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Monitoring the Chemical Composition of Polyolefins along the Molar Mass Axis with High-Temperature Size Exclusion Chromatography Coupled with an Infrared Detector (HT SEC-IR5)

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Series of ethylene/1-alkene and ethylene-propylene-diene copolymers are separated with size exclusion chromatography (SEC) at 150°C using 1,2,4-trichlorobenzene as the mobile phase. Methyl (CH_3–) and methylene (–CH_2–) groups in the separated polymer samples are monitored at specific wavelengths via a filter-based infrared detector (IR5). It is found that the ratio of CH_3/CH_2 may increase, be constant, decrease or change irregularly along the molar mass axis, depending on the sample under investigation. Because the CH_3/CH_2 profiles may be very different even for a given series of copolymers synthesized with the same catalyst, it is supposed that one or more experimental parameters, which are not strictly controlled throughout synthesis, are responsible for these substantial differences in the chemical composition along the molar mass axis. The correlation between the ratio of CH_3– to –CH_2– groups and the average chemical composition of the investigated series of polymer samples as well as the reproducibility of the measurements and the limit of detection of the SEC-IR5 measurements are evaluated. Coupling of SEC with the advanced IR5-detector enables the convenient and reliable characterization of the chemical composition of many polyolefin materials along their molar mass axis. The monitoring of the chemical composition may help to improve quality of synthesized copolymers.

1. Introduction

Polyolefins are of enormous economic importance and by volume account for more than 60% of the total synthetic polymer market. Their worldwide production stood at 200 million tons in 2020 and is forecasted to reach 250 million tons by 2030.[1] Many industrially produced polyolefins are copolymers,[2] which means that in addition to their molar mass distribution (MMD), their chemical composition distribution (CCD) (distribution of the comonomer) determines their physical properties.

The MMD of polyolefins is routinely analyzed with size exclusion chromatography (SEC) operated at high temperatures.[3–5] The average chemical composition of a copolymer can be determined by spectroscopic methods (mostly IR and NMR). The characterization of the CCD of polyolefins is often realized with crystallization-based techniques (Temperature Rising Elution Fractionation [TREF],[6] Crystallization Analysis [CRYSTAF],[7] and Crystallization Elution Fractionation [CEF][8]). Amorphous polyolefins, however, cannot be characterized with the aforementioned methods. In contrast, high-temperature interaction chromatographic methods,[9–14] which are based on the adsorption and desorption of macromolecules from a column packed with porous graphite, enable to separate and analyze copolymers over the full range of their chemical composition and thus characterize their CCD independent of crystallizability. The most comprehensive characterization of the bivariate

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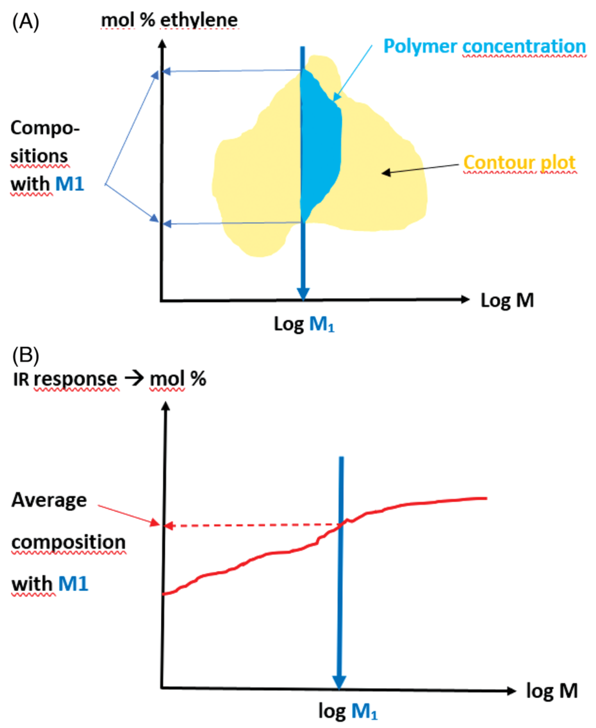

Figure 1. A) Plot CCD × MMD obtained with 2D-LC. B) CCD obtained with SEC-IR.

MMD × CCD distribution may be realized with two-dimensional liquid chromatography (2D-LC)[12,13] or by preparative fractionation, followed by the analysis of the fractions by nuclear magnetic resonance (NMR), SEC, TREF, high performance liquid chromatography (HPLC), differential scanning calorimetry (DSC), and other techniques.[14]

Two-dimensional liquid chromatography (2D-LC) or preparative fractionation enables to generate a contour plot illustrating both CCD and MMD distribution (**Figure 1**a). The 2D-LC contour plot shows the chemical composition of macromolecules as well as their concentration, which corresponds to each specific elution volume. This volume is usually transformed through a calibration into a molar mass (Figure 1a). On the other hand, coupling SEC with an infrared detector (SEC-IR) enables to obtain the average chemical compositions of macromolecules corresponding to each elution specific volume (transformed through a calibration into a molar mass (Figure 1b).

