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# SEC–FTIR characterization of semi-crystalline HDPE and PP

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**Abstract**

In SEC–FTIR, polymer separation according to molar mass, size exclusion chromatography (SEC) is coupled to a Fourier transform infrared (FTIR) analysis. Over the past few years, much effort was put into the determination of the chemical composition of a broad range of polyolefins as a function of molar mass using this technique (EPDM, LDPE, LLDPE).

In the current investigation, a pressure transducer is used to optimize the SEC–FTIR technique for the analysis of semi-crystalline materials like HDPE and PP. It was shown that the comonomer content (butene for HDPE and ethene for PP) decreased with increasing molar mass. For two HDPE samples which were produced by the dual reactor process this decrease occurred step wise with a constant comonomer amount on either side of the step. For all HDPE samples it was shown that the amount of end unsaturations decreases with molar mass. The concentrations of trans and side unsaturations were too low to be determined.

*Keywords*: Polymer analysis; Size exclusion chromatography; Fourier transform infrared

## 1. Introduction

Despite ethylene's simple structure, the field of polyethylene is a complex one with a very wide range of densities and melt indices and many different manufacturing processes. High density polyethylene (HDPE) is produced at low pressure and temperature. In contrast, low density polyethylene (LDPE) is produced by the high pressure process.

Another type of polyethylene is linear low density polyethylene (LLDPE) which is produced in a relatively cheap production process. Using a coordination catalyst, a comonomer is incorporated. The special catalyst allows the copolymerization of ethylene with olefins such as butene. Note that by introducing side branches, the crystallinity is reduced and an LDPE can be produced at comparatively low pressures.

*The general structure of LDPE, LLDPE and HDPE is as follows:*

- LDPE has a long-chain randomly branched structure. The short branches (control of the density) are not uniform in length but are mainly four or two carbon atoms long. The molar mass distribution (MMD) is moderately broad.
- LLDPE has branching introduced in the main chain by a comonomer (butene-1, hexene-1, octene-1). This branching is uniform of length and is randomly distributed along a given chain. The catalysts used to produce LLDPE are mostly Ziegler–Natta type. These catalysts introduce a lot of side chains in the low molar mass region, while in the high molar mass region, less comonomer is incorporated. The catalyst used to minimize this effect (metallocene types) generally also produces fairly narrow MMDs.
- HDPE is essentially free of both long and short branching, although very small amounts of side chains are deliberately incorporated to achieve specific product properties (density). The MMD depends on the catalyst used: Ziegler–Natta type produces narrow MMDs, Cr-type produces broad MMDs.

The principal effect of copolymerization is the reduction of crystallinity (density). In addition to the branches introduced by the comonomer, the branches which originate under the high pressure synthesis conditions, also contribute to the reduction in crystallinity. The performance of the final product is dramatically affected by the inclusion of a small amount of short-chain branches along the backbone of the polyethylene.

*Polypropylene:* Another important semi-crystalline material that was analyzed was polypropylene (PP). Commercial interest lies in homopolymers as well as in copolymers of PP. There are two distinct classes of copolymers having different application areas. Random copolymers are made in the same way as homopolymers, but a mixture of propene

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and comonomer is used instead of pure propene. These random copolymers have lower melting points and improved clarity. Usually, polymers containing 2–6 wt% of ethylene cover most applications. Impact (block) copolymers, made in a two-stage polymerization process, contain dispersed propene–ethylene elastomers in a homopolymer matrix which leads to increased toughness.

In this investigation, the size exclusion chromatography–Fourier transform infrared (SEC–FTIR) technique is used to characterize semi-crystalline materials like HDPE and random PP copolymers: the average comonomer content (expressed as the amount of methyl groups per 1000 carbon atoms, $CH_3$/1000C) and the amount of unsaturations can be determined as a function of molar mass. It is also possible to determine the comonomer distribution in the peak tails, where the amount of polymer is so low that the $CH_3$/1000C is very difficult to quantify. Quantitative analysis can be performed by spraying three layers of polymer on top of each other. All this information is of great importance in order to fully understand polymer properties. Measuring the heterogeneity leads to a better understanding of relations between material properties, processability and microstructure. The heterogeneity is not only determined by the type of catalyst, but by the entire reaction and production process.

