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Fractionation and Characterization of Impact Poly(propylene) Copolymers by High Temperature Two-Dimensional Liquid Chromatography

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Summary: Information regarding molar mass distribution (MMD) and chemical composition distribution (CCD) of complex polyolefins such as impact polypropylene copolymer (IPC) is important in order to fully understand their properties during processing and application. Precise analysis of such polymeric materials having multiple distributions in various molecular characteristics is a difficult task and single separation methods fail to provide enough information about their microstructure. Preparative fractionation and subsequent analysis of the separated fractions was found to be an effective method for their complete characterisation. In this work, a combination of preparative TREF with high temperature two-dimensional liquid chromatography was used for the separation and analysis of the complex components in a commercial IPC sample. In addition to the ethylene-propylene (block or segmented) copolymers and low molar mass isotactic polypropylene (iPP) homopolymer (as expected in the semicrystalline TREF fraction of an IPC), significant amounts of high molar mass iPP and polyethylene (PE) homopolymer were observed. The results showed that the TREF-HT-2D-LC combination can be used as a powerful analytical tool for the complete microstructural analysis of such complex EP copolymers.

Keywords: chemical composition separation; crystallization analysis fractionation; ethylene-propylene copolymers; high temperature two-dimensional liquid chromatography; impact polypropylene copolymer; TREF

Introduction

Impact polypropylene copolymer (IPC) is a commercial grade of polypropylene (PP), produced to improve the low temperature impact resistance of the PP homopolymer. Modified impact resistance together with excellent properties of PP makes this material highly useful in automotive and other applications. Commercially they are produced by a two-stage polymerization process, which results in the formation of extremely complex materials, consisting of iPP homopolymer, ethylene-propylene random/segmented or block copolymers and a small amount of polyethylene.[1–6] The amount and chemical structure of the various components in this system play a significant role in deciding the final impact performance. Therefore, a detailed microstructural analysis is necessary to understand the structure-property relationships. The use of combined methods of preparative TREF and several conventional analytical techniques such as HT-SEC, DSC, FTIR and HT ^{13}C NMR has been reported over the past decades by several authors.[6–9] Due to the complexity of the various products formed during IPC synthesis a complete molecular characterization of this material was not achieved by the above mentioned techniques. In this study, a multidimensional analytical approach

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developed by combining prep TREF with high temperature two-dimensional liquid chromatography (HT-2D-LC), was used for the chemical composition and molar mass separation of the chemically different components in this copolymer system.

Experimental Part

A non-stabilised commercial IPC sample (designated as 3V A) was obtained from Sasol polymers (Secunda, South Africa). The bulk sample has an ethylene content of 11.8 mol%, with a weight average molar mass (M_w) and dispersity (Đ) of 361 kg. mol^{-1}, and 6, respectively.

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 Speciality 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 crystallisation 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 crystallisation of the polymer. The crystallised mixture was then packed into a stainless steel column which was inserted into a modified gas chromatography oven for the elution step. Xylene (pre-heated) was used as eluent in order to collect the fractions at pre-determined intervals as the temperature of the oven was raised. The fractions were isolated by precipitation in acetone, followed by drying to a constant weight.

High Temperature Size Exclusion Chromatography (HT-SEC)

Molar mass measurements for all samples were performed at 150 °C using a PL GPC 220 high temperature chromatograph (Polymer Laboratories, Church Stretton, UK) equipped with a differential refractive index (RI) detector. The column set used consisted of three 300 × 7.5 mm i.d. PLgel Olexis columns together with a 50 × 7.5 mm i.d. PLgel Olexis guard column (Polymer Laboratories, Church Stretton, UK). The eluent used was 1,2,4-trichlorobenzene (TCB) at a flow rate of 1.0 mL/min with 0.0125% BHT added as a stabiliser. Samples were dissolved at 160 °C in TCB at a concentration of 1 mg/mL for 1- 2 hours and 200 μL of each sample was injected. Narrowly distributed polystyrene standards (Polymer Laboratories, Church Stretton, UK) were used for calibration.