Thus, SEC-IR directly offers additional information about the chemical composition along the molar mass axis. Moreover, SEC-IR is much simpler and faster compared to the 2D-LC or TREF-GPC technique.

Three approaches for high temperature (HT) SEC-IR have been described in the literature:

a) Off-line coupling of SEC to Fourier Transform Infrared (FTIR) spectroscopy, in which the eluent from the SEC column is deposited on a rotating germanium disk, and the polymer layer obtained after solvent evaporation is subsequently analyzed offline by FTIR. The IR absorption is finally applied for an evaluation of the chemical heterogeneity.[15–22]
b) On-line coupling of SEC to FTIR where branching levels in the eluent are measured in a heated flow-through cell placed inside an FTIR spectrometer,[23,24] that is, the full FTIR spectrum of the effluent is recorded and later evaluated.
c) On-line coupling of SEC to a band pass filter-based IR detector.[25–29] The filter enables to monitor the IR absorption of selected chemical groups (like methyl, methylene, or carbonyl).

Studies comparing FTIR and filter-based IR detectors have concluded that both can be used successfully for studying the chemical composition along the MMD in polyolefins.[15,24] Ortin et al.[25–28] described a new model of filter-based IR detector coupled to SEC and its application in the determination of short chain branching (SCB), as a function of molar mass. In this work the new model of the filter-based detector described by Ortin et al.[26–29] was applied for the high-temperature SEC-IR characterization of various polyolefin copolymers. Moreover, the repeatability and the limit of the IR detection approaches were evaluated.

2. Experimental Section

2.1. High-Temperature Size Exclusion Chromatography (HT SEC)

HT SEC-IR5 measurements were performed using a PolymerChar GPC-IR (PolymerChar, Valencia, Spain), equipped with a 200 µL sample loop, at 150°C. The mobile phase was 1,2,4-trichlorobenzene (TCB) (Across Organics, Schwerte, Germany) containing 0.5 g L^{-1} butylhydroytoluene (BHT, Merck, Darmstadt, Germany). The mobile phase flow rate was 1 mL min^{-1}. As stationary phase, three POLEFIN linear XL analytical columns, 300 × 8.0 mm (Polymer Standards Service, Mainz, Germany) were used. Detection was performed with a filter-based multiple band IR detector (model IR5-MTC, PolymerChar, Valencia, Spain) featuring a thermoelectrically cooled mercury-cadmium-telluride (MCT) sensor. The IR5 detector includes two narrow band filters tuned to the adsorption region assigned to CH_3 (at 2960 cm^{-1}) and CH_2 (2920 cm^{-1}) groups, as well as a broader filter used to collect absorbance from all C–H bonds in a polymer.[25–27] The heated flow-through cell contains 13 µL volume, exhibits a 1.8 mm path-length and is equipped with sapphire windows.

The MMD was evaluated using a polystyrene calibration (EasiCal PS-1, Agilent, Waldbronn, Germany) and WinGPC software version 8 (Polymer Standards Service GmbH, Mainz, Germany). The molar masses of PS standards were transferred to polyethylene equivalents using using the following Mark-Houwink coefficients from the literature: K_{PE}: 3.8 × 10^2 mL g^{-1}, α_{PE}: 0.73 and K_{PS}: 1.26 × 10^2 mL g^{-1}, α_{PS}: 0.702.[34]

For each measurement, ≈12 mg polymer was automatically mixed with 6 mL mobile phase. Simultaneously, the vials were flushed with nitrogen. Each sample was dissolved under shaking in the autosampler for 1 h at 150°C before injection.

2.2. Polymer Samples

The polymer samples were obtained from our partners working in universities, research institutes or the industry. A part

Table 1. Characteristics of ethylene-propylene copolymers synthetized with metallocene catalyst: Average chemical composition, weight average molar mass: M_w, polydispersity Đ.

Content of ethylene [mol%]	M_w [kg mol^{-1}]	Đ	References
18.6	180	2.0	[30]
33.2	1405	2.1	
42.5	2270	2.0	
45.2	1160	1.9	
48.2	405	3.2	
50.1	2075	2.2	
52.8	755	2.2	
57.8	1530	2.1	
60.5	290	2.2	
63.4	1585	1.9	
65.9	650	2.0	
73.7	2075	1.9	

Table 2. Characteristics of ethylene-propene copolymers synthesized with metallocene catalyst.

Content of ethylene [mol%]	M_w [kg mol^{-1}]	Đ	Reference
1.5	166.9	3.8	[31]
6.34	150.2	3.4	
7.9	105	4.7	
8.5	124.4	3.9	
13.2	92.9	4.0	
36.0	63.2	4.2	
58.7	83.1	3.8	
77.78	144.4	3.5	
90.53	198.2	3.4	
97.84	370.1	7.0	

of these samples has been described before (see references in **Table 1–5**). Where average molar masses and/or dispersities were not known from previous investigations, they were evaluated based on current SEC-IR5 measurements and are given as polyethylene-equivalent molar masses.

