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Comparison of Fractionation Methods for the Characterisation of Short Chain Branching as a Function of Molecular Weight in Ethylene 1-Olefin Copolymers

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Summary: Rapid and automated analysis of polyolefins is becoming essential for product development in industry. Quantifying short chain branching in ethylene 1-olefin copolymers is common practice. Several different methods are available to perform this type of analysis. Preparative fractionation followed by subsequent analysis of the fraction by SEC and NMR, SEC-FTIR and SEC-IR were studied towards their applicability in polyolefin research and product development environment. The method of choice is defined by prerequisites such as accuracy, labour and time demands but also in versatility and practicability. The most accurate method is limited in terms of sample throughput and the most practical method is limited towards resolution of very low branching. SEC-FTIR is capable to measure even heterogeneous low branched samples like bimodal high density polyethylene in rapid and satisfactory matter.

Keywords: fractionation of polymers; FT-IR; gel permeation chromatography (GPC); microstructure; molecular weight distribution; NMR; polyethylene (PE)

Introduction

Modern polyolefin copolymer development needs detailed understanding of the copolymer microstructure. Bimodal polyethylene copolymers are tailored towards molecular weight distribution and short chain branching distribution. Fractionation techniques are helping to understand catalyst and process influences on material properties and following changes for product development.

The combination of molecular weight distribution (MWD) and short chain branch content (SCB) per molecular weight slices (SCB(MW)) gives characteristic profiles for understanding material properties. As the average molecular weights and average comonomer concentration do not describe very well the material properties while the interpretation of full MWD-CCD profiles obtained via cross fractionation techniques can be valuable but challenging. Practical or common solutions are hyphenated techniques like SEC-FTIR,[1,2] SEC-IR (composition detectors or FTIR ratio method),[3] 3D-TREF,[4] and preparative fractionation[5] followed by SEC, TREF and FTIR[6] or NMR spectroscopy.

A robust compositional analysis of ethylene copolymers involves solvent and thermal fractionation followed of subsequent characterization of the fractions by size exclusion chromatography (SEC), NMR spectroscopy and other techniques. Although the resulting information on polymer composition is highly comprehensive, the efforts to acquire the wanted data are labour and time intensive.

Three types of SEC infrared detector methods are typically used: Online SEC-FTIR, where branching levels in SEC eluent are measured in a heated flow

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through cell which is placed in a FTIR spectrometer; SEC-IR using an infrared concentration and composition detector (heated flow through cell, detection of absorbance in different bands, MID-IR); and offline SEC-FTIR where sample eluent from the SEC is deposited on a rotating germanium disc and the solid deposit is subsequently analysed offline by FTIR for branching content.[1]

The profiles obtained from techniques like SEC-FTIR can be understood as a two-dimensional projection showing the average SCB per slice as a function of molecular weight from a three-dimensional plot of a sample's MWD and CCD. Limitations need to be considered, especially when materials such as bimodal pipe grades with overlapping molecular weight distributions and different comonomer concentrations are analysed. Nevertheless, such profiles however became essential for polyolefin research and development.

This article presents and discusses SCB(MW) profiles obtained from SEC-FTIR, SEC-IR (FTIR ratio method) and preparative fractionation according to molecular weight followed by SEC and NMR analysis of the fractions ($\text{PREP}_{\text{MW}} + \text{SEC} + \text{NMR}$).

Experimental Part

Three samples were selected for this study, a bimodal linear low density polyethylene-co-butene (ZN-LLDPE: Ziegler Natta catalysed, 4.1 mol% butene), a bimodal high density polyethylene-co-butene (ZN-HDPE: Ziegler Natta catalysed, 0.8 mol% butene), and a bimodal high density polyethylene-co-octene (SSC-HDPE: single site catalysed, 2.5 mol% octene).

