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Chemical Composition Distribution of Linear-low Density Polyethylenes by SEC-FT-IR*

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A method is described to measure the chemical composition of linear-low density polyethylenes as a function of molar mass. This technique combines polymer separation according to molar mass by size exclusion chromatography with chemical analysis by Fourier-transform infrared spectroscopy. The comonomer (octene, hexene, butene or propene) distribution in these ethene- α -olefin copolymers is determined. The influence of the type of catalyst, Ziegler *versus* metallocene, is thus determined.

Keywords: Size exclusion chromatography; Infrared spectroscopy; Polyolefins; Linear-low density polyethylene

INTRODUCTION

The molar mass and molar mass distribution of polymers can be measured experimentally by size exclusion chromatography (SEC). The overall comonomer content and the tacticity of the material can be obtained by Fourier-transform infrared (FT-IR) or nuclear magnetic resonance (NMR) spectroscopies. It is, however, impossible to obtain the comonomer distribution of copolymers with these techniques. One has to resort to hyphenated methodologies, which combine polymer separation with information-rich detection, in

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order to resolve these distributive properties.^[1] The recently developed SEC-FT-IR technique^[2] is extremely well suited to solve this problem. In this paper, we present the comonomer distribution in heterogeneous and homogeneous linear-low density polyethylenes (LLDPEs).

A broad range of LLDPE samples is used in the packaging industry. LLDPE is made by the copolymerization of ethene with α -olefins. The physical properties of these materials are affected by molar mass and molar mass distribution, as well as by the type, number and arrangement of comonomers along the polymer backbone. The catalyst and process employed, determine the distribution of the comonomer in the polymer. It is believed that the finer scale properties (clarity, sealability and processability) are associated with the comonomer distribution.^[3] Therefore, the synthesis and characterization of homogeneous and heterogeneous LLDPE copolymers is important.

EXPERIMENTAL

Apparatus

The SEC-FT-IR technique combines size exclusion chromatography with Fourier-transform infrared spectroscopy. The connection between these two techniques was made with a commercially available LC-transform unit (Model 303, Lab Connections, Marlborough Mass) in which the polymer fractions from SEC are collected on a disc rotating with a speed corresponding to the SEC flow rate. The LC-transform was connected in a sequential flow mode. This means that the entire eluent flow from the chromatograph was directed to the nebulizer of the LC-transform.

A Waters M150C GPC was used, operated at high temperature (injector compartment at 150°C, column oven at 140°C and solvent reservoir at 60°C). Distilled and stabilized trichlorobenzene (TCB) was used as mobile phase. The eluent flow was set at 0.5 mL/min. Four TSK GMHxL-HT columns were used. The injection volume was around 0.3 mL. The polymer solution was transferred from the SEC columns to the vacuum chamber of the LC-transform through a

heated transfer line (155°C). The temperature of the nozzle was programmed and optimized for the best nebulization of solvent in the vacuum chamber and most uniform and homogeneous deposit on the collection disc.

The collection disc was scanned with a Perkin Elmer 2000 Spectrum FT-IR spectrometer with a fast and sensitive MCT (mercury-cadmium-telluric) detector. In each radial segment of 3° on the disc, 50 infrared spectrum scans were summed. The resolution was 4 cm^{-1} with strong apodization.

For the LLDPE samples, the methyl bending vibration at 1378 cm^{-1} was used to determine the comonomer content. The normalization for this band was performed by measuring the difference in extinction at 2660 cm^{-1} and 2450 cm^{-1} . By normalizing the different peaks, the difference in film thickness across the collection disc was neutralized. Absolute propene, butene, hexene or octene contents were obtained with FT-IR-NMR calibration curves (for each type of comonomer another calibration curve is used). The ethene-octene calibration curve is given in Figure 1.