For determinations of reproducibility and the limit of detection, an ethylene/1-butene copolymer sample (Basell, Ludwigshafen, Germany) containing 5.2 wt% 1-butene was used.

Table 3. Characteristics of ethylene-propene copolymers synthesized with ZN catalyst.

Content of ethylene [mol%]	M_w [kg mol^{-1}]	Đ	Reference
0	652.1	7.4	[31]
5.63	557.3	5.5	
20.57	465.6	6.9	
30.07	503.8	8.4	
43.34	456.9	9.1	

Table 4. Characteristics of ethylene-1-hexene copolymers.

Content of 1-hexene [mol%]	M_w [kg mol^{-1}]	Đ	Reference
1.0	160	2.0	[10]
1.2	56	2.0	
1.4	278	2.0	
2.8	58	2.2	
4.3	123	2.2	
5.8	112	2.0	
6.2	280	2.0	
7.0	52	2.1	
8.4	223	2.2	
12.8	24	2.0	

Table 5. Characteristics of ethylene-propylene-2-ethylidene-5-norbornene terpolymers.

ENB [wt%]	Ethylene [wt%]	Propylene [wt%]	M_w [kg mol^{-1}]	Đ	Reference
0	49.2	50.8	332	2.4	[32]
5.2	47.9	46.9	353	2.6	
7.1	50.6	42.3	503	2.7	
9.8	48.2	42.0	394	2.7	
14.5	47.8	37.7	395	2.6	

3. Results and Discussion

3.1. SEC-IR5 of Ethylene-Alkene Copolymers

The IR5 detector monitors the presence of methyl and methylene groups, as well as the overall polymer concentration in the eluate.[25,26] The corresponding absorbance changes with the elution volume in SEC (**Figure 2**) and thus with the molar mass of the sample.

The CH_3/CH_2 ratio reflects changes in the chemical composition of a polymer with the elution volume as is illustrated in

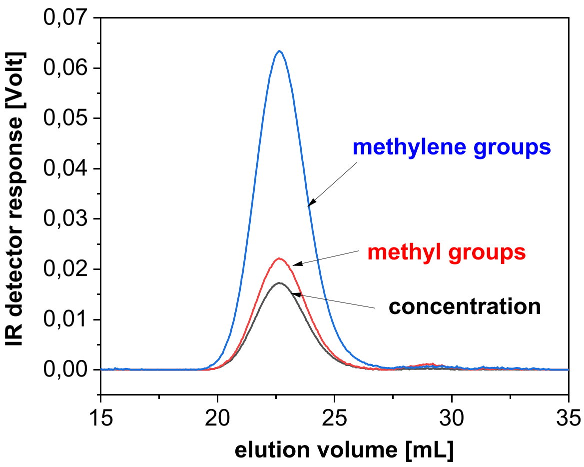

Figure 2. Chromatograms of an ethylene/propylene copolymer containing 52.8 mol% ethylene (Table 1).

