

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/235951795>

# Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC

DATASET · FEBRUARY 2012

---

CITATIONS

2

---

READS

44

5 AUTHORS, INCLUDING:



Vincent B. F. Mathot

University of Leuven

111 PUBLICATIONS 2,262 CITATIONS

SEE PROFILE

# Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC

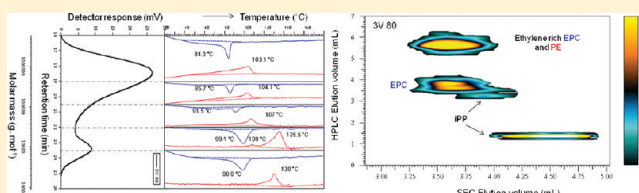
Sadiqali Cheruthazhekatt,<sup>†</sup> Thijs F. J. Pijpers,<sup>‡,§</sup> Gareth W. Harding,<sup>†</sup> Vincent B. F. Mathot,<sup>‡,§</sup> and Harald Pasch<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa

<sup>‡</sup>SciTe, Ridder Vosstraat 6, 6162 AX Geleen, The Netherlands

<sup>§</sup>Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

**ABSTRACT:** A new multidimensional fractionation technique, temperature rising elution fractionation (TREF) combined with high temperature size exclusion chromatography FTIR (HT-SEC-FTIR), HT-SEC-DSC and high temperature two-dimensional liquid chromatography (HT-2D-LC) is used for the comprehensive analysis of a commercial impact polypropylene copolymer. HT-SEC-FTIR provides information regarding the chemical composition and crystallinity as a function of molar mass. Thermal analysis of selected SEC fractions yields the melting and crystallization behavior of these fractions which is related to the chemical heterogeneity of this complex copolymer. The thermal analysis of the fractions is conducted using a novel DSC method — high speed or high performance differential scanning calorimetry (HPer DSC) — that allows measuring of minute amounts of material down to micrograms. The most interesting and complex “midelution temperature” TREF fraction (80 °C) of this copolymer is a complex mixture of ethylene-propylene copolymers (EPC's) with varying ethylene and propylene contents and sequence length distributions, as well as iPP. High temperature solvent gradient HPLC has been used to show that there is a significant amount of PE homopolymer and EPC's containing long ethylene sequences in this TREF fraction. High temperature 2D-LC analysis reveals the complete separation of this TREF fraction according to the chemical composition of each component along with their molar mass distributions.



## INTRODUCTION

Impact polypropylene copolymers (IPC) are a commercial grade of polypropylene (PP) which feature improved low temperature impact resistance. This class of polymers has seen growing demand in the thermoplastic market in recent times. The modified impact resistance of such heterophasic PP, together with the excellent properties of the polypropylene homopolymer such as rigidity and thermal and chemical resistance, makes the material highly useful in automotive and other applications.<sup>1,2</sup> Among the several methods reported for its production, the two-stage copolymerization process of propylene with ethylene is found to be the most effective and commercially adopted. The sequential multistage polymerization leads to the formation of highly complex materials consisting of many products, including amorphous, random, and segmented ethylene-propylene copolymers with different monomer sequence length distributions and molar mass distributions (MMD), as well as highly isotactic polypropylene and polyethylene homopolymers.<sup>3–6</sup> Preparative fractionation and subsequent analysis of the individual fractions is found to be an effective method for the complete characterization of such complex polymeric materials.<sup>7–10</sup> Offline coupling of SEC with FTIR is an established technique which has been used to

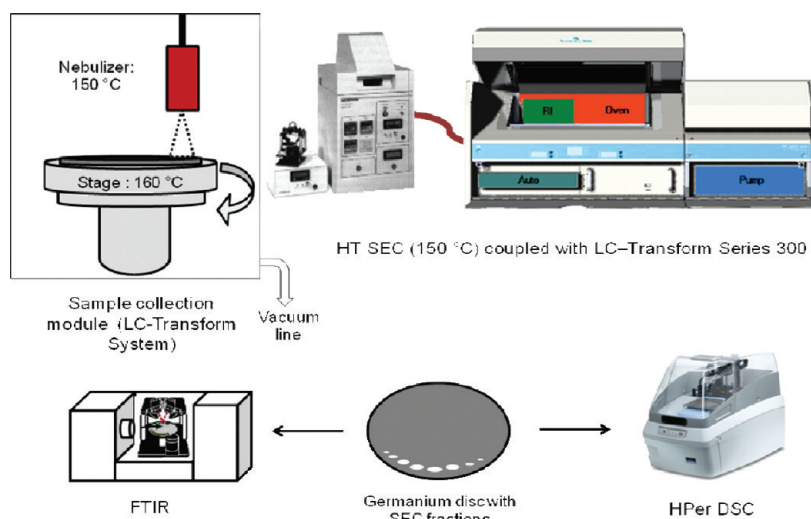
characterize the chemical composition distribution (CCD) across the molar mass distribution.<sup>11</sup>

Despite the fact that SEC-FTIR can indicate the level of ethylene and propylene crystallinity across these bimodal molar mass distributions, it is necessary to study the thermal behavior and crystallinity of these fractions thoroughly.<sup>12–15</sup> It has been reported that it is possible to couple SEC fractionation with standard DSC,<sup>16</sup> and even better with HPer DSC in order to study the short chain branching distribution along the MMD.<sup>17</sup> This is important due to the effect of molecular structure on the crystallization behavior, and thereby the final properties of the materials.<sup>18</sup> HPer DSC has the ability to measure very small sample masses while scanning at higher heating rates (up to 500 °C/min) than traditional, standard DSC. Fast scanning rates help to separate or reduce reorganizational thermal behavior, such as cold crystallization, recrystallization and decomposition which may occur during heating. The improvement in fast scanning DSC technology also offers the opportunity to detect weak transitions, including glass transitions which could not be determined by standard DSC.<sup>18</sup>

**Received:** December 13, 2011

**Revised:** January 25, 2012

**Published:** February 8, 2012



**Figure 1.** Polymer cross-fractionation techniques (SEC-FTIR and SEC-HPer DSC).

For many polymers, it has been proven that liquid chromatography is an efficient analytical technique for the fast separation of the polymer chains according to their chemical compositions.<sup>19</sup> However, the separation of polyolefins by high temperature liquid chromatography was only developed during the last couple of years by Pasch et al.<sup>20</sup> Initial work utilizing zeolites enabled the separation of polyolefins according to their chemical composition, however, the components could not be easily desorbed from the column packing.<sup>21,22</sup> Further development led to the separation of a blend of polypropylene and polyethylene based on the precipitation-redissolution mechanism on a modified silica gel column, using a solvent gradient of ethylene glycol monobutyl ether (EGMBE) (which is a good solvent for PP and not for PE) to 1,2,4-trichlorobenzene (TCB).<sup>20,21</sup> Most recently, research led to an HT-HPLC method capable of separating polypropylene according to tacticity in addition to the chemical composition separation of polyethylene from polypropylene.<sup>23</sup> This method is based on the adsorption-desorption mechanism and utilized the unique properties of the Hypercarb column.<sup>24</sup> To this date this is the only method for the swift and efficient separation of polyolefins and olefin copolymers according to their chemical compositions, where all components can be recovered from the column. The HPLC method separates polyolefin materials according to their chemical composition, although a slight molar mass influence on the retention volume has been observed for low molar masses. Despite this fact, the separation is governed mainly by the chemical composition or tacticity of samples; i.e., nearly baseline-separated peaks are obtained for all components. Several articles have been published based on the same separation methods for the analysis of polyolefins.<sup>25–30</sup> A new technique, high temperature thermal gradient interaction chromatography (HT-TGIC), has also been reported for the separation of olefin copolymers according to their comonomer content.<sup>31</sup> HT-HPLC allows one to estimate the chemical composition distribution (CCD) in such complex materials within a short period of time, which is a significant step forward for the characterization of these materials.