Crystallization Analysis Fractionation (CRYSTAF)

CRYSTAF experiments were carried out using a commercial CRYSTAF apparatus Model 200 (Polymer Char, Valencia, Spain). For each sample, approximately 20 mg of the sample was dissolved in 35 mL 1,2,4-Triichlorobenzene (TCB). Crystallisation was carried out under agitation in stainless steel reactors, equipped with automatic stirring and filtration devices. After dissolution, the temperature was decreased from 100 °C to approximately 30 °C at a rate of 0.1 °C/min. Fractions were taken automatically and the concentration of the solution was determined by an infrared detector, using 3.5 μm as the chosen wavelength.

Chromatographic System

All chromatographic experiments were performed using a new chromatographic system for high temperature two-dimensional liquid chromatography (see Figure 1) 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 SGIC 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-

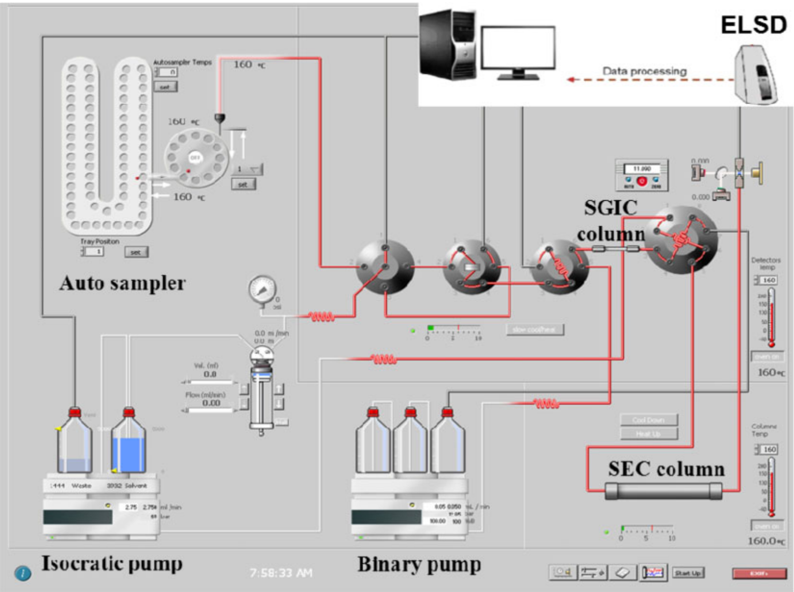

Figure 1.
Schematic representation of the HT-2D-LC system (Polymer Char).

pressure binary gradient pump was used for SGIC 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 SLM, a nebuliser temperature of 160 °C, and an evaporator temperature of 270 °C.

High Temperature Solvent Gradient Interaction Chromatography (HT-SGIC)

HT-SGIC was carried out using a Hypercarb column (Hypercarb®, Thermo Scientific, Dreieich, Germany) with the following parameters: 100 × 4.6 mm id., packed with porous graphite particles with a particle diameter of 5 μm, a surface area of 120 m^2/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 SGIC 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. The dwell volume (1.7 mL), void volume (1.1 mL) was measured according to the method described by Ginzburg et al.[10] That means there is an isocratic elution of 1-decanol (1.7 mL) before the start of the linear solvent gradient hits at the column. 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- SGIC and HT-SEC was achieved by using an electronically controlled eight-port valve system (VICI Valco instruments, Houston, Texas, USA) 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 Rapid H (Polymer

Laboratories, Church Stretton, UK) 100 × 10 mm id. 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 (SGIC) separation.

Results and Discussion

The molar mass distribution obtained for the bulk IPC sample by SEC analysis is given in Figure 2a. In SEC, the separation occurs according to the size of the molecules; therefore it cannot tell anything about the chemical structure and amount of the individual components in such a complex copolymer system. In order to obtain a chemical composition separation, the sample was further analysed by CRYSTAF and the CCD curve obtained is given in Figure 2b. As illustrated in Figure 2b, the major part of the sample crystallizes at higher temperatures in the range of approximately 70-90 °C. It is expected to be highly crystalline iPP homopolymer. The soluble fraction (30 °C) corresponds to the EP rubber. A close look at the CRYSTAF curve shows the crystallization of a small amount of material in the temperature range of approximately 35–70 °C, indicating the presence of semi-crystalline components.