SEC: Molecular weight distributions were determined by SEC according to ISO 16014-4:2003 and ASTM D 6474-99. A Waters GPCV2000 instrument, equipped with differential refractive index detector was used with 2 x GMHXL-HT and 1x G7000HXL-HT TSK-gel columns from Tosoh Bioscience and 1,2,4-trichlorobenzene (TCB, stabilized with 250 mg/L 2,6-Di-tert-butyl-4-methyl-phenol) as solvent at 140 °C and at a constant flow rate of 1 mL/min. 209.5 μL of sample solution were injected per analysis. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with at least 15 narrow MWD polystyrene (PS) standards in the range of 1 kg/mol to 12 000 kg/mol. Mark Houwink constants for PS and PE used are as per ASTM D 6474-99. All samples were prepared by dissolving close to 10 mg of polymer in 10 mL (at 140 °C) of stabilized TCB and keeping for max. 3 hours at maximum 160 °C with continuous gentle shaking prior sampling into the SEC instrument.

SEC-FTIR: A Waters GPC2000 instrument, equipped with heated flow cell from Polymer Laboratories (at 140 °C) connected via a heated transfer line (at 140 °C) was used with 2 x Olexis and 1x Olexis Guard columns from Polymer Laboratories and TCB as solvent at 140 °C and at a constant flow rate of 1 mL/min. The heated flow cell is mounted on a sample plate located in a Perkin Elmer Spectrum 100 equipped with a mercury cadmium telluride (MCT) detector, cooled with liquid nitrogen. A series of FTIR spectra was then collected during the chromatographic run. The spectrometer settings were 16 accumulations, scan range from 3000–2700 cm^{-1} and resolution of 8 cm^{-1}. A background spectrum was taken under SEC run conditions and substracted from each spectrum collected during the chromatographic run. A new background spectrum was taken prior to each chromatographic run. 423.5 μL of sample solution were injected per analysis. The column set was calibrated using universal calibration as described above. All samples were prepared by dissolving about 8 mg of polymer in 4 mL (at 140 °C) of stabilized TCB and further treaded as described above. The spectral data was converted into chromatograms using root-mean-square (RMS) absorbance over the 3000–2700 cm^{-1} spectral region. The molecular weight distributions were calculated from the generated chromatogram and universal calibration.

The short chain branching calibration set covered a broad range of different branched polyethylenes in order to generate most universal calibration. This set included over 100 samples, both single site and fractions of Ziegler Natta catalysed medium high molecular weight polyethylene-co-butene, polyethylene-co-hexene, and polyethylene-co-octene as well as n-alkanes covering a branching level from 0 to 67 methyl groups per 1000 total carbons (CH_3/1000TC). The branching degree of all calibration set samples was determined by ^{13}C melt-state NMR or calculated for the n-alkanes and the same set was used to generate the calibrations for methods A and B.

Method A: Evaluation of short chain branching was performed via multivariate analysis by applying a chemometric model generated from partial least square regression (PLS1).[2] Outlier detection for individual measurements was generated from probability values obtained through the chemometric software (Infometrix Pirouette and Instep). Calibration samples having probabilities >0.95 were considered as outliers.

Method B: The evaluation towards short chain branching was performed by calculation of the ratio of methyl (CH_3) to methylene (CH_2) groups. This ratio was defined as the ratio of absorbance intensities at 2964 cm^{-1} (assigned as related to methyl groups) and at 2928 cm^{-1} (assigned as related to methylene groups) at each corresponding retention time.[3] The ratio CH_3/CH_2 was calibrated to branching as methyl groups per 1000 total carbons (CH_3/1000TC) using a linear relationship to results obtained via melt-state NMR results. All FTIR spectra were baseline corrected prior ratio calculation. The baseline correction was performed using an iterative method of finding baseline variables. First, all included variables are used to compute a linear trial baseline. Only variables with points lying on or below the trial baseline were retained as baseline variables and another trial computed. As this process was repeated, fewer variables remain in the baseline. When only 1% of all included variables were left in the baseline or when the number of baseline variables did not decrease, the process stops and the actual baseline was computed on the retained variables. Thus, the nature and number of variables was determined to be in the baseline varied from sample to sample. We observed that this kind of baseline correction significantly improved the quality of the ratio method calibration.