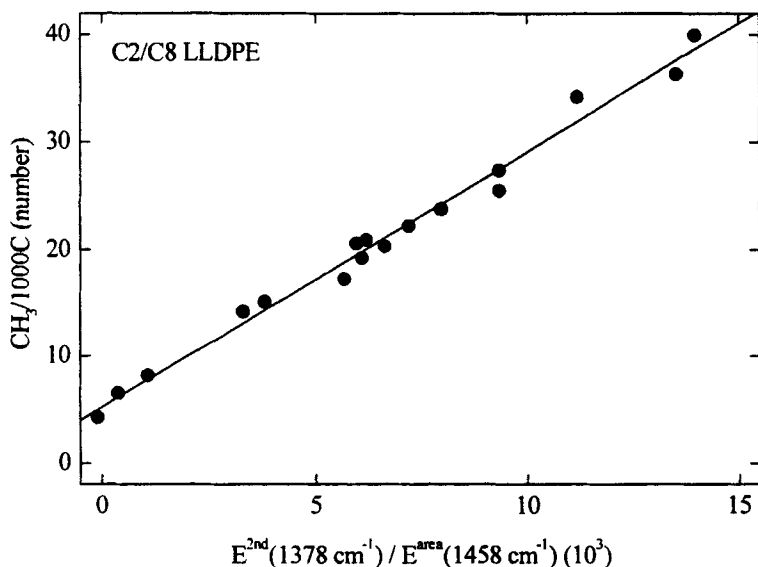


FIGURE 1 The octene FT-IR-NMR calibration curve for LLDPE.

Polymer Sample Preparation

The polymer samples were dissolved (0.1 w%) in 1,2,4-trichlorobenzene (TCB), which was distilled prior the use, over a period of 4 h at 150°C and stabilized with di-*tert*-butyl-*p*-cresol (DBPC) at a concentration of 1 g/L. The solutions were filtered at high temperature (150°C) using a Millipore filtration set-up (1.2 mm) positioned in a Hereaus LUT oven operating at 150°C.

RESULTS AND DISCUSSION

The quantitative FT-IR analysis of the disc (which is related to the chemical composition) as a function of the position on the disc (which is related to retention volume and hence molar mass) is translated into a chemical composition distribution (CCD) plot (chemical composition as a function of molar mass).

Eight different LLDPE samples were prepared and characterized with the SEC-FT-IR technique (Tab. I). The two heterogeneous ethene–octene copolymers (LLDPE I and LLDPE II) show a decrease in comonomer content (expressed as the number of methyl groups per 1000 carbon atoms: CH₃/1000C) with increasing molar mass (Fig. 2).

The Ziegler type catalyst used to synthesize these heterogeneous copolymers has at least two active sites. One of the sites produces low molar mass PE with high comonomer content, while the other site produces high molar mass PE with a low comonomer content. This

TABLE I Comonomer, weight average molar mass, polydispersity, and density

Sample	Comonomer	M_w^* (g/mol)	M_w^*/M_n^*	Density (kg/m ³)
LLDPE I	octene	81,000	6.2	888
LLDPE II	octene	87,000	5.7	907
LLDPE III	octene	105,000	2.1	853
LLDPE IV	octene	229,000	2.1	872
LLDPE V	butene	107,000	2.3	878
LLDPE VI	butene	155,000	2.2	910
LLDPE VII	propene	98,000	2.2	NA
LLDPE VIII	propene	134,000	2.1	NA