This study focuses on the molecular complexity of IPC and the analysis of different IPC components as separated by TREF and SEC using offline coupling with FTIR and HPer DSC, with emphasis on those TREF fractions exhibiting multimodal molar mass distributions. A single SEC separation and deposition is found to be sufficient for HPer DSC analysis. Melting and

crystallization of an IPC sample and its 80 °C TREF fraction were studied. These investigations were complemented by fractionation and analysis using HT-HPLC and HT-2D-LC.

## EXPERIMENTAL SECTION

A nonstabilized commercial IPC (designated as 3 V) was obtained from SASOL Polymers (Secunda, South Africa). The IPC sample has a comonomer (ethylene) content of 10.48 mol %, with a weight-average molar mass ( $M_w$ ) and dispersity ( $D$ ) of 228 kg·mol<sup>−1</sup> and 3.5, respectively.

**Size Exclusion Chromatography (SEC).** Molar mass measurements for all samples were performed at 150 °C using a PL GPC 220 high temperature chromatograph (Polymer Laboratories, Church Stretton, U.K.) equipped with a differential refractive index (RI) detector. The column set used consisted of three 300 × 7.5 mm PLgel Olexis columns together with a 50 × 7.5 mm PLgel Olexis guard column (Polymer Laboratories, Church Stretton, UK). The eluent used was TCB at a flow rate of 1.0 mL/min with 0.0125% 2,6-ditert-butyl-4-methylphenol (BHT) added as a stabilizer. Samples were dissolved at 160 °C in TCB at a concentration of 1 mg/mL for 1–2 h (depending on the sample type) and 200 µL of each sample was injected. Narrowly distributed polystyrene standards (Polymer Laboratories, Church Stretton, U.K.) were used for calibration.

**Temperature Rising Elution Fractionation (TREF).** Preparative TREF was carried out using an instrument developed and built in-house. Approximately 3.0 g of polymer and 2.0 w/w % Irganox 1010 (Ciba Specialty Chemicals, Switzerland) were dissolved in 300 mL of xylene at 130 °C in a glass reactor. The reactor was then transferred to a temperature-controlled oil bath and filled with sand (white quartz, Sigma-Aldrich, South Africa), used as a crystallization support. The oil bath and support were both preheated to 130 °C. The oil bath was then cooled at a controlled rate of 1 °C/h in order to facilitate the controlled crystallization of the polymer. The crystallized mixture was then packed into a stainless steel column which was inserted into a modified gas chromatography oven for the elution step. Xylene (preheated) was used as eluent in order to collect the fractions at predetermined intervals as the temperature of the oven was raised. The fractions were isolated by precipitation in acetone, followed by drying to a constant weight.

### Deposition of SEC Fractions by the LC Transform Interface.

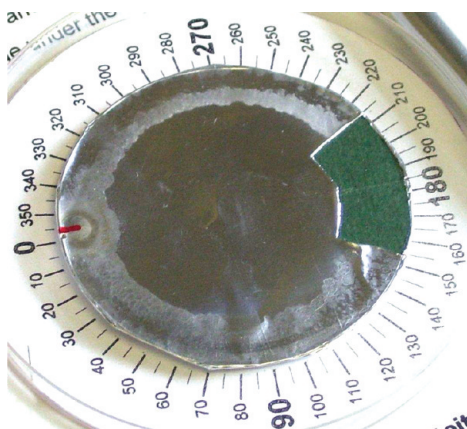
An LC-Transform series model 300 (Lab Connections) was coupled to a PL GPC 220 (Polymer Laboratories, Church Stretton, England) in order to collect the SEC eluate. Samples were dissolved at 160 °C in TCB at a concentration of 2 mg/mL, with 200 µL of each sample being injected. The SEC column outlet was connected to the LC transform interface (see Figure 1) through a heated transfer line set at 150 °C.

The fractions were deposited by rotating a germanium disk (sample target in the LC-transform) at a speed of 20°/min. The disk stage and nozzle temperatures of the LC-transform were set to 160 and 150 °C, respectively. For HPer DSC sample preparation an aluminum foil was wrapped around the germanium disk in such a way as to ensure good contact with the disk, with the opaque side of the foil being used for collection of the polymer deposits. The surface roughness of the opaque side of the foil enables comparatively higher adhesion as compared to the glossy side of the Al foil.<sup>32</sup> The bulk sample was collected by deposition of the entire sample at a single point on the germanium disk (no rotation). All the samples for SEC-FTIR and SEC-HPer DSC were prepared under the same deposition and cooling conditions in order to ensure comparable sample and thermal histories.

**FTIR Analyses of the Deposited Fractions.** FTIR analyses of the deposited SEC fractions were performed on a Thermo Nicolet iS10 Spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC-transform FTIR interface connected to a standard transmission baseplate. Spectra were recorded at a resolution of 8 cm<sup>-1</sup> with 16 scans being recorded for each spectrum. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

**Differential Scanning Calorimetry (DSC).** Melting and crystallization behavior of the bulk material and 80 °C TREF fraction were measured on a TA Instruments Q100 DSC system, calibrated with indium metal according to standard procedures. A heating rate of 10 °C/min was applied across the temperature range of 0–180 °C. Data obtained during the second heating cycle were used for all thermal analysis calculations. Measurements were conducted in a nitrogen atmosphere at a purge gas flow rate of 50 mL/min.

**High Performance Differential Scanning Calorimetry (HPer DSC).** Thermal properties of the SEC LC-Transform deposits were investigated using a Perkin-Elmer DSC 8500 (situated at SciTe's laboratory, Katholieke Universiteit Leuven, Belgium). A single deposition on the aluminum foil delivers enough material (not weighed as yet) for measurement at 50 °C/min, in both cooling and heating regimes. The foil is cut between various rotation angles for sample analysis (see Figure 2). The sample on the foil is folded into a



**Figure 2.** Example of an aluminum-covered disk after cutting out a sample for HPer DSC measurement. The portion of the aluminum foil removed is between 155° and 215°. This equates to the removal of the portion of the SEC eluate deposited between retention volumes of 20.75 to 24.75 mL.

flat package for analysis. For each sample, the first heating, first cooling, and second heating curves have been measured and plotted (endo up, exo down). All transitions observed turn out to be either crystallization (during cooling) or melting (during heating), and possibly recrystallization.

**Chromatographic System.** All chromatographic experiments were performed using a new chromatographic system for high-temperature two-dimensional liquid chromatography constructed by

Polymer Char (Valencia, Spain), comprising of an autosampler, two separate ovens, 2D switching valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven was used for the HPLC column, while the second oven, where the injector and a switching valve were located, was used for the SEC column. The autosampler is a separate unit connected to the injector through a heated transfer line. A high-pressure binary gradient pump was used for HPLC in the first dimension and an isocratic pump was used for SEC in the second dimension. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: A gas flow rate of 1.5 L/min, a nebulizer temperature of 160 °C, and an evaporator temperature of 270 °C.

**High Temperature HPLC.** HT-HPLC was carried out using a Hypercarb column (Hypercarb, Thermo Scientific, Dreieich, Germany) with the following parameters: 100 × 4.6 mm i.d., packed with porous graphite particles with a particle diameter of 5 μm, a surface area of 120 m<sup>2</sup>/g, and a pore size of 250 Å. The flow rate of the mobile phase was 0.5 mL/min. The column was placed in the column oven maintained at 160 °C. The HPLC separations were accomplished by applying a linear gradient from 1-decanol to TCB. The volume fraction of TCB was linearly increased to 100% within 10 min after the sample injection and then held constant for 20 min. Finally, the initial chromatographic conditions were re-established with 100% 1-decanol. Samples were injected at a concentration of 1–1.2 mg/mL, with 20 μL of each sample being injected.