## 2. Experimental

### 2.1. Experimental set-up

Hyphenated techniques, which connect polymer separation with information rich detection, are able to reveal the chemical heterogeneity of polymers as a function of molar mass [1]. The SEC–FTIR technique combines SEC (polymer separation) with FTIR (polymer characterization). The connection between the high temperature Waters M150C GPC (operated at 150°C) and the Perkin–Elmer 2000 Spectrum FTIR spectrophotometer is made by the LC-transform model 303 of Lab Connections [2–6]. With this technique, the average chemical composition of a polymer can be measured as a function of molar mass [7,8].

To make the analysis of semi-crystalline materials such as HDPE and PP possible a pressure transducer model CVC $2^{II}$ was connected to the LC-transform collection module. In this way the pressure in the vacuum chamber can be controlled in a range of 1–1060 mbars with an accuracy of ±2 mbars.

### 2.2. Evaporation conditions

The most critical step in the SEC–FTIR analysis is the deposition of the polymer film on the disc. The evaporation of the solvent in the vacuum chamber has to be sufficiently rapid to avoid any accumulation of solvent on the surface of the disc during the run [3]. When liquid is accumulated on the disc, the film morphology is not uniform. In some cases, polymer is sprayed away from the disc. Normally the solvent evaporation rate is controlled with the ultrasonic nozzle power, the spray temperature, and the oven temperature (vacuum conditions) resulting in smaller more uniform polymer particles. Under such conditions homogeneous films are obtained on the discs which in turn give good FTIR measurements.

For semi- and high crystalline polyolefines, a high temperature is needed in order to keep the polymer in solution. Due to increased solvent evaporation rates under vacuum conditions the polymer crystallizes inside the ultrasonic nozzle. Using a pressure transducer the pressure in the chamber is increased slightly resulting in a decreasing solvent evaporation velocity. By optimizing the temperature program and chamber pressure the crystallization of polymer in the nozzle can be avoided, resulting in a homogeneous and clean film deposited on the collection disc.

### 2.3. Considerations on semi- and high crystalline materials

With high temperature SEC–FTIR, there are two complications:

1. the semi-crystalline nature of polyolefins;
2. the low volatility of the mobile phase [4].

Solubilities (and hence the tendency to precipitate in a sprayed droplet) of polyolefins depend upon molar mass and, for polyethylene, PP and for EPDM, depends also upon the degree of branching. In TCB, PP is generally less soluble than polyethylene. Thus, under the same experimental conditions, there will be some variation in film morphology obtained from different polyolefins. The film quality refers to the properties of the film that are relevant to obtain accurate and precise results from the interpretation of the FTIR spectra as a function of molar mass. These include: thickness, uniformity, 'wedging', Christiansen effect, molecular interactions, and polarization effects. The absorbance at a specific IR frequency depends on the thickness of the film. If the film is too thick, the absorbance of a highly absorptive band may not obey the Lambert–Beer law. Film inhomogeneity can cause offsets in the absorption band intensity of the spectrum. The Christiansen effect is caused by the scattering of radiation. The extent of scattering depends on the particle size of sample deposited on the disc and refractive index differences. Scattering can cause both baseline curvature and derivative-like absorption band shape changes. Molecular interactions can cause shifts of absorption bands. Polarization effects may lead to changes in relative intensities in a spectrum due to crystal orientation.

The resolution is determined by the range of molecular sizes contributing to each FTIR scan. This is determined by both the SEC fractionation obtained and the degree to which the interface remixes different molecular sizes. A compromise between sensitivity and resolution is involved: the more the molecules are allowed to mix (i.e. increase film thickness), the higher the sensitivity but the lower the resolution.

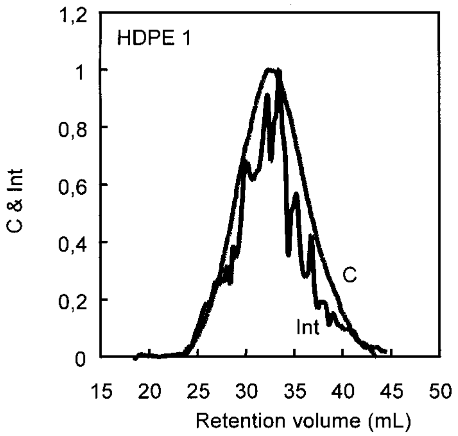

Fig. 1. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for HDPE 1.