SEC-FTIR and SEC-IR are hereafter referred to as method A and B. The short chain branching was determined as methyl branching per 1000 total carbons (CH_3/1000TC) and may be corrected for up to two methyl chain end groups per polymer chain in order to obtain the short chain branching level (SCB/1000TC).[3]

NMR: Melt-state NMR was performed on a dedicated solid-state Bruker Avance III NMR spectrometer (wide-bore AV III 500), operated at ^{1}H and ^{13}C Larmor frequencies of 500.13 and 125.75 MHz respectively. All measurements were undertaken using a commercial Bruker MAS probehead specially optimised for higher sensitivity. Nitrogen gas was used for all pneumatics to limit thermal sample oxidation. Compensation for MAS frictional heating and decompression-cooling was undertaken using temperature calibration data measured on lead nitrate. All measurements were conducted at $\varpi r/2\pi = 3$ kHz MAS. Shimming was undertaken on the ^{1}H resonance of the molten sample with a full-width at half-maximum (FWHM) ≤ 25 Hz being deemed acceptable. Typically $\pi/2$ pulse lengths of 10 μs (25 kHz) were used on both channels. For further details of the optimised melt-state MAS method the reader is directed to the literature.[7–11] A combination of 16 dummy scans and 1024 real scans were used with a 3 s recycle delay. All samples were measured at 150 °C.

Preparative fractionation ($PREP_{MW}$ + SEC + NMR): Fractionation was performed by the solvent gradient method.[5,12]

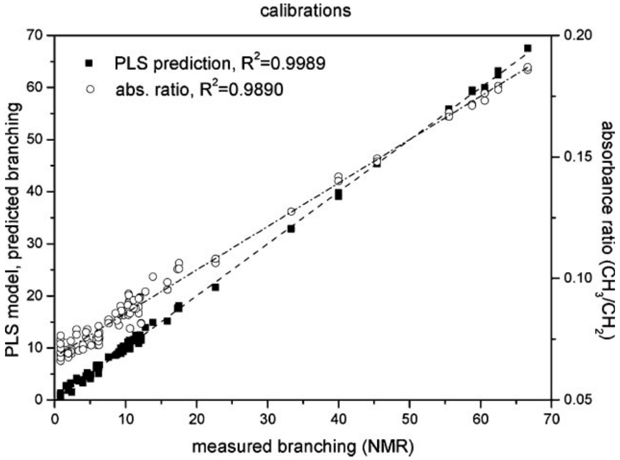

Figure 1.
PLS and ratio calibration, method A and B.

The polymers were fractionated according to molecular weight using a semi automated fractionation instrument, PREP mc2 from PolymerChar, with xylene used as solvent and di-ethylene-glycol-mono-buthyl-ether (DEGMBE) as non-solvent. Both solvents contained stabilizer Irganox 1010 in a concentration of 600 mg/L. Dissolution and precipitation steps were repeated with different solvent/non-solvent mixtures from high amount of non-solvent to pure solvent giving 8 fractions. The fractions were precipitated at room temperature by adding acetone, filtered and dried in vacuum. Each fraction obtained was analysed subsequently by SEC and ^{13}C NMR spectroscopy.

Results

The applicability of FTIR detectors in high temperature SEC for analysing polyolefin composition has been discussed in detail in literature.[12,13] The classical method of preparative fractionation followed by subsequent analysis of the fractions remains most accurate. A few options are available for online detection of short chain branching in polyethylenes. The method of choice is clearly based on the need of optimising time load versus accuracy. Due to measuring in dilute solution and TCB having several (total) absorption regions in its spectrum, three problematic issues occur in SEC-FTIR and SEC-IR: Firstly the low sample concentration at the detector, mainly at the tailings of the molecular weight distribution; secondly very low branching in the sample results in minor spectral differences (in dilute solution); and finally heterogeneous copolymers i.e. heterogeneous fractions per slice molecular weight result in spectra of average branching. For spectra of heterogeneous fractions it may be difficult to predict (method A) or calculate (method B) the average short chain branching. A combination of all three problematic aspects is very well possible for samples such as multi modal high density polyethylenes.