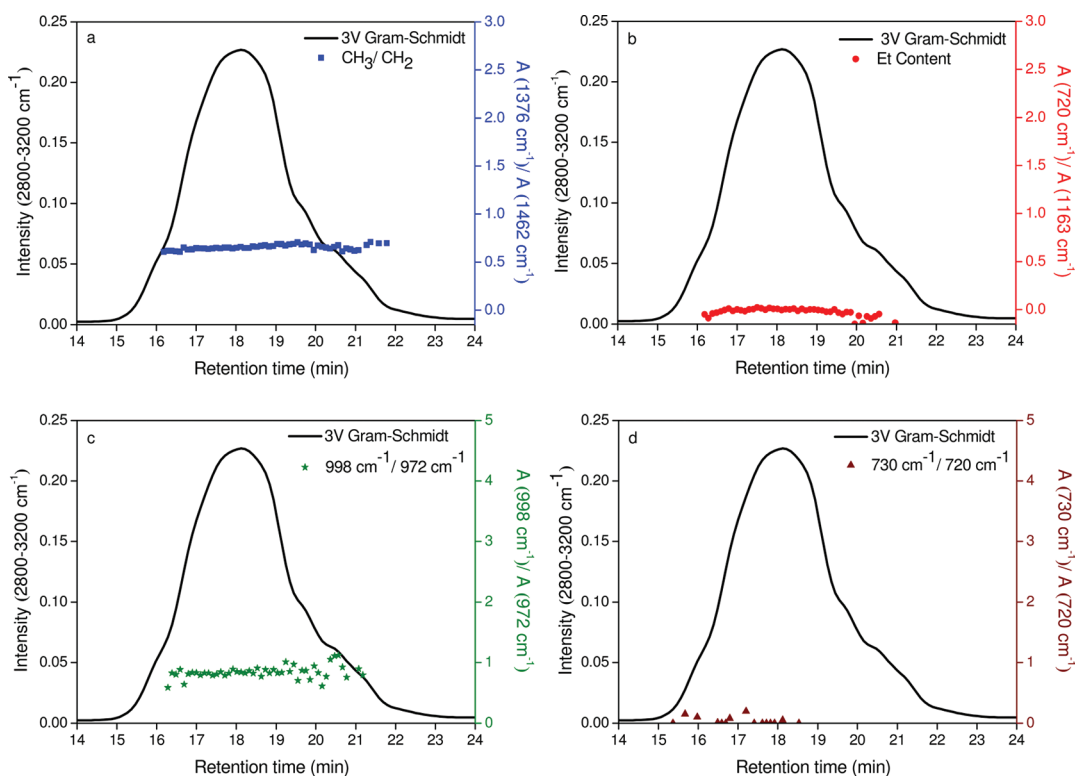
**High Temperature Two-Dimensional Liquid Chromatography (HT-2D-LC).** The coupling of HT-HPLC and HT-SEC was achieved by using an electronically controlled eight-port valve system (VICI Valco instruments, Houston, TX) equipped with two 100 μL sample loops. A 110 μL sample loop was used for injection into the first dimension. The flow rate for the first dimension was 0.05 mL/min, using the same gradient as for one-dimensional analysis, adjusted for the longer analysis time. TCB was used as the mobile phase for the second dimension at a flow rate of 2.75 mL/min. The second dimension column used was a PL Rapide H (Polymer Laboratories, Church Stretton, U.K.) 100 × 10 mm i.d. column with a 6 μm particle diameter. The column was placed in the top heated oven, maintained at 160 °C. Detection was performed with an ELSD using the same settings as for the one-dimensional (HPLC) separation.

## RESULTS AND DISCUSSION

This study explores the combination of selective fractionation with highly sensitive thermal analysis to investigate the correlation between molecular properties (chemical composition and molar mass) and thermal behavior. In a first step the bulk IPC sample has been investigated followed by TREF fractionation and the analysis of the most complex part of the sample, the midtemperature (80 °C) TREF fraction (3 V 80). Up to now the investigation of such complex polyolefins by SEC-HPer DSC cross-fractionation is at a preliminary stage.

**Analysis of the Bulk Sample.** When HT-SEC is coupled to FTIR, information about the chemical composition as a function of molar mass can be obtained. Using the LC-transform approach, a polymer concentration profile similar to the response from the conventional RI detector of the SEC instrument is obtained by integrating the spectral peak area over the 2800–3200 cm<sup>-1</sup> range of the FTIR spectrum.<sup>33,34</sup> This time-based representation of the total IR absorbance over this range during elution as a function of the total amount of the polymer sample is termed the Gram-Schmidt (GS) plot. The composition distribution can be determined from the deposition on the disk by analyzing the characteristic fingerprint region for particular functional groups. The propylene content was quantified by the ratio of the areas of the CH<sub>3</sub> and CH<sub>2</sub> bending bands at 1376 and 1462 cm<sup>-1</sup>, respectively. The ethylene content was quantified by the area ratio of the bands





**Figure 3.** SEC-FTIR analysis of the bulk sample (3 V) illustrating (a) the propylene ( $\text{CH}_3/\text{CH}_2$ ) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c and d), respectively.

at 720 and 1163  $\text{cm}^{-1}$ , which is used to determine the comonomer composition within EP block copolymers.<sup>11,35,36</sup>

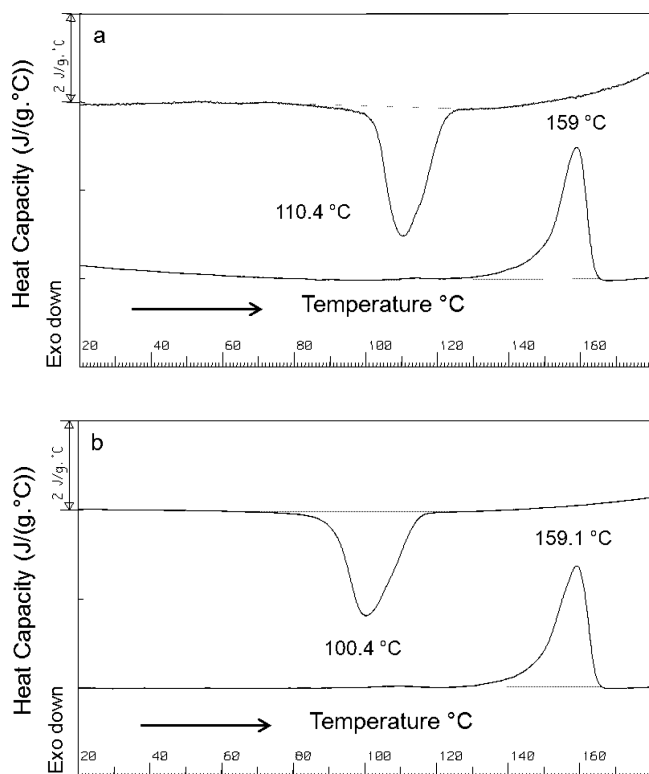
Figure 3 illustrates the SEC-FTIR results for the bulk sample (3 V). A uniform propylene concentration and its crystallinity distribution (Figure 3a and 3c) were observed across the GS curve for the bulk sample. The ethylene content and its crystallinity distribution (Figure 3b and 3d) have a lower value across the GS plot. This means that either the methylene ( $\text{CH}_2$ ) sequence lengths are short or that the number of methylene chain units is few, due to the relatively low ethylene content in the bulk copolymer sample.

It is possible to construct a crystalline distribution of ethylene and propylene (crystalline parts of PE and PP) across the GS. The two absorptions at 998 and 730  $\text{cm}^{-1}$  are the result of molecular vibrations from crystalline PP and PE regions, respectively. The absorption bands at 998 and 841  $\text{cm}^{-1}$  are known to originate from long repeating monomer units in the crystalline 3-fold helical structure of iPP. The band at 972  $\text{cm}^{-1}$  is associated with short helix segments from the amorphous region of PP. The relative intensity of the two bands at 998 and 972  $\text{cm}^{-1}$  can be used to estimate the level of PP crystallinity in the sample.<sup>37–41</sup> Similar to the propylene content distribution, a uniform propylene crystallinity distribution is observed across the GS plot. Because of the presence of crystalline ethylene sequences, the peak at 720  $\text{cm}^{-1}$  splits and an additional peak appears at 730  $\text{cm}^{-1}$ .<sup>33,42</sup> The relative ethylene crystallinity can be determined from the ratio of the absorbance at 730  $\text{cm}^{-1}$  to 720  $\text{cm}^{-1}$ . In the present sample the value of 730  $\text{cm}^{-1}$ /720  $\text{cm}^{-1}$  ratios across the GS curve was found to be zero, which indicates that either the sample does not contain any long crystallizable ethylene sequences or that the relative amount of long ethylene sequences in the sample is too low to be detected by SEC-FTIR of the bulk material.