Polymer recovery is the amount of polymer deposited on the collection disc compared to the amount injected into the chromatograph. Imperfect aerosol generation can result in splashing, droplet and particle ricochet, and other effects that result in sample not being deposited on the disc. It is very hard to obtain clean FTIR data if the film breaks up. Some temperature profiles improve the film quality at low molecular weight, but none improve the quality at higher molecular weights. This is because the amount of sample present at this elution volume is not high enough to form a continuous film. Increasing the injected sample volume or the concentration of the polymer in the sample will improve the quality of the film in the edges of the MMD, but has two negative consequences. The first unfavourable effect is the loss of separation resolution in the GPC columns, and the second is the formation of a very thick film in the bulk of the material on the collection disc. This thick film will saturate the FTIR absorption bands and obstruct the measurement of FTIR peak intensities [4]. A way to increase the polymer deposit in the peak tails is to perform the experimental run more than one time using always the same collection disc. This will lead to a very thick film in the bulk of the material on the collection disc, but will improve the quality of the film in the edges of the MMD without any loss in separation resolution in the GPC columns. To obtain good FTIR results in the bulk, a normal run can be carried out and the results of the two discs obtained can be compared. Disadvantages of this analysis are: time consuming and higher price per analysis.

### 2.4. Molar mass distribution curve reconstruction with FTIR

With IR it is possible to reconstruct the molecular mass distribution. At a certain elution volume (or collection disc position) the total amount of material present is calculated (including any background material on the disc) by taking the area under the CH bending peak between 1450 and 1400 cm$^{-1}$. This reconstruction is called the chemogram.

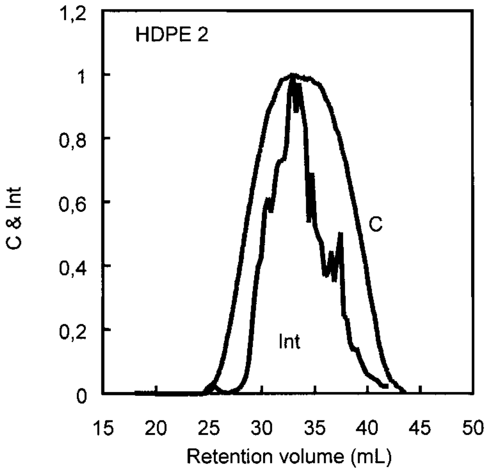

Fig. 2. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for HDPE 2.

In order to check if all the polymer material injected into the chromatograph was deposited as a film on the collection disc, the mean chemogram is plotted over the SEC-RI MMD.

This is a very important indication that the experiment was carried out successfully.

### 2.5. FTIR conditions and calibration of the unsaturations

The amount of branching is calculated with a second derivative method. In the past [7], the second derivative parameters worked well for VLDPE samples with high content of branching. The branching in polyethylene with less branches had to be recalibrated with optimized second derivative parameters. Furthermore a new calibration was made to determine the end-group unsaturation using two PE samples: one with 100 C=C end-groups/1,00,000C and one with 160 C=C/1,00,000. The amount of unsaturations is determined at 908 cm$^{-1}$, which corresponds to the –C=C–H bending vibration. It is also corrected for the film thickness.

At 965 cm$^{-1}$ a band can be seen for trans (in backbone) unsaturation and at 895 cm$^{-1}$ for vinylidene unsaturation $-CH_2-C(=CH_2)-CH_2-$.

For the calibration of the random C2 in the PP samples, a band at 730 cm$^{-1}$ was used. This band was corrected for the film thickness with a band at 840 cm$^{-1}$. The calibration was carried out using samples with C2 contents of 3.2, 2.9, and 1.7 mol/mol%.

## 3. Results and discussion

### 3.1. Molar mass distribution curve reconstruction

The use of SEC–FTIR for the characterization of semi-crystalline products such as HDPE and PP is illustrated for three HDPE (HDPE 1: a Cr catalyst was used in a single reactor process, HDPE 2 and HDPE 3: both were made with

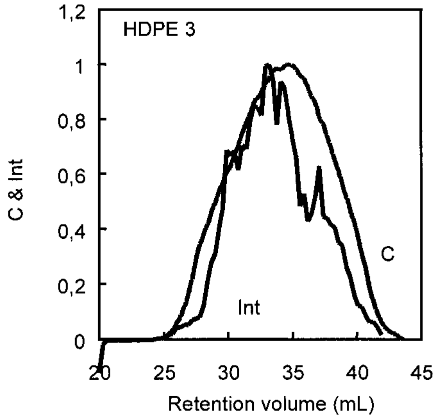

Fig. 3. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for HDPE 3.