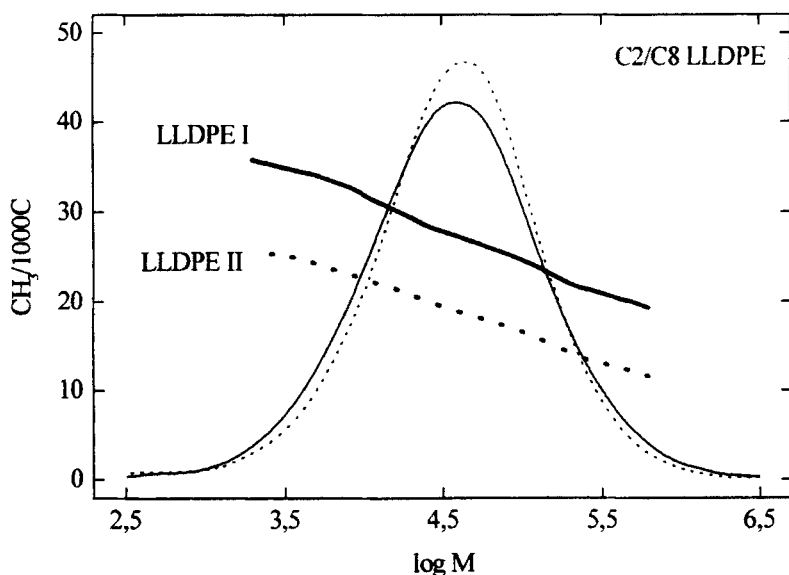


FIGURE 2 CCD plot of LLDPE I and LLDPE II.

means that the long PE chains have relatively less comonomer than the short ones. The comonomer distribution is inhomogeneous.^[4, 5] With single-site catalysts, homogeneous ethene–octene LLDPE III and LLDPE IV, ethene–butene LLDPE V and LLDPE VI, and ethene–propene LLDPE VII and LLDPE VIII copolymers were synthesized and characterized. From Figures 3–5, it is clear that the comonomer content is constant with molar mass, as expected.

From the SEC-FT-IR CCD and the molar mass distribution, the bulk comonomer weight percentage (C_n wt%) can be calculated according to Eq. (1)

$$C_{n_{\text{bulk}}} = \frac{\sum_i C_{n_i} \cdot c_i}{\sum_i c_i} \quad (1)$$

with $C_{n_{\text{bulk}}}$ the calculated bulk C_n wt%, C_{n_i} the C_n wt% of the i -th chromatogram slice, and c_i the concentration of the i -th chromatogram slice. The values obtained with this expression are summarized in Table II and compared with the off-line bulk values.

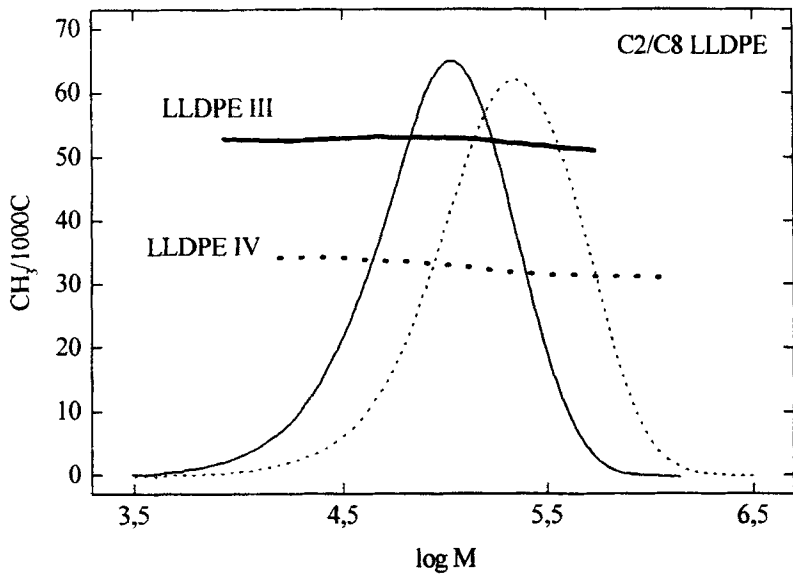


FIGURE 3 CCD plot of LLDPE III and LLDPE IV.

