for polyethylene NBS 1475. Figure 3 presents the data obtained for 1–17 mg/mL concentrations. The linearity of the data is satisfactory.

Reproducibility of elution temperature: An important parameter for the quality of an analytical temperature-rising elution fractionation method is the reproducibility of the elution temperature (volume) for a characteristic peak. The elution temperature (T_{peak}) was taken as the temperature of the bath that corresponded to the maximum signal of the detector. T_{peak} was recorded using the second data channel. Figure 4 shows the elution temperatures that correspond to the peaks of the samples injected for the calibration curve presented in Figure 3.

The elution time is reproducible for concentrations greater than 3 mg/mL. A very

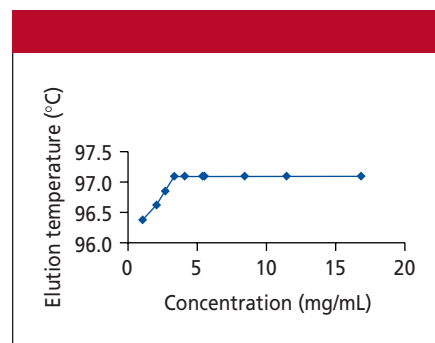


Figure 4: Variation of the peak elution temperature for polyethylene NBS 1475 as a function of the concentration of the sample solution.

small decrease can be detected only for lower concentrations. Figure 5 illustrates the chromatograms for three injected concentrations after baseline subtraction.

Method resolution: The power of an analytical temperature-rising elution fractionation method is its ability to resolve different polyethylenes that differ by only their short-chain branching distribution. Based upon the linear relationship between the elution temperature and the degree of branching, we can represent the short-chain branching distribution as the weight fraction of the eluted species versus elution temperatures. For this purpose, we subtracted the baseline and normalized the peak.

Figure 6 shows the short-chain branching distributions obtained using the described analytical temperature-rising elution fractionation method for the two polyethylene standards. The temperature domains in which the polyethylene NBS 1475 and polyethylene NBS 1476 standards are eluted are similar with the reported data for highly crystalline polyethylene and

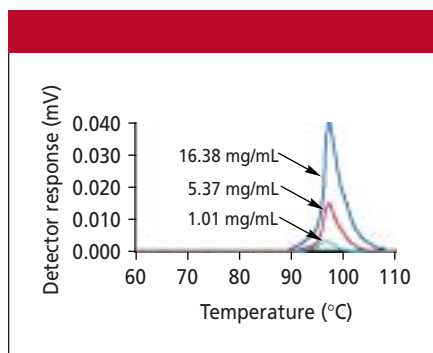


Figure 5: Analytical temperature-rising elution fractionation chromatograms of polyethylene NBS 1475 for three injected concentrations (1.01 mg/mL; blue; 5.37 mg/mL; pink; 16.38 mg/mL; black).

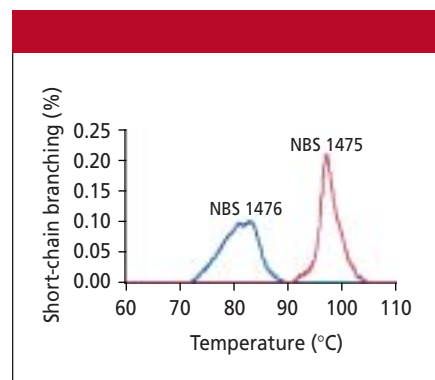


Figure 6: Short-chain branching distributions for two types of polyethylenes: linear (polyethylene NBS 1475) and branched (polyethylene NBS 1476).

branched polyethylene, respectively (11, 18,19).

It is important to mention that the resolution depends upon the temperature program (18). The resolution can be improved for complex samples by using slower temperature gradients for both crystallization and elution steps.

Conclusions

To develop an automated analytical temperature-rising elution fractionation method we needed two equally important things: a suitable commercial system (or a minor modification of a commercial system) and a reproducible method with this system.

In this article, we have presented a simple method to obtain an analytical temperature-rising elution fractionation system using a minor modification of a commercially available GPC instrument and a temperature-programming system. We also have established several guidelines for the analytical temperature-rising elution fractionation system qualification that use the accepted procedure for the validation of chromatographic systems.

An important parameter for the identification of compounds using HPLC systems is the reproducibility of the elution time for different analyzed compounds. For the analytical temperature-rising elution fractionation method, this reproducibility is translated into the reproducibility of the elution temperature. Using the system described above, we obtained a reproducibility of ± 0.05 °C for polyethylene NBS 1475 concentrations greater than 3 mg/mL and as great as 20 mg/mL.

For quantitative analyses of mixtures using the HPLC methods, a good calibration curve — peak area versus injected mass — is essential. In the analytical temperature-rising elution fractionation method, the mixture is composed of fractions that have different melting temperatures in solution. These fractions are recorded as a single chromatogram, which is used to obtain a short-chain branching distribution. For this reason, a linear calibration curve must be verified for a broad domain of concentrations before determination of short-chain branching distribution. Using our system, we found an excellent linear correlation between peak area and injected mass of the polymer for a domain of 0.1–17 mg/mL concentrations, which provides the possibil-

ity of a quantitative determination of short-chain branching distribution.

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