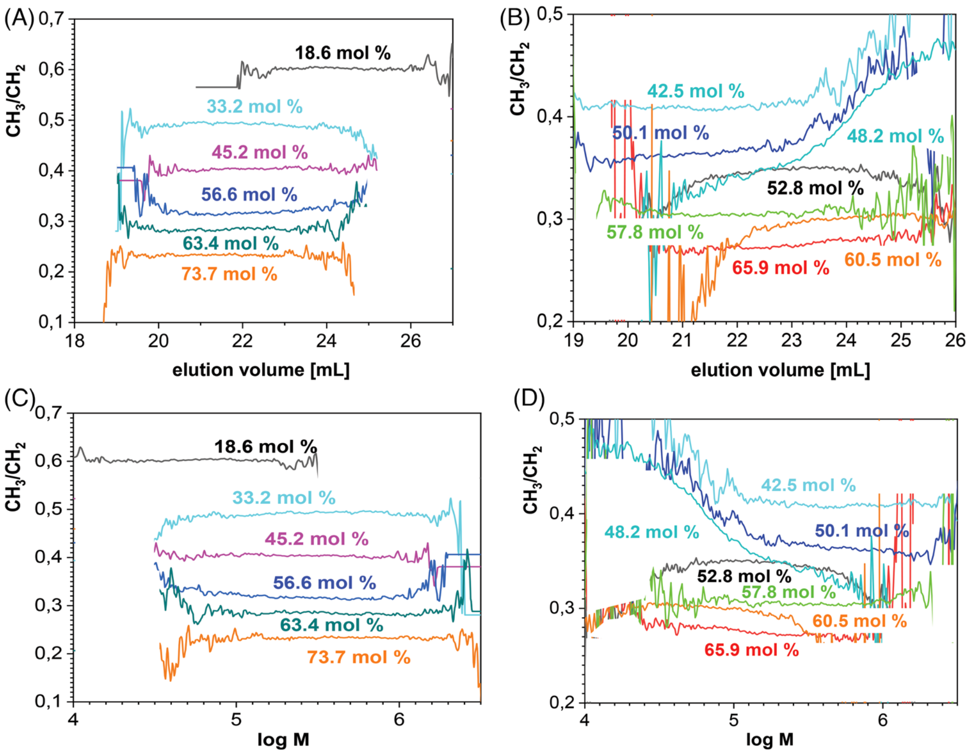

Figure 3. A,B) CH_3/CH_2 ratios as a function of elution volume of ethylene/propylene copolymers (Table 1). C,D) CH_3/CH_2 ratios as a function of equivalent polyethylene (PE) molar mass.

Figure 3a and b, that is, it reflects the chemical composition of the polymer along its molar axis (Figure 3c and d). As shown in Figure 3, the baseline and both edges of the peaks yield scattered values CH_3/CH_2 because the signal intensity in these regions is very low (i.e., it is the noise of measurement). The majority of the ethylene/propylene (EP) samples (Table 1) exhibit a constant CH_3/CH_2 ratio along the molar mass axis (Figure 3c and d), indicating that most of these samples (Table 1) are chemically homogeneous. The EP sample containing 48.2 mol % ethylene shows the largest decrease in the CH_3/CH_2 ratio with increasing molar mass.

Plotting the CH_3/CH_2 ratios which correspond to the top of the peaks of the elugram against the average chemical composition of the samples enables to obtain a calibration line (**Figure 4**). The quality of any calibration depends on the chemical homogeneity of the samples. We have deliberately not removed any samples from the series, which were outliers according to the SEC-IR results. In difference to the paper by T. Frijns-Bruls et al.,[28] we will focus on differences in the shape of the CH_3/CH_2 relation.

Surprisingly, the point corresponding to the most chemically nonhomogeneous sample (48.2 mol%, Figure 3b) in this series fits into the linear calibration (Figure 4) quite well. We notice that, although the concentration of components was the primary changed parameter in the synthesis, several of the samples manifest inhomogeneity (especially sample 48.2 mol%) – probably an experimental parameter was not controlled enough throughout the synthesis.

Such a calibration line may be used to evaluate changes in the CCD. It shows that the chemical composition of the sample with 48.2 mol% ethylene decreases from 59 to 39 mol% with increasing molar mass (Figure 3d), that is, considerably.

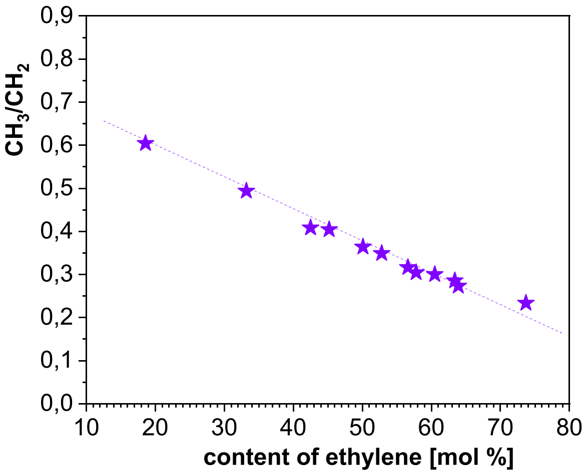

Figure 4. Dependence of CH_3/CH_2 ratio on the average content of ethylene in EP copolymers (Table 1).

Another type of CH_3/CH_2 profile was found in another series of EP copolymers (Table 2) synthesized also with a metallocene catalyst (**Figure 5**).

While the EP sample containing 58.3 mol% ethylene shows a substantial decrease in the CH_3/CH_2 ratio with increasing molar mass, the EP sample with 13.2 mol% shows an increasing CH_3/CH_2 ratio (Figure 5). According to the calibration for these

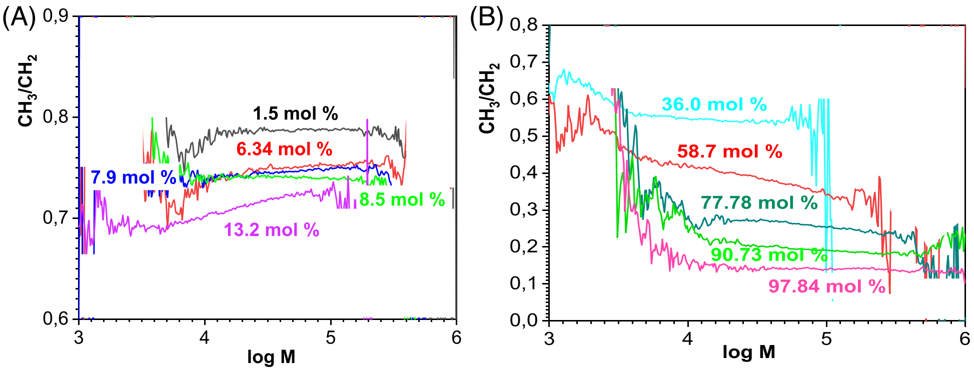

Figure 5. CH_3/CH_2 ratio as a function of equivalent PE molar mass of EP copolymers (Table 2).