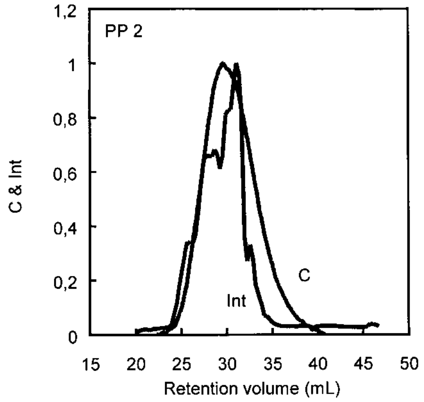

Fig. 5. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for PP 2.

Ziegler–Natta catalysts in a two reactor process) and three random PP copolymers (PP 1, PP 2, PP 3, made using a Ziegler–Natta catalyst) with different molecular structure (MMD, comonomer distribution and content).

To prove that semi-crystalline materials can be determined by SEC–FTIR, a reconstructed chemogram is plotted over the SEC-RI MMD. Figs. 1–3 show results for HDPE and Figs. 4–6 show results for PP.

The general shape and location of the maximum are similar in the concentration chromatogram and reconstructed chemogram for the HDPE and PP samples as can be seen in Figs. 1–6. That the reconstructed chemogram is less smooth then the on-line measured concentration chromatogram can be expected since the reconstructed chemogram is influenced by physical processes (aerosol generation, film formation on disc, evaporation of the solvent) and by FTIR measuring effects (film thickness, background material on disc). Taking this into account it can be concluded that there is acceptable agreement between the concentration chromatogram and the reconstructed chemogram for the presented HDPE and PP products. The differences found in the peak tails result from a discontinuous film since the amount of sample is too small in this area, i.e. the deposited film on the collection disc breaks up in islands. It is very difficult to determine the comonomer distribution and amounts of unsaturations in these peak tails.

For polymers having broad MMDs, such as HDPE 2 and 3 which are produced in a two reactor process, it is even more difficult to find a temperature program that allows the deposit of a continuous film along the complete MMD. This behaviour can be observed especially for HDPE 2 which has a very broad MMD.

### 3.2. The chemical distribution

*HDPE:* The SEC–FTIR method developed for semi-crystalline materials reveals the mean chemical composition as a function of the molar mass. The comonomer content ($CH_3$/1000C) of the HDPE samples is given as a function of molar mass in Figs. 7, 9 and 11, while the amount of unsaturation as a function of molar mass is given in Figs. 8, 10, and 12.

It can be seen that the amount of comonomer and end unsaturations decreases with increasing molar mass for all

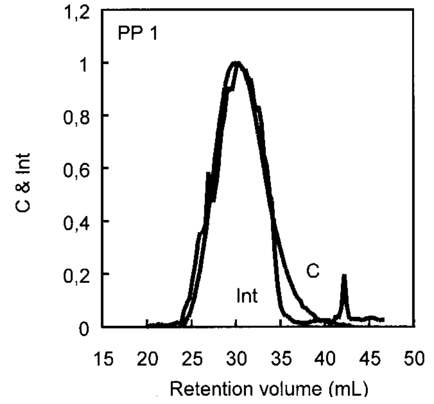

Fig. 4. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for PP 1.

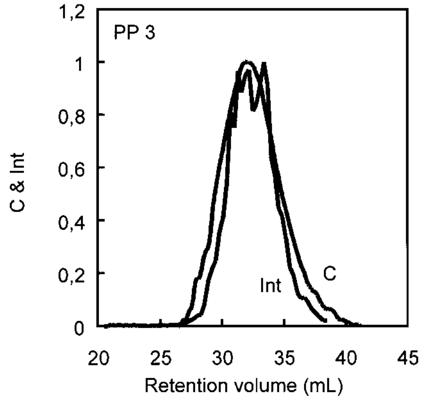

Fig. 6. Concentration chromatogram from SEC, C (arbitrary units), and reconstructed chemogram from SEC–FTIR, Int (arbitrary units), are given as a function of retention volume for PP 3.