As reported by several authors,[3,4,6] due to the low concentration of some

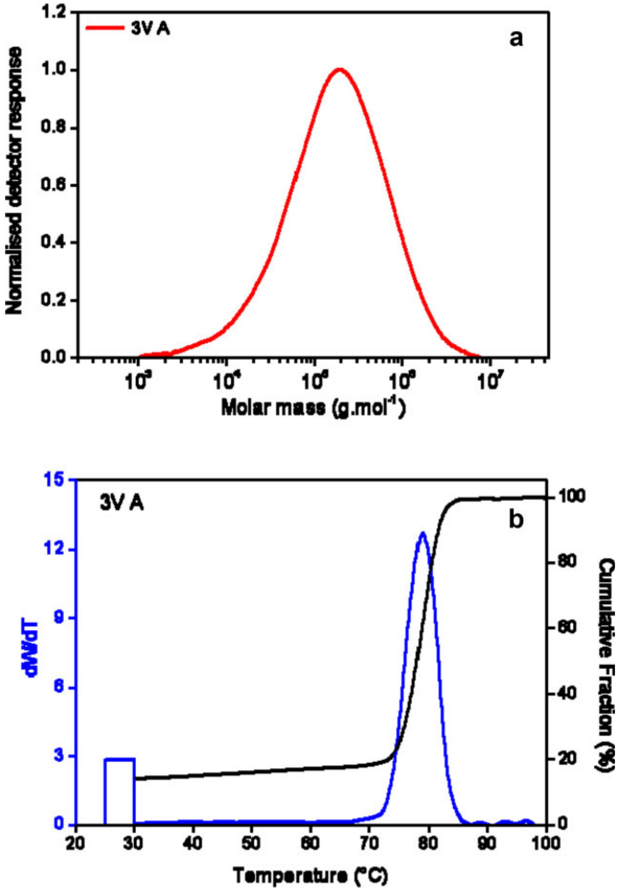

Figure 2.
MMD (a) and CCD (b) curves obtained for the bulk IPC sample by HT-SEC and CRYSTAF analysis, respectively.

components, the bulk sample analysis does not provide complete CCD information. The ethylene content value for this copolymer is very low (11 mol %), and it is distributed over a wide range of chemical compositions. Therefore, it is very difficult to analyse the components in the temperature range of 35–70 °C which are present only in minute concentrations. In addition, CRYSTAF fractionation is based on the crystallizability of the components and, therefore, cannot fractionate amorphous materials such as ethylene-propylene copolymers having high ethylene contents.

In order to achieve a complete chemical composition separation, we decided to use a recently developed interaction-based fractionation technique, high temperature solvent gradient interaction chromatography (HT-SGIC). In SGIC, the separation occurs above the melting and crystallization temperature of the polyolefins, so that the crystallization will not be a factor to affect the resolution in separation. A solvent gradient method developed by Macko and Pasch[11] was used to perform the SGIC separation. The resulting chromatogram obtained after isocratic and gradient elution is given in Figure 3. The sample eluted in two regions and showed only two iPP components (low and high molar mass). Peaks corresponding to EP copolymers or PE homopolymer were not observed. It is obvious that even highly sophisticated fractionation techniques such as HT-SGIC fail to provide information regarding the amount and chemical structure of these minor components, due to their low concentration in the bulk sample. Therefore, a pre-fractionation in preparative scale is necessary for a detailed microstructural analysis of such complex materials.

In the next step the sample was fractionated via prep TREF to accumulate the individual components in higher concentrations (see Refs. [7–9] for the details). TREF also separates according to the crystallizability of the polymer chains, which in turn is related to their macromolecular chain structure or chemical composition. Similar to CRYSTAF, soluble, semicrystalline and highly crystalline components were fractionated, and subjected to further analysis. A detailed analysis of one of the midelution temperature TREF fractions (60 °C) will be discussed in the coming section.