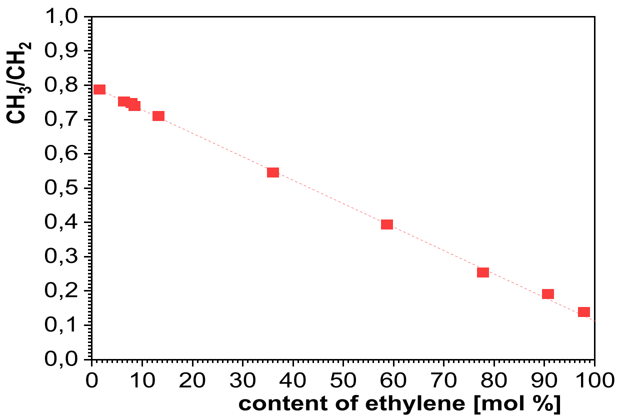

Figure 6. CH_3/CH_2 ratio as function of the average content of ethylene in EP copolymers (Table 2).

copolymer samples (**Figure 6**), the content of ethylene in the sample with 58.3 mol% decreased from 73 to 52 mol%, while in the sample with 13.2 mol% it increased from 13 to 16 mol% ethylene.

Samples with increasing or decreasing CH_3/CH_2 ratios were found also in other series of EP copolymers (data not shown) synthesized with metallocene catalysts. While the majority of samples showed a constant or almost constant CH_3/CH_2 ratio, similar deviations were found, as described previously. On the other hand, in some series of EP copolymers synthesized with metallocene catalysts (data not shown) all samples had constant or nearly constant CH_3/CH_2 ratios.

The CH_3/CH_2 profiles of EP copolymers synthesized with ZN catalysts (Table 3) are shown in **Figure 7**.

Two samples exhibit almost constant CH_3/CH_2 ratios, the CH_3/CH_2 rations of two samples are decreasing and the EP sample containing 43 wt% ethylene shows a pronounced increase as well as a decrease of the CH_3/CH_2 ratio. Taking the corresponding calibration (Figure 7b) into account, the ethylene content in the samples with 20 wt% and 30 wt% varies in the range of 15 wt%, while it varies in the range of 25 wt% in the sample with 43 wt% ethylene.

Various trends in CH_3/CH_2 profiles were found also for ethylene/1-butene, ethylene/1-hexene and propylene/4-methylpentene copolymers. For example, from the plots in **Figure 8** we can see that the CH_3/CH_2 ratio is decreasing for samples containing 5.8, 7.0, and 12.8 mol% hexene in EH copolymers (Table 4) while the CH_3/CH_2 ratio of the sample with 6.2 mol% hexene is increasing with increasing molar mass. The remaining samples show a homogeneous chemical composition as the CH_3/CH_2 ratio is constant along the molar mass.

Thus Figure 8 is an example of considerable diversity in the CH_3/CH_2 profiles. While samples in the range of 1–4 mol% 1-hexene exhibit flat profiles, the CH_3/CH_2 ratio of samples containing 6.2 and 8.4 mol% 1-hexene increases and the CH_3/CH_2 ratio of samples containing 5.8, 7.0, and 12.8 mol% 1-hexene decreases. The sample containing 12.8 mol% is the most inhomogeneous (composition between 8 and 15 mol% 1-hexene). The chemical inhomogeneity of the samples is apparently the reason for the substantial scattering of data points around the calibration line in Figure 8b. This substantially decreases the quality of the calibration curves in comparison to previous reported ones (e.g., Frijns-Bruls et al.[28]). Considering the calibration line, the ethylene content in the sample containing 12.8 mol% ethylene decreases from 20 to 9 mol% with increasing molar mass, while in the sample containing 6.2 mol% ethylene it increases from 7 to 17 mol%. These are substantial changes in the 1-hexene content along the molar mass axis.

An overlay of calibrations, as created from the provided data regarding the average composition of EP and EH samples, is shown in **Figure 9**.

The majority of points fall onto the same line, but the calibration line of one set of EP copolymers is shifted. A disagreement we also found in the past for other series of copolymers, when data were provided by different laboratories. Due to significant differences in ethylene content for the same CH_3/CH_2 ratio (a difference of 10 mol% ethylene) the ethylene content presented by Chitta et al.[30] should be evaluated again.