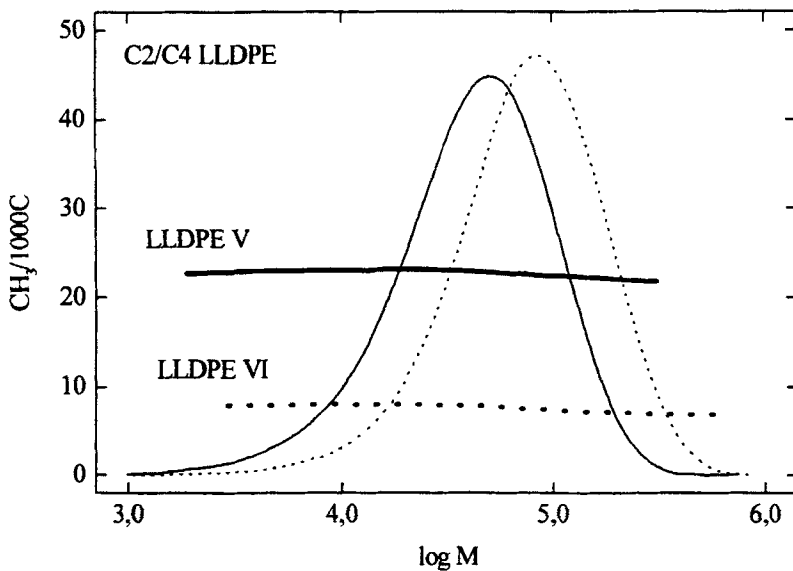


FIGURE 4 CCD plot of LLDPE V and LLDPE VI.

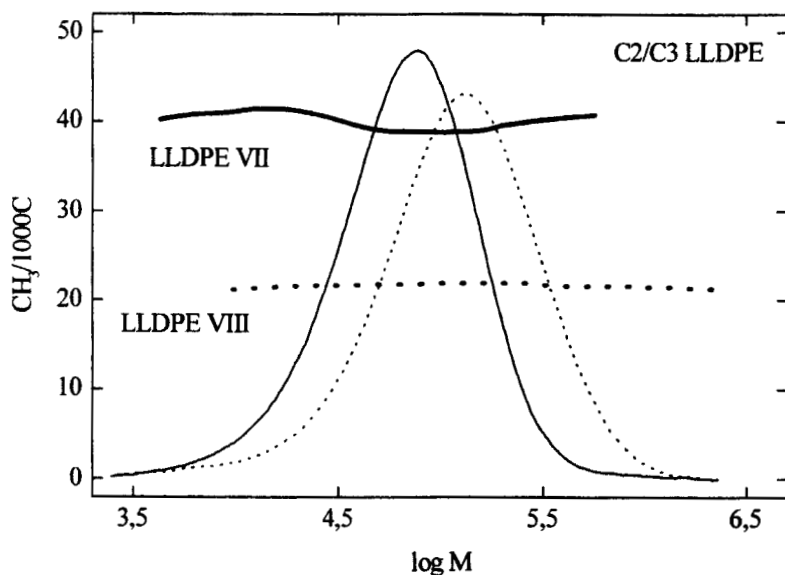


FIGURE 5 CCD plot of LLDPE VII and LLDPE VIII.

TABLE II Total mass of polymer material accessible with SEC-FT-IR, total off-line and calculated $CH_3/1000C$

Sample	Mass (%)	$CH_3/1000C$	
		Off-line	Calculated
LLDPE I	98	28.2	28.0
LLDPE II	97	19.1	20.3
LLDPE III	99	51.2	52.1
LLDPE IV	98	31.9	30.5
LLDPE V	97	21.6	21.2
LLDPE VI	99	8.3	8.9
LLDPE VII	98	39.2	38.5
LLDPE VIII	99	20.7	21.3

CONCLUSIONS

The SEC-FT-IR technique is extremely well suited to measure the chemical composition of polymers as a function of molar mass. In LLDPE copolymers, as an example, the octene, hexene, butene or propene distribution is measured. Differentiation between Ziegler type and metallocene type catalysts is possible.

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