The SEC-FTIR (method A) and SEC-IR (method B) obtained SCB(MW) profiles of the three samples in this study are shown in Figure 2–4. The obtained branching level is methyl groups per 1000 total carbons, shown as A1 and B1 respectively. It can be assumed that, depending on the type of catalyst, two methyl groups are present at the chain ends. An end group correction was performed and is shown in the figures as method A2 and B2. Additionally, the chemometric modelling allows using outlier probabilities (OP) obtained from the

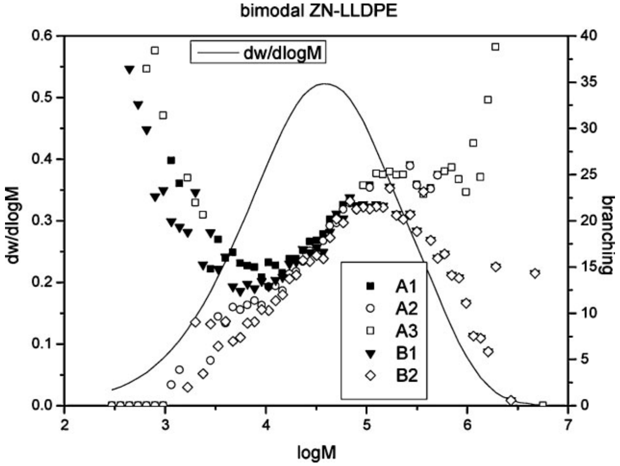

Figure 2.
SEC-FTIR and SEC-IR analysis of a bimodal ZN-LLDPE; methods A1 = OP $<$ 0.96, CH_3/1000TC; A2 = OP $<$ 0.96, SCB/1000TC; A3 = OP $>$ 0.96, CH_3/1000TC; B1 = CH_3/1000TC; B2 = SCB/1000TC.

chemometric software to filter the results according to its reliability. Data points having probability values of >0.96 were considered as outliers. These results are shown as methods A1 (OP < 0.96) and A3 (OP > 0.96) respectively.

Methods A and B are showing significantly different results for the ZN-HDPE sample, for the other two, ZN-LLDPE and SSC-HDPE, comparable results were obtained. Both calibrations are giving good correlations between the solution state FTIR and the ^{13}C NMR. The differences become pronounced when the sample is becoming more challenging, fulfilling the above mentioned problematic issues A to C. The analytical difficulty of polyethylene copolymers in SEC-(FT)IR is clearly increasing from uni to multi reactor grades and from single site to multi site catalyst systems. In this study the ZN-HDPE appears to be the most challenging sample.

Both method A and method B can in principle also be applied to other type of IR

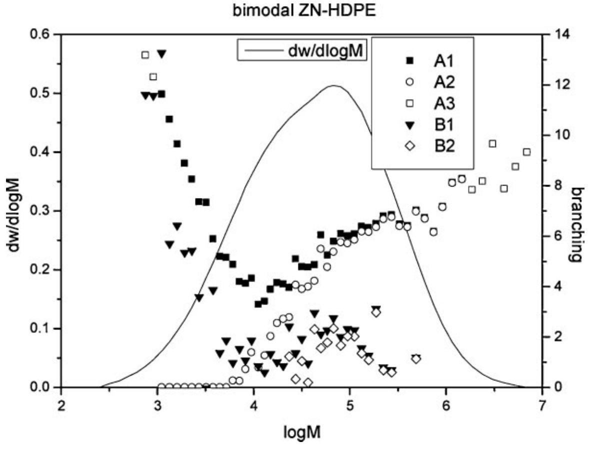

Figure 3.
SEC-FTIR and SEC-IR analysis of a bimodal ZN-HDPE; methods A1 = OP $<$ 0.96, CH_3/1000TC; A2 = OP $<$ 0.96, SCB/1000TC; A3 = OP $>$ 0.96, CH_3/1000TC; B1 = CH_3/1000TC; B2 = SCB/1000TC.

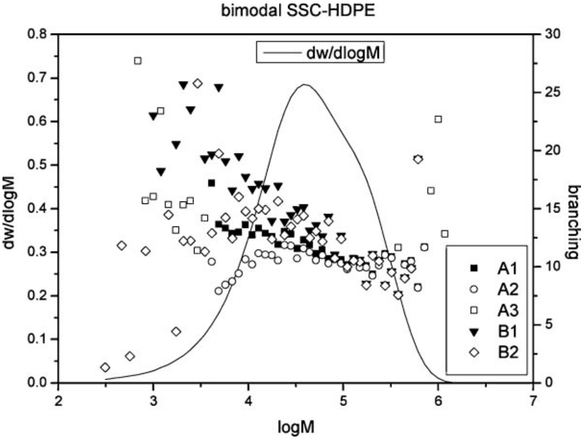

Figure 4.