We conclude that EP copolymers prepared with metallocene catalysts yield more homogeneous CH_3/CH_2 profiles than EP samples prepared with ZN catalysts. However, in both groups, examples of profiles indicating chemical composition inhomogeneity along the molar mass axis were found. Similarly, CH_3/CH_2 profiles were constant or increased or decreased with the increase of molar mass for series of EB and EH copolymers. Such non-homogeneous samples may mix randomly with homogeneous samples or there may be a systematic trend. We hypothesize that

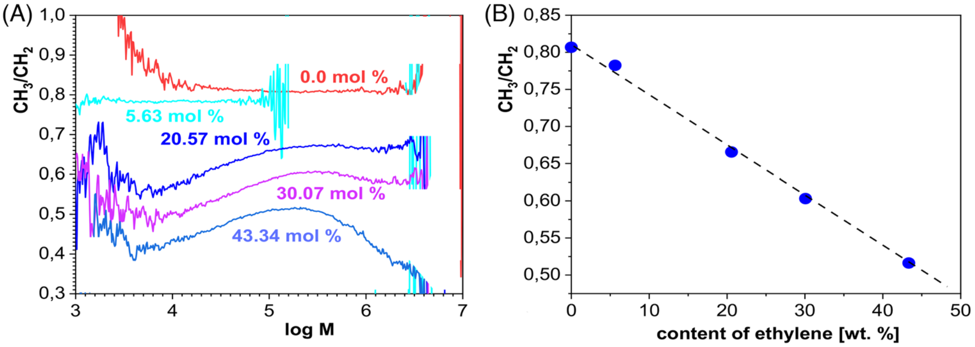

Figure 7. A) CH_3/CH_2 ratio as function of equivalent PE molar mass, B) CH_3/CH_2 ratio as function of the average content of ethylene in EP copolymers (Table 3).

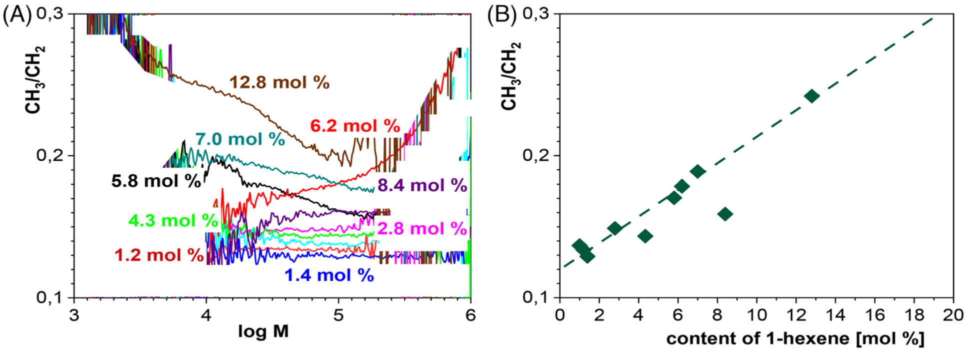

Figure 8. A) CH_3/CH_2 ratio as function of equivalent PE molar mass. B) CH_3/CH_2 ratio of the top of peaks as function of the average content of ethylene in ethylene/1-hexene copolymers (Table 4).

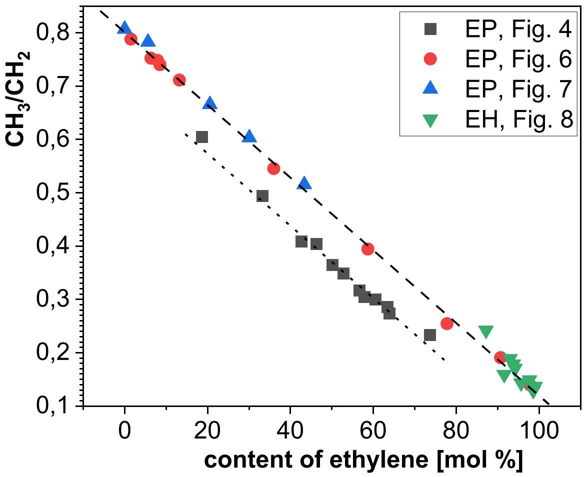

Figure 9. CH_3/CH_2 ratio at the top of the peaks as a function of the average content of ethylene in ethylene/propene and ethylene/1-hexene copolymers.

this may be related to experimental parameters, which were eventually not sufficiently controlled during the synthesis of the samples. Consequentially, the incorporation of comonomers changed with the molar mass of the copolymers – as shown, often substantially. When CH_3/CH_2 ratios are not monitored, then these trends may not be recognized. If they would be recognized, it could help to increase the quality (homogeneity) of the synthesized copolymers.