The coupling of SEC with FTIR provides information on the propylene distribution and its crystallinity distribution across the molar mass distribution for this copolymer sample. On the other hand, it is difficult to determine the ethylene distribution and its crystallinity distribution for the bulk sample by using this technique. Since the amount of ethylene within this copolymer is small (10.5 mol %), it is difficult to differentiate it from the major component of the material which is isotactic polypropylene.

The DSC result for the bulk sample is displayed in Figure 4a showing a single distinct peak maximum for melting at 159 °C. This can be related to the melting process of the iPP matrix, since this melting endotherm is also observed in a pure iPP homopolymer sample and shows a similar melting temperature.<sup>43,44</sup> DSC on the bulk sample does not reveal any melting or crystallization events corresponding to the IPC components such as EPR, EPC, or PE homopolymers.

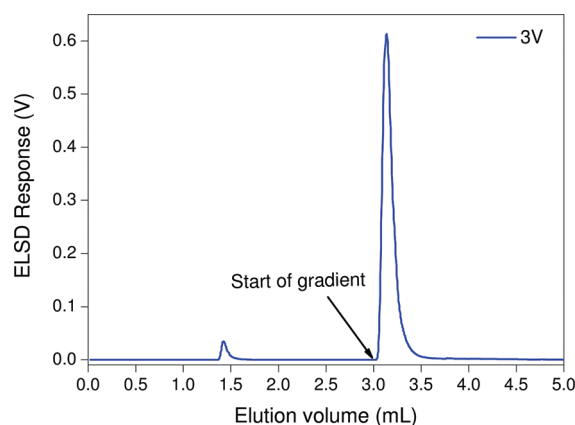
HPer DSC analysis of the bulk sample revealed that at 50 °C/min cooling and heating the peak maximum temperatures for crystallization and melting are approximately 100 and 159 °C, respectively, see Figure 4b. Compared to the standard DSC scan rate of 10 °C/min the crystallization temperature has shifted by 10 °C toward the lower temperature side with increasing the cooling rate from 10 °C/min to 50 °C/min. However, the peak maximum temperature of melting does not change, probably reflecting reorganization during heating, not nullified by heating at 50 °C/min because it would ask for a much higher heating rate. As is seen from Figure 4b, the cooling curve is broadened at 50 °C/min compared to the cooling curve at 10 °C/min, Figure 4a, the reason being that—when the sample mass is kept constant like in Figure 4 because the same sample packed in aluminum was used in both cases—the lowest scan rates induce the narrowest DSC peaks, while increasing the



**Figure 4.** HPer DSC results for the bulk sample, (a) DSC 1st cooling and 2nd heating curves at 10 and 50 °C/min, respectively, and (b) 1st cooling and 2nd heating curves, both obtained at a scan rate of 50 °C/min.

scan rate will broaden these peaks,<sup>18</sup> as is the case here for the cooling curves.

A chemical composition separation of the sample can be achieved by HT-HPLC where elution takes place regarding the E/P content. Figure 5 indicates that the bulk sample elutes in



**Figure 5.** HT-HPLC chromatogram obtained after isocratic and gradient elution for the bulk IPC copolymer sample (3 V).

two regions, the first elutes in 1-decanol while the second elutes after the start of the gradient elution. All iPP standards, with the exception of the very low molar mass standards, elute in these two zones meaning that the PP chains are partially retained on the Hypercarb column from 1-decanol, being desorbed in the gradient from 1-decanol to TCB.<sup>45</sup> No peaks corresponding to EPR, EPC, or PE homopolymer were observed in the

chromatogram for the bulk sample due to the low concentration of these components.

A first information on the thermal properties as a function of molar mass can be obtained by combining HT-SEC and HPer DSC. As is shown in the Experimental Section, different molar mass fractions are collected using the LC Transform system. The SEC depositions (approximately 0.4 mg of total weight), forming a continuous film on the aluminum foil, were divided into five separate SEC fractions. These fractions are subsequently subjected to HPer DSC measurements providing well resolved melting and crystallization curves.

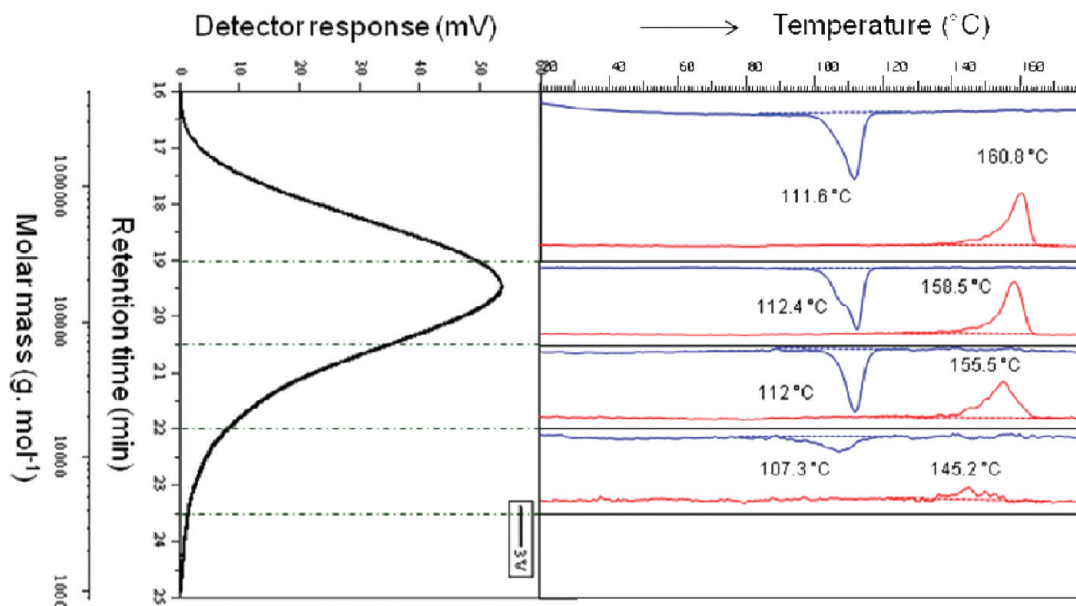
The capability of measuring minute amounts of material from fractionations stems from the fact that by increasing the scan rate the sensitivity of the DSC is increased. However, the thermal lag also increases and, thus, smaller samples are to be taken in order to keep the thermal lag acceptable, meaning at the same level as is accepted for standard DSC. In practice, for HPer DSC, milligrams down to micrograms of material are being used, and the present, limited amounts available from the fractionations pose no problem for the HPer DSC.

Figure 6 combines the results from the first cooling and second heating HPer DSC curves for the SEC fractions of 3 V. The HPer DSC curves for each SEC fraction range are compared to the overall SEC chromatogram in terms of retention time as well as its calibrated molar mass distribution.

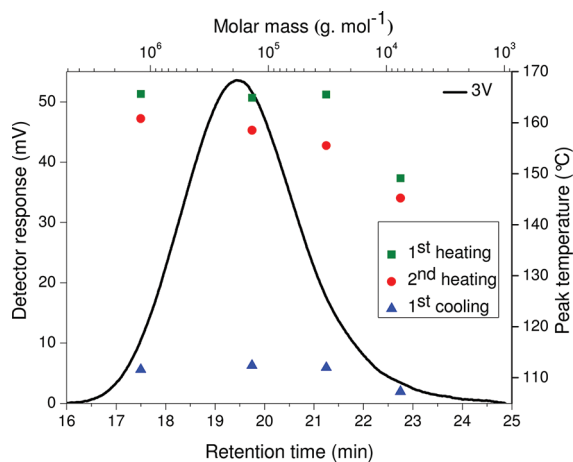
Figure 7 illustrates the molar mass dependence on the melting peak temperatures. The peak melting temperatures increase within the temperature range 145–165 °C, indicating the presence of crystalline iPP. The fractions eluting from 20.5 min onward show some broadening. This could indicate compositional heterogeneity in addition to the well-known stronger dependence of the crystallization and melting temperatures on molar mass in the lower mass range. A simple SEC separation is not able to reveal such subtleties, especially not for a bulk sample with relatively low comonomer content. SEC fractionation followed by HPer DSC analysis is a promising combination to provide important information regarding the chemical composition of the bulk sample.