SEC-FTIR and SEC-IR analysis of a bimodal SSC-HDPE; methods A1 = OP < 0.96, CH_3/1000TC; A2 = OP < 0.96, SCB/1000TC; A3 = OP > 0.96, CH_3/1000TC; B1 = CH_3/1000TC; B2 = SCB/1000TC.

detectors (SEC-IR). For example a infrared detector in combination with two or more optical filters (measuring absorbance in different IR bands could be used as alternatives to the more complex MCT FTIR spectrometer cooled with liquid nitrogen. This may result also in simpler analysis solutions. The most important for detecting even low amounts of short chain branching are sensitivity and signal to noise capabilities of the detector. Besides this the FTIR spectrometer is a flexible detector option also in respect to other solvents and polymers.

Comparison of SEC-(FT)IR results with the most accurate classical method PREP$_{MW}$ + SEC + NMR is shown in Figure 5–7. Each sample was fractionated according to molecular weight into 8 fractions. More fractions could have been obtained, however this would have made the fractionation procedure even more laborious.

The obtained branching trends are very well in line for all three methods in case of ZN-LLDPE and SSC-HDPE. In case of the bimodal ZN-HDPE the method B is reaching its resolution limits (compare Figure 3 and 6). Differences between the classical

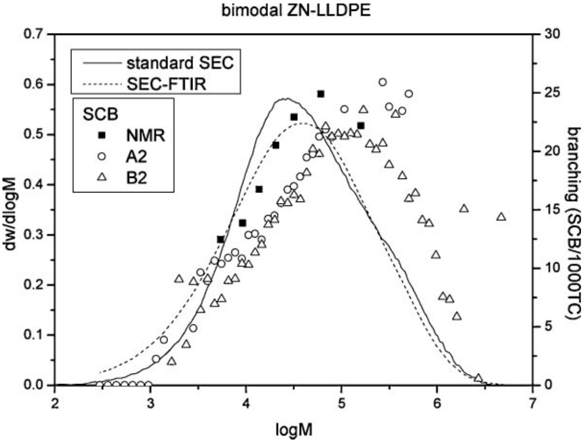

Figure 5.

SEC, NMR, SEC-FTIR and SEC-IR analysis of a bimodal ZN-LLDPE; methods A2 = OP < 0.96, SCB/1000TC; B2 = SCB/1000TC.

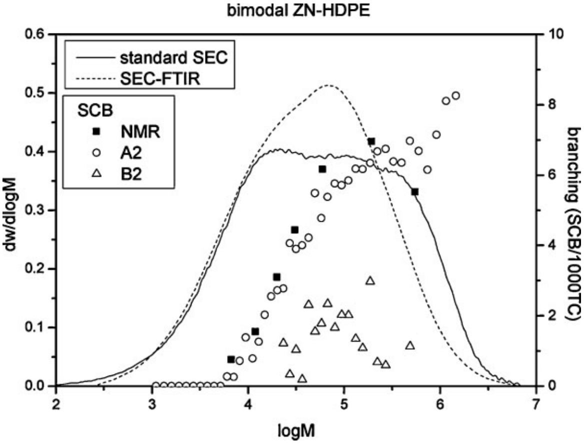

Figure 6.
SEC, NMR, SEC-FTIR and SEC-IR analysis of a bimodal ZN-HDPE; methods A2 = OP < 0.96, SCB/1000TC; B2 = SCB/1000TC.

method and SEC-FTIR may result from two origins, the degree of branching may vary and the molecular weight may vary. The degree of branching is based on its determination method and their measuring principles in general and, as discussed here, on method and sample limitations. The differences in molecular weight may result from very different SEC instrument setups. While the standard SEC is typically optimised towards sample separation i.e. size exclusion, meaning having concentrations as low as possible, the SEC-FTIR is a compromising technique. For good FTIR resolution the sample concentration (at the detector) should be as high as possible. Therefore the SEC setup in case of SEC-FTIR is using fewer columns, higher sample solution concentrations and larger injection volumes, all resulting in worse molecular weight distribution resolution. Nevertheless, using both techniques, SEC and SEC-FTIR lead to very valuable information about MWD and SCB(MW). The ZN-