3.2. SEC-IR5 of Ethylene-Propylene-Diene Terpolymers

Tackx and Bremmers[17] have shown that SEC-FTIR using the LC-Transform approach enables to profile the distribution of methyl and diene along the molar mass in ethylene-propylene-diene (EPDM) samples. We have applied SEC-IR5 for the analysis of 6 EPDM samples (Table 5) and the ratios of CH_3/CH_2 of ethylene-propene-ethylidene-norbornene are shown in **Figure 10**a. An almost constant ratio of CH_3/CH_2 indicates homogeneity most of these polymer samples. Only the EPDM sample containing 5.2 wt% ENB manifests a drift in composition along the molar mass axis (Figure 10a).

Although the plot in Figure 10a indicates that the majority of the samples is chemically homogeneous (except with the one containing 5.2 wt% ENB), the CH_3/CH_2 ratio corresponding to the top of the peaks did not correlate linearly with either the average chemical composition of the EPDM (Figure 10b) nor with the average ethylene or propylene content. Apparently, the specific IR response of the diene must be taken into account, because the CH_3/CH_2 ratio does not reflect the presence of any monomer in EPDM alone. Thus, a linear calibration could not be established. However, the chemical inhomogeneity of the sample with 5.2 wt% ENB is reflected in the CH_3/CH_2 profile. An independent HPLC measurement showed[33] that just this particular

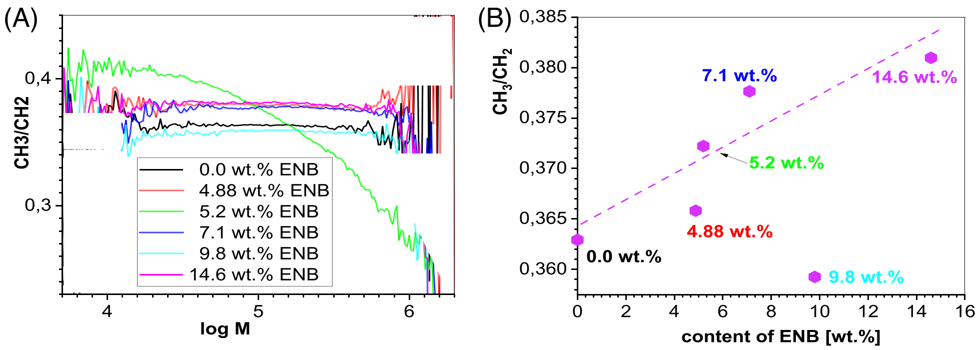

Figure 10. A) CH3/CH2 ratio of EPDM terpolymers (Table 5) as a function of the equivalent PE molar mass). B) Relation between CH_3/CH_2 ratio of EPDM terpolymers and the average content of ENB.

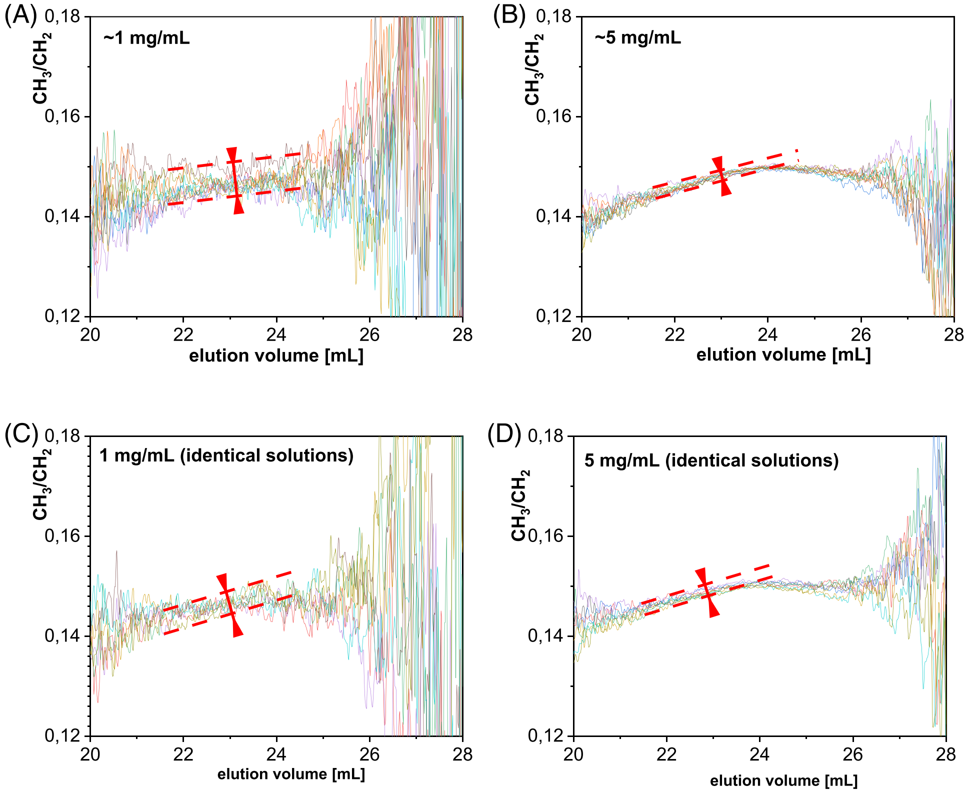

Figure 11. Ratio CH_3/CH_2 obtained after SEC-IR5 analysis of 10 solutions of ethylene/1-butene containing 5.2 wt.% of 1-butene.

sample exhibits a bimodal CCD. As shown, SEC-IR5 may reveal such a sample.