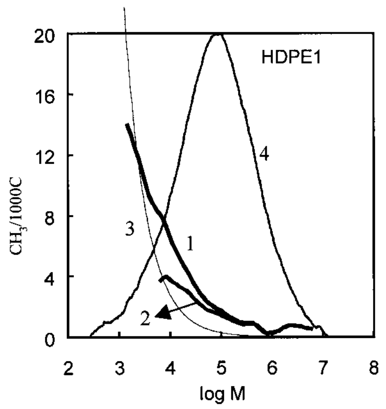

Fig. 7. Comonomer content of HDPE 1 as a function of molar mass, measured by SEC–FTIR. Lines 1–4 represent the number of CH$_3$/1000C (not corrected for end-groups), the CH$_3$/1000C corrected for end-groups, the amount of end-groups, and the molar mass distribution (arbitrary units), respectively.

the HDPE products presented here. For both two reactor HDPE products (HDPE 2 and 3 in Figs. 9–12) the decrease in CH$_3$/1000C seems to be step wise with two regions with constant but different amount of comonomer.

The distributions obtained depend highly on the synthesis routes as can be seen when the process conditions are taken into account.

The one reactor product (HDPE 1, Figs. 7, 8) was produced using a Cr-type catalyst. Butene was added as comonomer during the polymerization process. Using NMR the CH$_3$/1000C was determined to be 0.6. The comonomer distribution shows a decreasing comonomer content with increasing molar mass.

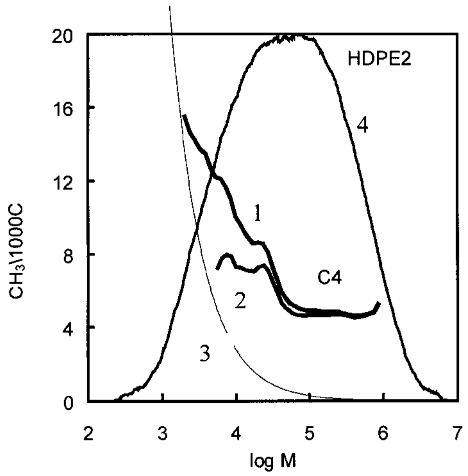

Fig. 9. Comonomer content of HDPE 2 as a function of molar mass, measured by SEC–FTIR. Lines 1–4 represent the number of CH$_3$/1000C (not corrected for end-groups), the CH$_3$/1000C corrected for end-groups, the amount of end-groups, and the molar mass distribution (arbitrary units), respectively.

Both two reactor HDPE products (HDPE 2 and 3) are produced using a Ziegler–Natta catalyst. These HDPE products have very broad molecular weight distributions because they are produced in a two reactor process. The comonomer used to produce these samples is butene. The comonomer profiles (corrected for end-groups) obtained show that both are heterogeneous samples where the butene content for the high molar mass region is different compared to the low molar mass region. This is a direct result of the dual reactor polymerization process. For HDPE 2 (Fig. 9) the bulk C3 wt% calculated from SEC–FTIR measurements is 4.9 CH$_3$/1000C which agrees reasonably with the off-line FTIR bulk value of 5.4 CH$_3$/1000C. Note that the CH$_3$/1000C value obtained by SEC–FTIR is an average value over the region where accurate FTIR measurements are obtained. The distribution in the peak tails is therefore not taken into account. The off-line bulk value is obviously an averaged value over the complete polymer. Differences between the CH$_3$/1000C amount determined by both methods can thus be accounted for.

The amount of unsaturations can be measured successfully by infrared spectroscopy (end, side and trans unsaturations). Coupling SEC to IR to characterize the amount of unsaturations as a function of molar mass is a logical step. In

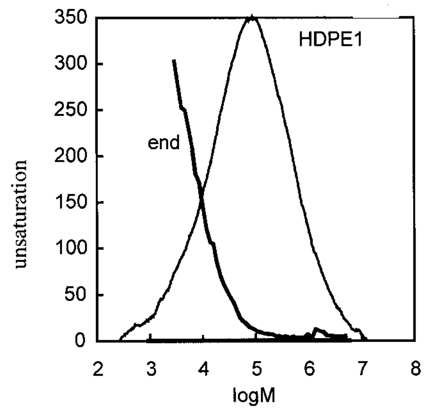

Fig. 8. Amount of end unsaturations per 1,00,000C of HDPE 1 as a function of molar mass, measured by SEC–FTIR.