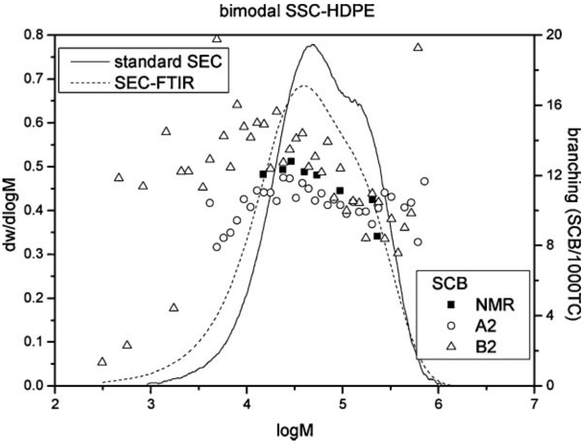

Figure 7.
SEC, NMR, SEC-FTIR and SEC-IR analysis of a bimodal SSC-HDPE; methods A2 = OP < 0.96, SCB/1000TC; B2 = SCB/1000TC.

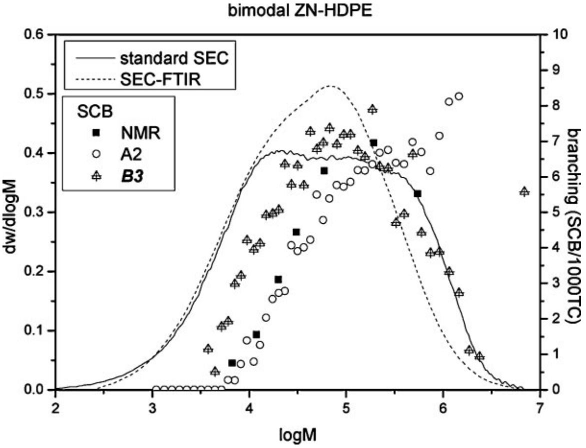

Figure 8.
SEC, NMR, SEC-FTIR and SEC-IR analysis of a bimodal SSC-HDPE; methods A2 = OP < 0.96, SCB/1000TC; B3 = SCB/1000TC using dedicated calibration.

LLDPE showed this difference in terms of a slight shift along the x-axis (log M) of the branching comparing NMR and FTIR results (Figure 5).

The calibration sets for methods A and B were selected to cover a wide range of different types of short chain branched polyethylenes in order to obtain a most universal calibration. This is a limiting factor when evaluating very difficult samples especially with method B (compare Figure 3 and 6). A dedicated calibration for a specific type of sample can be created and applied to obtain improved results. This was performed for sample ZN-HDPE. This sample is a bimodal ethylene-co-butene made by Ziegler-Natta type catalyst. The dedicated calibration (method B3) was created using the SEC-FTIR results of ZN-LLDPE (method A1) in the region of log M = 3.5–4.9 (same catalyst type, same comonomer, low branching region). The results are shown in Figure 8. As expected, the branching level is now much closer to data obtained by method A2 but also very much closer to NMR data (compare Figure 6 and 8). The mayor disadvantage of a calibration of that kind is the application possibility to a very limited range of samples.

Conclusion

All three presented methods are suitable for determination of short chain branching as a function of molecular weight, differing in accuracy of molecular weight and branching level and thereby in their application towards low or highly branched samples, unimodal or multimodal compositions. SEC-FTIR (method A) is fast, accurate and versatile towards SCB determination for a wide variety of polyethylenes while SEC-IR (method B) requires less complex samples or dedicated calibrations. The multivariate analysis enables to observe very small spectral differences from dilute polymer solution. Very universal calibrations can be obtained especially for method A; additionally, the chemometric approach allows a data filtering based on e.g. outlier probability calculations to present only most reliable results in an automated way. SEC-FTIR allows the analysis of even heterogeneous high density polyethylene and is an exellent substitute for the PREP$_{MW}$-Sec-NMR method to obtain SCB(MW).

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