The first information regarding MMD and CCD for the 60 °C TREF fraction was obtained by SEC and CRYSTAF analysis and the results are shown in Figures 4a and b. A clear bimodal molar mass distribution

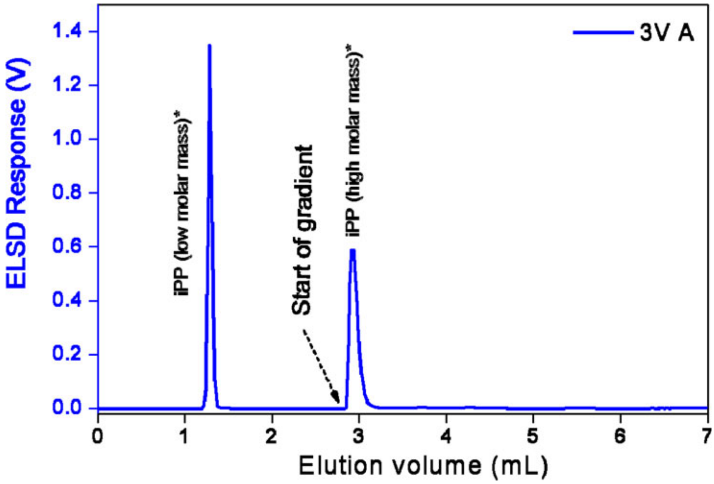

Figure 3.
HT-SGIC chromatogram obtained for the bulk IPC sample. [Note: *peaks are assigned according to the elution profile observed for iPP standards using the same solvent gradient under similar experimental conditions].

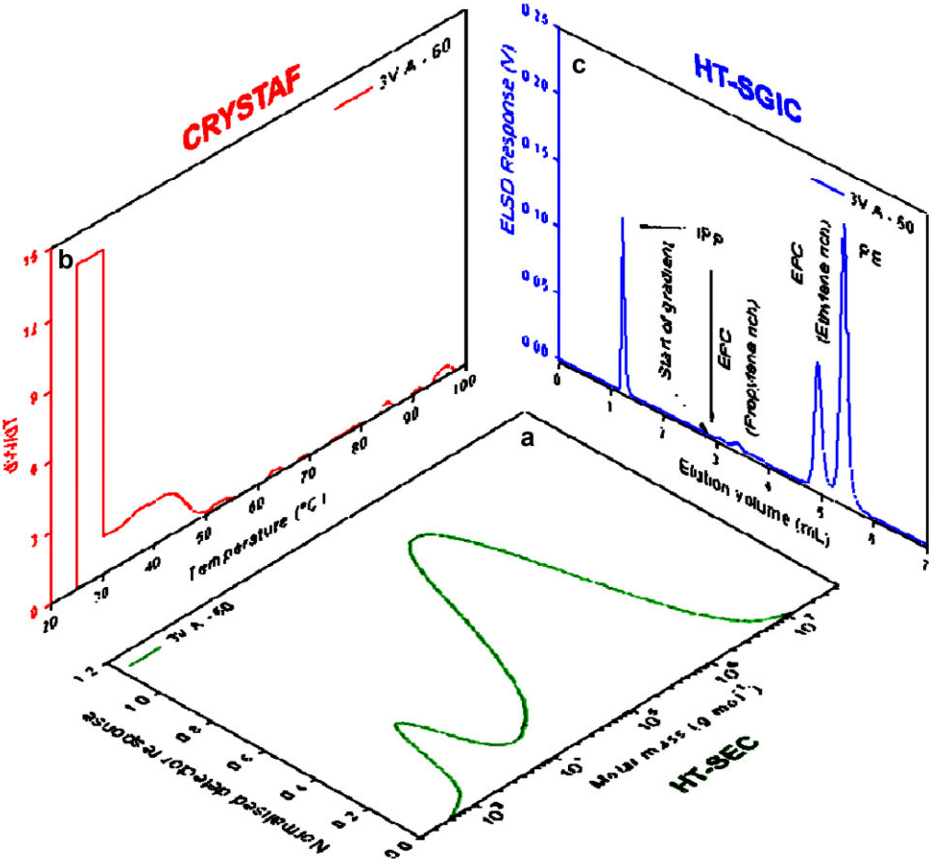

Figure 4.
HT-SEC, CRYSTAF and HT-SGIC analysis of the 60 °C TREF fraction.