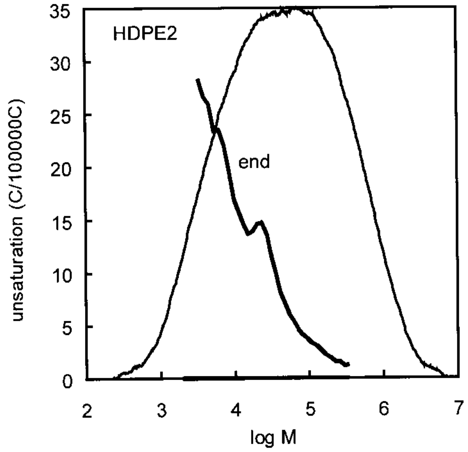

Fig. 10. Amount of end unsaturations per 1,00,000C of HDPE 2 as a function of molar mass, measured by SEC–FTIR.

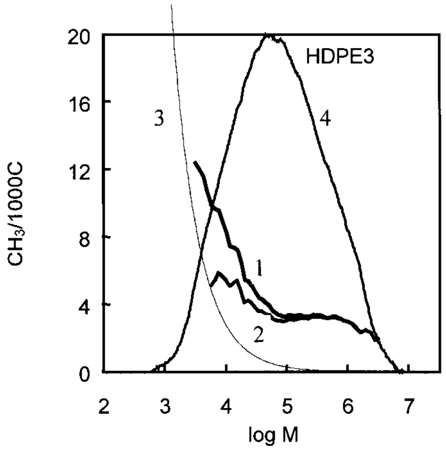

Fig. 11. Comonomer content of HDPE 3 as a function of molar mass, measured by SEC–FTIR. Lines 1–4 represent the number of $CH_3$/1000C (not corrected for end-groups), the $CH_3$/1000C corrected for end-groups, the amount of end-groups, and the molar mass distribution (arbitrary units), respectively.

this report it is demonstrated that SEC–FTIR is a useful technique for the measurement of end unsaturations in polymers. The decrease in the amount of end unsaturations can be seen clearly for the HDPE samples analyzed (Figs. 8, 10, and 12). Similar analysis done on LDPE and LLDPE samples, also resulted in determinations of the amount of end unsaturations as a function of molar mass. However, some limitations are observed. For instance, it is known that for polymers produced using a Cr-type catalyst, the amount of end unsaturations is higher (one order higher) than for the polymers produced using Ziegler–Natta catalysts. Although this tendency is confirmed by SEC–FTIR measurements, a direct comparison between SEC–FTIR and off-line bulk determinations revealed that the total amount of end unsaturations determined by SEC–FTIR is sometimes lower than determined by off-line bulk FTIR determinations.

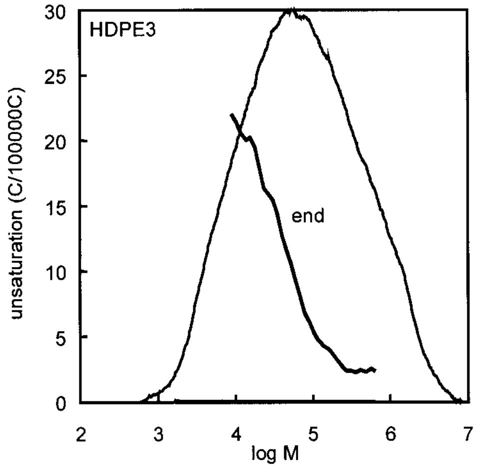

Fig. 12. Amount of end unsaturations per 1,00,000C of HDPE 3 as a function of molar mass, measured by SEC–FTIR.

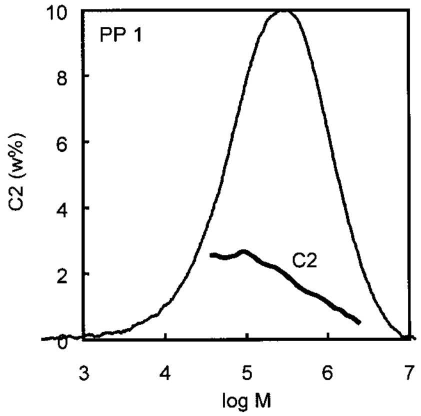

Fig. 13. Ethene content (wt%) measured with SEC–FTIR as a function of molar mass, $M$, is plotted over the molar mass distribution (arbitrary units) for PP 1.