As has been shown in these first and preliminary experiments, traditional bulk sample analysis even using the highly sophisticated HT-HPLC method cannot provide sufficient information regarding the different components in these complex copolymers. New analytical approaches are needed to obtain more detailed information about the different components, in particular when they are present in small concentrations. It is clear that for thorough characterization of such materials, the components with vastly differing chemical composition must be separated so that these components can be analyzed separately in higher concentrations. In principle, preparative TREF can be considered as a suitable method for the separation, isolation, and complete analysis of the individual components in the copolymer system, as one expects these would show different fractionation behavior based on the components' different crystallizabilities from solution.<sup>7,10,11</sup>

As has been shown previously by us and others, IPC can be separated into three major fractions, namely the highly crystalline iPP, the amorphous EP rubber and a “midtemperature” fraction that is speculated to contain segmented EP copolymers. This fraction elutes in the temperature range of 60–80 °C and amounts only to about 5 wt % of the total sample. It is assumed to be the most complex fraction, at the same time being very important for the phase formation in these multiphase copolymers. In the following section, this



**Figure 6.** HPer DSC 1st cooling and 2nd heating curves for the SEC fractions of the bulk sample (3 V) at scan rates of 50 °C/min, along with the overall SEC elution profile. The left half of the figure depicts the molar mass distribution as recorded by the RI detector, while the right half of the figure depicts the individual HPer DSC results from each fraction as cut out from the aluminum foil at the specific retention time windows.

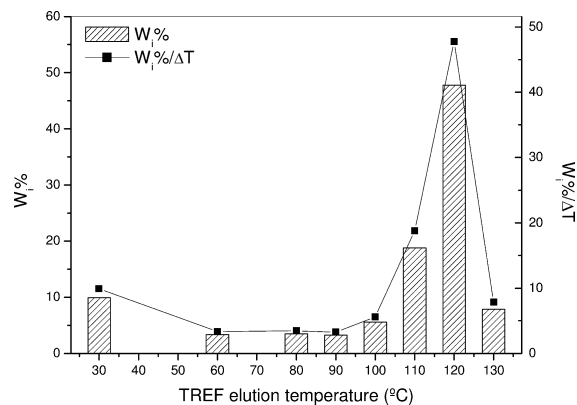


**Figure 7.** SEC curve of the bulk product 3 V showing the retention time axis and molar mass axis, indicating the peak maximum temperatures of the HPer DSC cooling and heating curves of the SEC fractions at 50 °C/min.

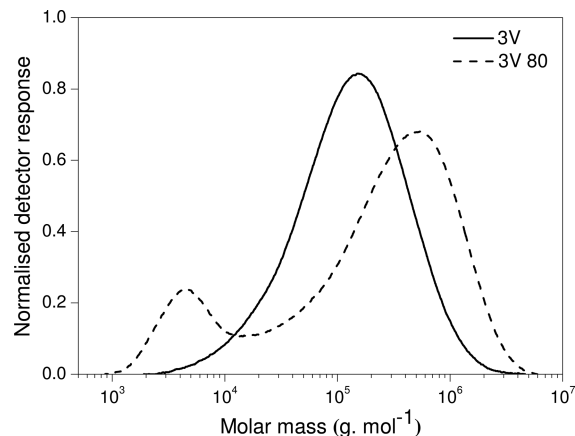
fraction shall be studied in detail to reveal its compositional complexity.

**Analysis of the 80 °C TREF Fraction (3 V 80).** The TREF fractionation of the bulk sample is presented in Figure 8. As has been discussed previously, the 30 °C TREF fraction contains mainly the EP rubber while the 100–130 °C TREF fractions contain mainly iPP.<sup>11</sup>

The molar mass distributions for the bulk sample 3 V and its 80 °C TREF fraction are compared in Figure 9. The 80 °C fraction shows a clear bimodality in MMD, which indicates compositional heterogeneity due to the coelution (from TREF) of nonidentical components. Multimodal distributions are often observed for these midelution temperature TREF fractions due to the coelution of semicrystalline EPCs and PP homopolymers, due to the tacticity distribution of PP.<sup>11</sup> The PP homopolymer does not elute entirely at temperatures >100 °C



**Figure 8.** Mass distribution and mass fraction per temperature increment for the TREF fractions of copolymer 3 V.<sup>11</sup>

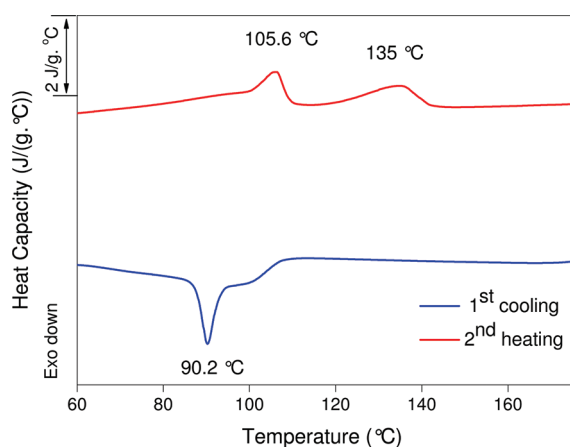


**Figure 9.** SEC curves for the bulk sample (3 V) and its 80 °C TREF fraction (3 V 80).

due to the fact that chains of lower tacticity become soluble at the same lower temperatures as the EPC phase of similar solubility.

TREF-SEC does not supply information on the chemical composition of these TREF fraction. It is clear that even the knowledge of MMD available from SEC analysis for the 80 °C TREF fraction is not sufficient to define the compositional heterogeneity, since SEC separates polymers according to the hydrodynamic volume of the molecules. It is important to understand the exact nature of the molecular species in this important fraction since they affect thermal, mechanical, and optical properties by the way they constitute the various phases present after cooling, like crystalline, amorphous, and possible rigid amorphous phases etc. In addition, on the molecular level, with respect to mechanical properties, the crystallites and their connections play an important role; such organization strongly depends on the way of crystallization as determined by the molecular architecture and the cooling conditions.

Two melt endotherms were observed for the 80 °C TREF fraction by standard DSC analysis, see Figure 10, which



**Figure 10.** Two DSC melt endotherms present in the 80 °C TREF fraction (3 V 80). Heating and cooling rates were 10 °C/min.

indicates the compositional heterogeneity in the midtemperature eluting fraction. It is impossible to assign the melting endotherms from the standard DSC technique, for this specific complex TREF fraction, to a chain structure, since a single peak could result from one component overruling others, as is seen in the case of the bulk material. Possibly, one of the melting endotherms is due to the propylene rich segments of the EPC, while the other is due to the melting of the ethylene rich segments, crystallized in their respective crystal structures. However, due to variations in the tacticity of polypropylene, as well as comonomer content for the copolymers, it is possible that either monomer type could melt at both the observed temperatures. A more in-depth analysis is needed in order to assign the crystallization and melting transitions to particular chain types.