3.3. Repeatability, Dependence on Concentration, and Limit of Detection

With the aim to check the quality of measurements with the IR5-detector, 10 solutions of an ethylene/1-butene copolymer sample were prepared and the solutions were prepared in similar concentrations (≈1.0 and ≈5.0 mg mL^{-1}). Moreover, solutions with the identical concentration (1 and 5 mg mL^{-1}) were injected. The CH_3/CH_2 ratios corresponding to all measurements were calculated and the results are illustrated in **Figure 11**.

Figure 11 shows that reproducibility of the measurements was smaller at smaller concentration and increased with increasing concentration. We notice that noise in the data influences reproducibility of the IR5-measurements to a larger extent at smaller concentrations compared to larger concentrations. This is because the signal-to-noise ratio increases at higher concentrations. A comparison of Figure 3a–d confirm that small variations of the concentration do not influence the reproducibility substantially.

Injections of 10 solutions with different concentrations of the ethylene/1-butene sample exhibited linear dependences between the IR response and the polymer concentration, as illustrated in **Figure 12**.

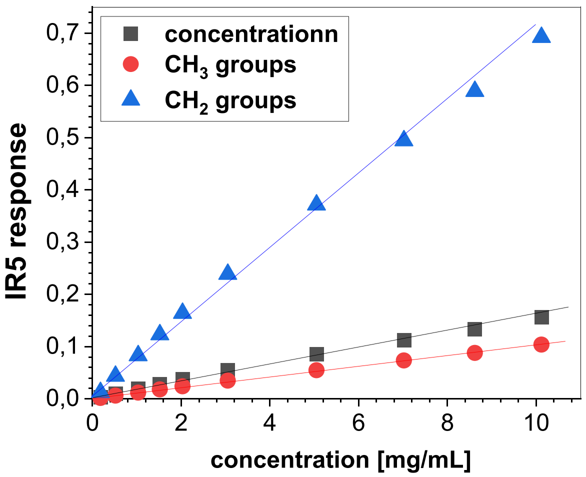

Figure 12. IR5 responses obtained after SEC-IR5 analysis of 10 solutions of EB (5.2 wt% 1-butene) with different concentrations.

Table 6. Reproducibility and limit of detection data for the IR5.

Sample	Mean (CH_3/CH_2)	Standard deviation (CH_3/CH_2)	Limit of detection [mg mL^{-1}]	Linearity (R^2) of concentration dependence
EB (5.2 wt% 1-butene)	0.14483	0.000638	0.09	0.99723

Taking the base line noise of the recorded IR5-concentration signal into account, the limit of detection (defined as 3 × noise) was calculated for the tested polymer sample (**Table 6**).

The obtained results confirm high reproducibility, linear response, and suitable detection limit of the IR5-detector. The obtained results are similar to those obtained with different polymer samples by Ortin et al.[26] Our data confirm that changes in the CH_3/CH_2 profiles, which were described above, are many times larger than errors connected to the SEC-IR5 measurements.

4. Conclusion

This study shows that the high temperature SEC-IR (with a filter-based infrared detector model IR5, PolymerChar, Valencia, Spain) technique is a powerful tool for monitoring the CCD as a function of the molar mass of various polyolefins. The monitoring of methyl and methylene groups can be performed as part of routine SEC measurements. Thus, in addition to the MMD, the CCD along the molar mass axis can be determined for many polyolefin materials.

It was found that the ratio of the IR signals that correspond to methyl and methylene groups (CH_3/CH_2 ratio) along the molar mass axis of a polymer sample may be constant, increasing or decreasing with increasing molar mass. In some samples, first an increase and at lower molar masses a decrease was found. Such variations in CH_3/CH_2 profiles were found even within individual series of copolymers that were prepared with the same catalyst, including metallocene catalysts, which usually produce chemically very homogeneous polymers. It is hypothesized that one or several experimental parameters, which were eventually not strictly controlled during polymer synthesis, may cause such changes in the CCD along the molar mass axis. Consequentially, some samples in a series exhibit different CH_3/CH_2 profiles. Monitoring the CH_3/CH_2 ratio through SEC measurements was, however, seldom performed in the past.

As is illustrated in this work, the advanced HT SEC-IR5 instrument enables to reveal inhomogeneities in the CCD of polyolefins and thus the HT SEC-IR technique is a useful tool for evaluating and understanding the molecular structure of polyolefins.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chemical composition, FTIR, polyolefins, size exclusion chromatography

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