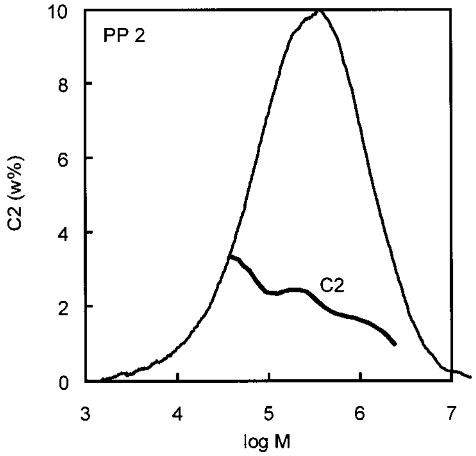

Fig. 14. Ethene content (wt%) measured with SEC–FTIR as a function of molar mass, $M$, is plotted over the molar mass distribution (arbitrary units) for PP 2.

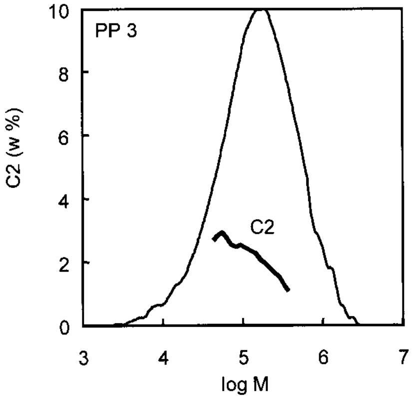

Fig. 15. Ethene content (wt%) measured with SEC–FTIR as a function of molar mass, $M$, is plotted over the molar mass distribution (arbitrary units) for PP 3.

Probably the SEC–FTIR determination of the absolute amounts is less accurate due to the low concentrations of the end unsaturations in combination with thin films on the collection disc (values are per 1,00,000C!). Note however, that SEC–FTIR is the only way to determine the end unsaturations as a function of molar mass. More accurate determinations of the absolute amounts of $CH_3$/1000C can possibly be obtained when several layers are deposited on top of each other. The amount of side and trans unsaturations is difficult to determine even by normal FTIR measurements due to low concentrations. Since the concentrations on the SEC–FTIR disc are much smaller, it is not very surprising that almost no side and trans unsaturations are found. Based on these results it is concluded that no quantitative and also no qualitative information about trans and side unsaturations can be determined using SEC–FTIR.

*Polypropylene:* The PPs presented in Figs. 13–15 are random copolymers made with a Ziegler–Natta catalyst. The SEC–FTIR results show a decreasing ethene content with increasing molar mass. The bulk C2 wt% calculated from SEC–FTIR measurements is 1.8, 2.0 and 2.1 wt% for the PP samples presented in Figs. 13–15, respectively. For the PP product presented in Fig. 15 the off-line bulk value of 2.5 wt% was determined. This agrees reasonably with the on-line determination of 2.1 wt% even though the SEC–FTIR region in which the C2 amount could be determined is limited.

## 4. Conclusions

The results obtained in this investigation prove that it is possible to analyze semi-crystalline materials like HDPE and PP using a pressure transducer in combination with the SEC–FTIR technique. This progress broadens the possibilities of the SEC–FTIR technique. Moreover, SEC–FTIR demonstrated to be a useful technique for the measurement of the distribution of end unsaturation as a function of molar mass. The concentration side and trans unsaturations are too low to be determined. It is now possible to determine the average chemical composition as a function of molar mass of a large range of experimental and commercial polyolefins:

- EPDM: the ethene, propene and third monomer content can be measured as a function of molecular mass.
- LLDPE (both Ziegler–Natta catalyst and metallocene catalyst), LDPE, and HDPE: the comonomer distribution and the amount of unsaturations can be determined, even for bimodal distributions.
- PP: the ethene content can be determined as a function of molar mass.
- Polyolefins grafted with anhydrides (PP, PE, EPDM): the anhydride distribution can be determined.
- Ethene–styrene copolymers.

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