SEC-FTIR (Figure 11), has been used for the determination of the chemical composition and crystallinity distributions across the molar mass distribution for fraction 3 V 80. The fraction exhibits a gradual increase in the  $\text{CH}_3/\text{CH}_2$  ratio (Figure 11a) across the bimodal molar mass distribution, indicating higher propylene content within the low molar mass component. The  $720\text{ cm}^{-1}/1162\text{ cm}^{-1}$  area ratio (Figure 11b) of this fraction indicates the presence of ethylene within the higher molar mass component only. The  $998\text{ cm}^{-1}/972\text{ cm}^{-1}$  ratio (Figure 11c) is essentially zero for low retention volumes and increases only at higher retention volumes where the low

molar mass component of the fraction elutes which is revealed to be mostly polypropylene. Ethylene crystallinity (Figure 11d) is only observed at low elution volumes. It is concluded that the lower molar mass component of the bimodal distributions consists principally of propylene homopolymer only; whereas EPC's with different monomer distributions and longer crystallizable ethylene sequences are present within the higher molar mass component.

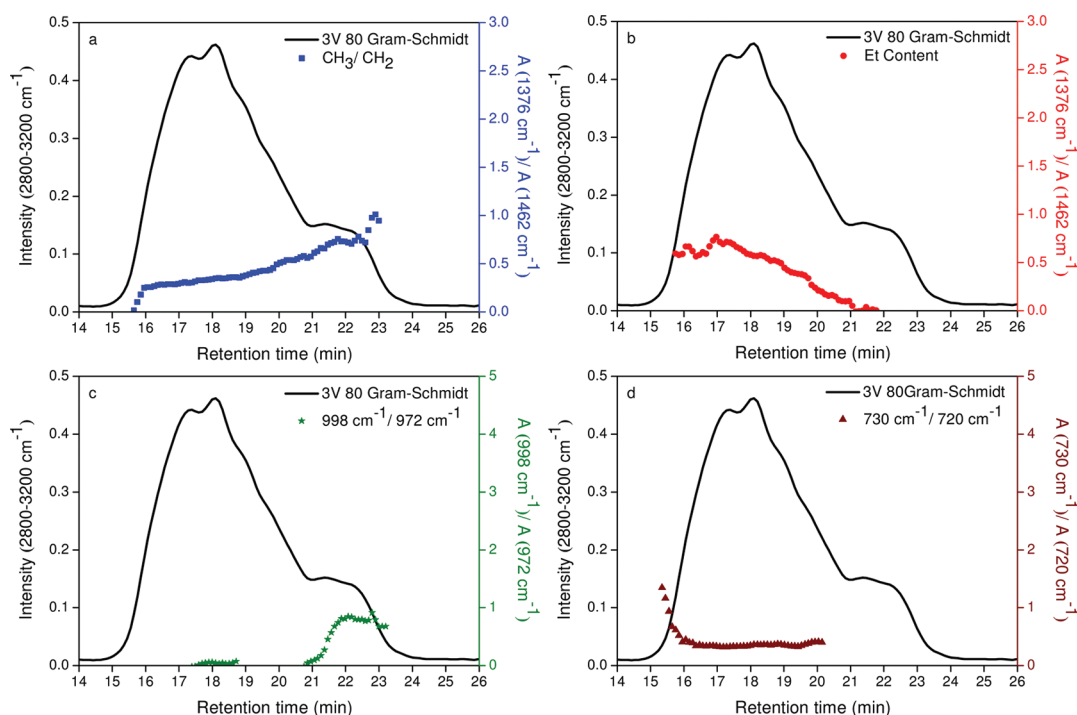
TREF-(SEC-HPer DSC) turns out to be an excellent tool for probing the crystallization and melting effects observed for complex polymer mixtures. What is difficult to realize with standard DSC is relatively easily revealed by the HPer DSC analysis of the TREF-SEC fractions as seen in Figure 12. All of the first three (high molar mass) SEC fractions have broad melting endotherms, indicating that these fractions probably contain a complex mixture of ethylene-propylene copolymers, possibly ethylene-rich copolymers and/or segmented EP copolymers; possible branched to almost linear, semicrystalline polyethylene, and finally, possibly low tacticity polypropylene homopolymer. This is in agreement with the SEC-FTIR results (Figure 11), which show that the copolymers which are richest in ethylene elute at low retention times (higher molar mass) and that there is a gradual increase in the propylene concentration with increasing retention time (decreasing molar mass). Crystalline polypropylene is found within the low molar mass fraction while crystalline polyethylene or PE segments of segmented EP copolymers are found in the higher molar mass fraction.

SEC fractions (Figures 12 and 13) at retention times of 16 to 22 min show a melting peak in the range of 103 to 107 °C (lower than  $T_m$  of HDPE and  $T_m$  of iPP). This suggests that there are insufficiently long iPP or PE segments to form highly stable crystallites of appreciable dimensions and perfection dissolving at 80 °C during TREF and eluting in this specific molar mass region of the TREF fraction.<sup>46</sup> SEC-FTIR results indicate that this fraction contains ethylene-propylene copolymers to a significant extent, with mainly longer ethylene sequences. Increasing melting temperature with retention time is observed even for late eluting fractions. SEC fractions eluting between 22 and 26.5 min show melting endotherms at 135 and 130 °C, respectively. The SEC-FTIR data (Figure 11) indicate the presence of high amounts of propylene in these fractions, with little or no ethylene present. These SEC fractions contain mostly propylene-rich copolymers or polypropylene homopolymers with lower tacticity and molar mass, which probably results in the formation of crystallites with reduced lamellar thickness and lower perfection as compared to highly crystalline iPP.<sup>47–49</sup> The lower tacticity and by that lower crystallizability is quite obvious if one compares the maximum peak temperatures of melting in this range of e.g. a molar mass fraction of 10000 g/mol (approximately 135 °C for the present case) with the one for the bulk sample 3 V 0 h (approximately 150 °C).

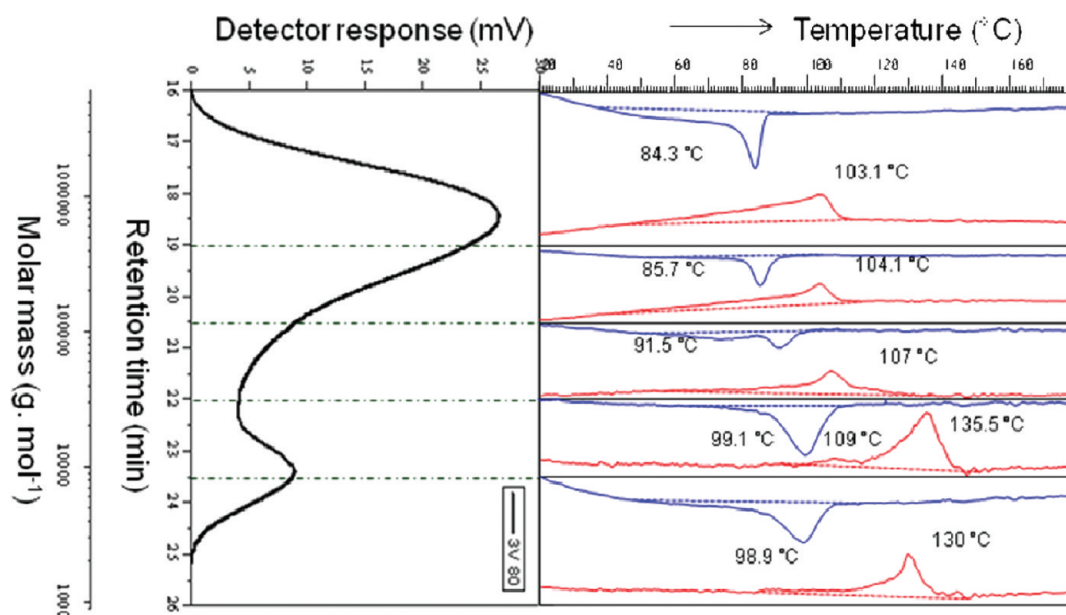
Finally, it has to be pointed out that the data as obtained by SEC-FTIR in principle have to be compared with the results obtained from the first heating experiment of the DSC, because then the thermal and sample histories by deposition on the disk are the same. For the present qualitative discussion, however, using the results from the second heating curves is acceptable because these are qualitatively analogous to the first heating curves; see Figures 7 and 13.