(Figure 4a) was observed for this TREF fraction indicating the compositional heterogeneity due to the co-elution of the chemically different components during TREF separation.[7] Even TREF – SEC cannot provide any information regarding the chemical nature of the components. As discussed before SEC separation is based on the molar mass or chain length of the polymer molecules, not according to their chemical structure. CRYSTAF analysis provides information about the chemical nature of the components present in this TREF fraction (see Figure 4b). The presence of EPC copolymer having crystallisable E/P sequences (broad peak in the temperature range of 30-50 °C) was observed. But the major part of this TREF fraction is soluble, which again limits the separation efficiency. These results indicate that even a TREF-CRYSTAF combination is not a suitable choice for the complete CCD determination of such complex EP copolymers. As shown in Figure 4c, a clear chemical composition separation of the soluble (amorphous) and semicrystalline components was obtained by using HT–SGIC. EP copolymers having varying E/P contents or sequence length distributions and significant amounts of the PE homopolymer were observed in this 60 °C TREF fraction.

Finally a complete separation in terms of chemical composition and molar mass was achieved by using HT-2D-LC. The 2D-LC contour plot (see Figure 5) shows that this semicrystalline TREF fraction is a complex mixture of low and high molar mass iPP, high molar mass EPC and PE

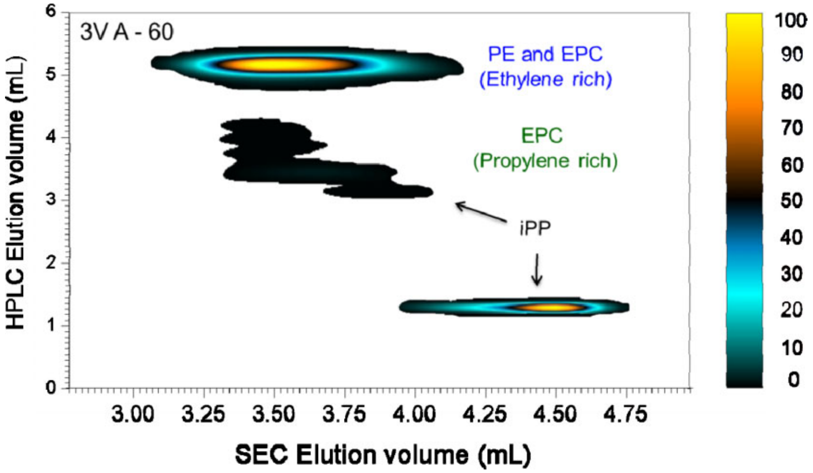

Figure 5.
HT-2D-LC contour plot for the 60 °C TREF fraction.

homopolymer. In this way, separation of the EPC having similar molar mass and different microstructure was obtained. These results prove that TREF-HT-2D-LC is a powerful analytical tool for the complete microstructural analysis of complex polyolefins, where the conventional analytical techniques or their combinations fail to provide detailed information regarding their molecular characteristics.

Conclusion

Impact polypropylene copolymer is a complex polymeric material having multiple distributions in various molecular characteristics, such as molar mass and chemical composition. The bulk sample analysis by using conventional analytical techniques like HT-SEC and CRYSTAF cannot provide sufficient information regarding the compositional heterogeneity due to the low concentration of the individual components. A pre-fractionation in preparative scale (prep TREF) was done to accumulate the individual components in sufficient concentrations for their further analysis. A detailed microstructural analysis of an important semicrystalline TREF fraction (60 °C) was accomplished by using a highly selective and advanced separation method, high temperature two-dimensional liquid chromatography (HT-2D-LC). In addition to the EP (block or segmented) copolymers and low molar mass iPP (as expected in the semicrystalline TREF fraction of an IPC), significant amounts of high molar mass iPP and PE homopolymer were observed. These results prove that this multidimensional approach is a valuable analytical tool for the analysis of such complex polyolefins.

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