It is evident from the TREF-(SEC-FTIR) and TREF-(SEC-HPer DSC) results that there is an overlapping of EPC with





**Figure 11.** SEC-FIR analysis of fraction 3 V 80, illustrating (a) the propylene ( $\text{CH}_3/\text{CH}_2$ ) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c and d), respectively.

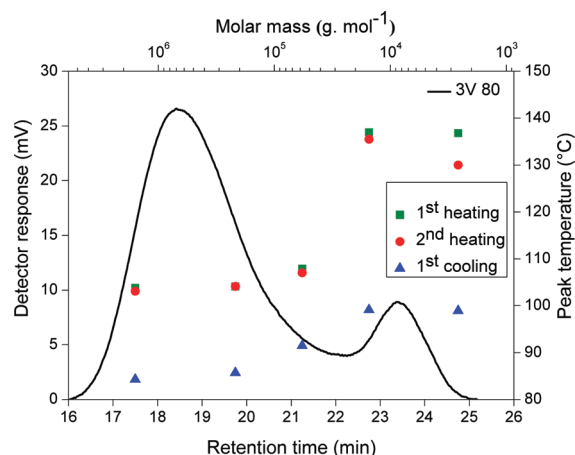


**Figure 12.** SEC curve of fraction 3 V 80 showing the retention time axis and molar mass axis, as well as the HPer DSC cooling and heating curves for the SEC fractions as "retention time boxes". HPer DSC scan rates were 50 °C/min.

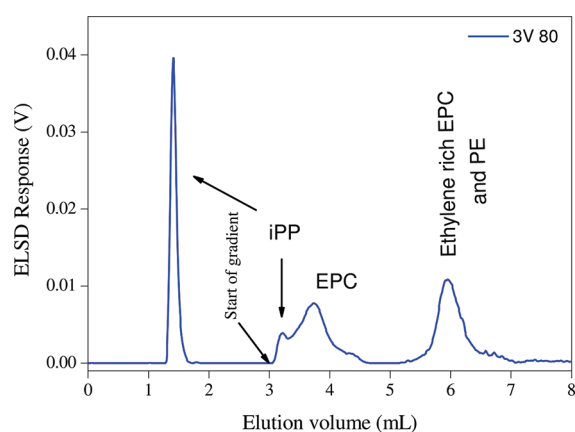
iPP due to the tacticity distribution for this midelution temperature fraction (3 V 80). A complete separation of these components according to the chemical composition by using TREF is not possible, undoubtedly also due to cocrystallization of the components at the same temperature. Separation of blends of polyolefins containing iPP, sPP, aPP, and PE on a Hypercarb stationary phase with a gradient from 1-decanol to TCB has been previously reported.<sup>23,50</sup> In order to further investigate the 80 °C TREF fraction and confirm the results obtained from HPer DSC we separated the components in this fraction of an IPC sample using the same method

reported for the blend. The results of this separation are given in Figure 14.

The low molar mass isotactic PP elutes in 100% 1-decanol at approximately 1.5 mL, followed by the retained iPP components that are desorbed by the gradient. Although the chemical composition is the primary parameter and governs the separation, the molar mass of the components also plays a role, especially for low molar masses. The EPC and linear PE are also fully retained due to their selective adsorption on the column packing, being only eluted in the gradient. It can be seen that the Hypercarb column is very selective with respect to



**Figure 13.** SEC curve of fraction 3 V 80 showing the retention time axis and molar mass axis, indicating the peak maximum temperatures of the HPer DSC cooling and heating curves for the SEC fractions at 50 °C/min.



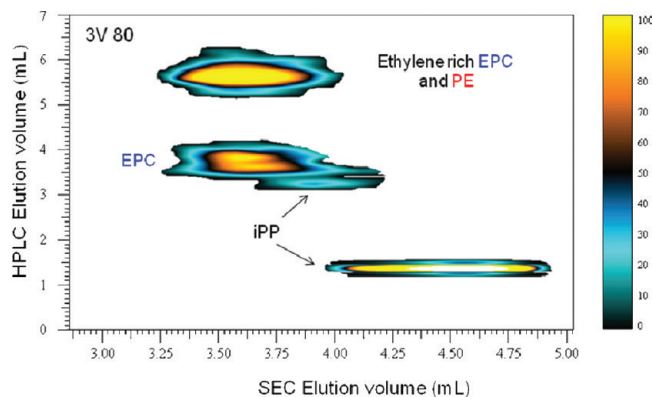
**Figure 14.** Chromatogram obtained after isocratic and gradient elution for fraction 3 V 80.

the chemical composition of the polymers, differentiating even with respect to their microstructure.

In order to study the influence of the molar mass of the components on the elution volume in HPLC, the fraction 3 V 80 was analyzed by HT-2D-LC. The corresponding contour plot is presented in Figure 15.

All components of fraction 3 V 80 are well separated from each other by both chemical composition and molar mass. It can be seen that the iPP has a lower molar mass component which elutes in pure 1-decanol and a second slightly higher molar mass component eluting in the gradient.<sup>44</sup> While EPC with different ethylene and propylene sequences as well as PE homopolymer having similar molar masses eluted according to their interaction on the Hypercarb column. There is a clear separation between the iPP and EPC copolymers. EPC dominated by longer propylene sequences elute closer to iPP while those dominated by longer ethylene sequences elute together with PE homopolymer (eluting at approximately 6.0 mL). As a result the HT-2D-LC represents a complete characterization of this TREF fraction in terms of both molar mass and chemical composition, accomplished within a relatively short analysis time.

The ethylene–propylene random/segmented copolymers (which constitute the bulk of the midelution TREF fractions)



**Figure 15.** HT-2D-LC contour plot for the fraction 3 V 80.

improve the adhesion between the EPR phase and the iPP matrix by acting as a compatibiliser between the phases. Therefore, the role of such fractions is very important for the overall properties of impact copolymers. From an analytical point of view, SEC-HPer DSC yields further insight into the thermal and mechanical properties of such complex materials, while HT-HPLC can completely separate the components in the midelution temperature fractions according to their chemical composition. Thus, these techniques are found to be very important for the industrial, as well as academic fields.

## CONCLUSIONS

The molecular characteristics (molar mass, chemical composition, and tacticity distributions) and thermal behavior (melting and crystallization) of a commercial impact polypropylene and its midelution temperature TREF fraction were investigated using various multidimensional analytical techniques such as SEC-FTIR, SEC-HPer DSC, and high temperature two-dimensional liquid chromatography. Analysis of the bulk sample by the above-mentioned techniques does not provide any in-depth information regarding the chemical composition and thermal behavior of the various components in this complex polymer system. For this reason, fractionation of the bulk sample and a more detailed study on one of the midelution temperature TREF fractions has been carried out in order to identify the complex components in the total polymer system and evaluate their effect on the thermal properties.

SEC-FTIR results indicate the presence of EPC copolymer and iPP homopolymer as the main constituents of the 80 °C TREF fraction. The crystallinity distribution of ethylene and propylene across the MMD by this technique indicates the presence of crystallizable ethylene sequences in the high molar mass component, with highly crystalline PP being found in the low molar mass component. Thermal analysis of the SEC fractions by HPer DSC provides information on the thermal properties of the different molar mass fractions, and, thereby, the compositional heterogeneity of the components. SEC-HPer DSC results also confirm the presence of EPC copolymers with crystalline sequences of ethylene and propylene with varying sequence lengths as well as ethylene homopolymers in the high molar mass SEC fractions, while crystalline PP homopolymer is found in the low molar mass SEC fractions. The ability to measure the thermal behavior of very small sample masses (SEC fractions) with HPer DSC enables the investigation of the thermal properties across the MMD of this complex midelution temperature TREF fraction. The combination of the two cross-fractionation techniques is found to be highly useful

for the mapping of the CCD across the molar mass slices for these complex TREF fractions.

The presence of PE homopolymer and EPCs containing long ethylene sequences in the 80 °C TREF fraction was proven by HT-HPLC. This is the first time that individual components in the midelution temperature TREF fraction of an IPC were separated according to their chemical composition using high temperature solvent gradient HPLC, which is based on the selective adsorption and desorption of the polymer molecules on a Hypercarb stationary phase at 160 °C. Finally, a complete separation of each component according to their chemical composition and molar mass was achieved through HT-2D-LC. The overall results demonstrate that these multidimensional techniques are found to be excellent analytical tools, necessary for a proper understanding of the molecular characteristics and thermal behavior of complex polymer fractions.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: hpasch@sun.ac.za.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The involvement of PerkinElmer UK/USA is much appreciated by T.P. and V.M. Also the support for SciTe from the EU-FP7-NaPolyNet/Coordination Support Action NMP-2007-2.1-3/Characterization of nanostructured materials, see <http://www.napolynet.eu>, is highly valued.

## REFERENCES

- (1) Maier, C.; Calafut, T. Polypropylene, The Definitive User's Guide and Databook. In *Polypropylene*; Plastics Design Library; Elsevier Inc.: Amsterdam, 1998; pp 11–25.
- (2) Galli, P.; Haylock, J. C.; Simonazzi, T. Manufacturing and Properties of Polypropylene Copolymers. In *Polypropylene: Structure Blends and Composites*, Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; Vol. 2, p 1.
- (3) Tortorella, N.; Beatty, C. L. *Polym. Eng. Sci.* **2008**, *48*, 1476–148.
- (4) Fan, Z. Q.; Zhang, Y. Q.; Xu, J. T.; Wang, H. T.; Feng, L. X. *Polymer* **2001**, *42*, 5559–5566.
- (5) Tan, H.; Li, L.; Chen, Z.; Song, Y.; Zheng, Q. *Polymer* **2005**, *46*, 3522–3527.
- (6) Hongjun, C.; Xiaolie, L.; Dezhu, M.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* **1999**, *71*, 93–101.
- (7) Francis, M.; Mirabella Jr. *Polymer* **1993**, *34*, 1729–1735.
- (8) Xue, Y.; Fan, Y.; Shuqin, B.; Xiangling, J. *Eur. Polym. J.* **2011**, *47*, 1646–1653.
- (9) Zacur, R.; Goizueta, G.; Capiati, N. *Polym. Eng. Sci.* **1999**, *39*, 921–929.
- (10) Rafael, A.; García, B. C.; María-Teresa, E.; Inmaculada, S.; Almudena, F.; Caveda, S. *Macromol. Res.* **2011**, *19*, 778–788.
- (11) de Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* **2010**, *295*, 366–373.
- (12) Karger, K. J.; Kallo, A.; Szafner, A.; Bodor, G. *Polymer* **1979**, *20*, 37–43.
- (13) Zhisheng, F.; Junting, X.; Yanzhong, Z.; Zhiqiang, F. *J. Appl. Polym. Sci.* **2005**, *97*, 640–647.
- (14) Hongjun, L. C.; Xiaolie, M. D.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* **1999**, *71*, 103–113.
- (15) Luruli, N.; Pijpers, T.; Brüll, R.; Grumel, V.; Pasch, H.; Mathot, V. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2956–2965.
- (16) Mathot, V. B. F.: The Crystallization and Melting Region. In *Calorimetry and Thermal Analysis of Polymers*; Mathot, V. B. F., Ed.; Hanser Publishers: Munich/Vienna/New York, 1994; Chapter 9, pp 231–299.
- (17) Krumme, A.; Basiura, M.; Pijpers, T.; Poel, G. V.; Heinz, L. C.; Brüll, R.; Mathot, V. B. F. *Mater. Sci.* **2011**, *17* (3), 260–265.
- (18) Poel, G. V.; Mathot, V. B. F. *Thermochim. Acta* **2007**, *461*, 107–121.
- (19) Pasch, H.; Trathnigg, B. *HPLC of Polymers*, 1st ed.; Springer: Berlin, 1998.
- (20) Heinz, L. C.; Pasch, H. *Polymer* **2005**, *46*, 12040–12045.
- (21) Macko, T.; Pasch, H.; Brüll, R. *J. Chromatogr. A* **2006**, *111*, 81–87.
- (22) Macko, T.; Denayer, J. F.; Pasch, H.; Baron, G. V. *J. Sep. Sci.* **2003**, *26*, 1569–1574.
- (23) Macko, T.; Pasch, H. *Macromolecules* **2009**, *42*, 6063–6067.
- (24) Pereira, L. J. *Liq. Chromatogr. Related Technol.* **2008**, *31*, 1687–1731.
- (25) Albrecht, A.; Heinz, L. C.; Dieter, L.; Pasch, H. *Macromol. Symp.* **2007**, *257*, 46–55.
- (26) Macko, T.; Brüll, R.; Alamo, G.; Thomann, Y.; Grumel, V. *Polymer* **2009**, *50*, 5443–5448.
- (27) Macko, T.; Cuttillo, F.; Busico, V.; Brüll, R. *Macromol. Symp.* **2010**, *298*, 182–190.
- (28) Dolle, V.; Albrecht, A.; Brüll, R.; Macko, T. *Macromol. Chem. Phys.* **2011**, *212*, 959–970.
- (29) Chitta, R.; Macko, T.; Brüll, R.; Doremaele, G. V.; Heinz, L. C. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1840–1846.
- (30) Macko, T.; R. Brüll, R.; Alamo, R. G.; Stadler, F. J.; Losio, S. *Anal. Bioanal. Chem.* **2011**, *399*, 1547–1556.
- (31) Cong, R.; deGroot, W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062–3072.
- (32) Zhu, W. W.; Allaway, J. R. *J. Chromatogr. A* **2004**, *1055*, 191–196.
- (33) Noel, L. V.; Baldo, L.; Bremmers, S. *Polymer* **2001**, *42*, 5523–5529.
- (34) Liu, M. X.; Dwyer, J. L. *Appl. Spectrosc.* **1996**, *50*, 349–356.
- (35) DesLauriers, P. J.; Rohlfing, D. C.; Hsieh, E. T. *Polymer* **2002**, *43*, 159–170.
- (36) Tso, C. C.; DesLauriers, P. J. *Polymer* **2004**, *45*, 2657–2663.
- (37) Liang, C. Y.; Pearson, F. G. *J. Mol. Spectrosc.* **1960**, *6*, 290–306.
- (38) Luongo, J. P. *J. Appl. Polym. Sci.* **1960**, *3*, 302.
- (39) Andreassen, E. Infrared and Raman Spectroscopy of Polypropylene. In *Polypropylene: An A-Z reference*; Karger-Kocsis, J., Ed.; Kluwer Publishers: Dordrecht, The Netherlands, 1999; p 320.
- (40) Painter, P. C.; Watzek, M.; Koenig, J. L. *Polymer* **1977**, *18*, 1169.
- (41) Monasse, B.; Haudin, J. M. Molecular Structure of Polypropylene Homo- and Copolymers. In *Polypropylene: Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; p 3.
- (42) Cossar, M.; Teh, J.; Kivisto, A.; Mackenzie, J. *Appl. Spectrosc.* **2005**, *59*, 300–304.
- (43) Schick, C. *Anal. Bioanal. Chem.* **2009**, *395*, 1589–1611.
- (44) Burfield, D. R. *Macromolecules* **1983**, *16*, 702–704.
- (45) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* **2011**, *47*, 319–329.
- (46) Zhang, C.; Shangguan, Y.; Chen, R.; Zheng, Q. *J. Appl. Polym. Sci.* **2011**, *119*, 1560–1566.
- (47) Mahdavi, H.; Nook, M. E. *Polym. Int.* **2010**, *59*, 1701–1708.
- (48) Zhang, C.; Shangguan, Y.; Chen, R.; Wu, Y.; Chen, F.; Zheng, Q.; Hu, G. *Polymer* **2010**, *51*, 4969–4977.
- (49) Tan, H.; Li, L.; Chen, Z.; Songa, Y.; Zheng, Q. *Polymer* **2005**, *46*, 3522–3527.
- (50) Macko, T.; Brüll, R.; Zhu, Y.; Wang, Y. *J. Sep. Sci.* **2010**, *33*, 3446–3454.