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Monitoring the chemical heterogeneity of metallocene-catalysed copolymers of ethylene and higher 1-olefins using CRYSTAF and SEC-FTIR

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Abstract: Copolymers of ethylene with 1-decene, 1-tetradecene and 1-octadecene were prepared using the catalyst system *rac*Et[Ind]$_2$ZrCl$_2$/MAO and were analysed with regard to chemical heterogeneity using crystallisation analysis fractionation (CRYSTAF), differential scanning calorimetry (DSC) and size exclusion chromatography coupled to FTIR (SEC-FTIR). The melting and crystallisation temperatures from DSC decrease linearly with increasing amount of comonomer, independently of the nature thereof. The decrease in crystallisation temperature from CRYSTAF of copolymers with higher 1-olefin content indicates a small dependence on the length of the side chain. The chemical heterogeneity of the copolymers as analysed by DSC and CRYSTAF broadens with increasing comonomer concentration.

Introduction

Many properties of a polymer are determined by the complicated interaction of molecular weight distribution, average chemical composition and chemical composition distribution. The average chemical composition can be determined by spectroscopic methods (e.g., IR and NMR) and the molecular weight distribution can be analysed for example by size exclusion chromatography. However, for a comprehensive understanding of the physico-mechanical properties of polymers it is necessary to consider the chemical heterogeneity. Also referred to as chemical composition distribution it is a fundamental parameter of any copolymer and one can distinguish between inter- and intramolecular (1st order and 2nd order) chemical heterogeneity. The former concept means that within one macromolecule the branches are not uniformly distributed along the molecular weight axis, while intermolecular heterogeneity implies that among different macromolecules the comonomer distribution is not uniform. The chemical heterogeneity of a copolymer can in principle be analysed by (molecular weight independent) fractionation according to composition (CRYSTAF or TREF) and the coupling of size exclusion chromatography with chemoselective detection (e.g., SEC-FTIR). It must be kept in mind that SEC-FTIR only yields an average chemical composition vs. the molecular weight distribution. CRYSTAF has been introduced into polymer fractionation in the 90s and separates polymers according to their composition [1-3]. From the Flory-Huggins theory, a linear relationship between the content of a comonomer and the crystallisation or melting temperature can be deduced for random copolymers following Eq. (1) [4,5].

$$T_m \cong T_m^o - \frac{R \cdot (T_m^o)^2}{\Delta H_u} \cdot X_{com} \tag{1}$$

T_m and T_m^o are the melting points of the copolymer and the homopolymer, respectively, ΔH_u is the heat of fusion per crystallised unit, and X_com is the fraction of comonomer incorporated. As a consequence the melting point depression is independent of the nature of the non-crystallisable comonomer provided that the latter cannot be incorporated into the crystal lattice. Monrabal proved the validity of this relationship for the crystallisation of ethylene/1-octene copolymers from solution and we previously showed a linear depression of the melting point for random copolymers of propene and higher linear 1-olefins [6-8]. The coupling of SEC and FTIR is a powerful technique for profiling the chemical composition along the molecular weight axis. It can be achieved by a flow cell or via the LC-transform interface. Despite the savings compared to conventional methods in both labour and time there are comparatively few applications of hyphenated SEC-FTIR to the analysis of polyolefins [9-13]. The copolymerisation of ethylene with higher 1-olefins using metallocene catalysts has been subject to extensive investigation and reviews on many aspects have been published [14-17]. Nevertheless, there is only limited information in the scientific literature about the chemical heterogeneity of the resulting copolymers. It is the aim of this study to investigate the copolymerisation of ethylene with higher 1-olefins with special focus on the chemical heterogeneity.

Results and discussion

Three series of copolymers of ethylene with 1-decene, 1-tetradecene and 1-octadecene were prepared with varying amounts of comonomer added (Tab. 1). As can be seen from Fig. 1, the peak crystallisation temperature of the copolymers, $T_\mathrm{c\,(CRYSTAF)}$, drops with increasing comonomer content. Interesting is the fact that simultaneously the compositional heterogeneity broadens. While for the samples with low comonomer content a relatively sharp crystallisation peak is observed, the curve for the samples with higher amounts shows tailing to lower crystallisation temperatures and flattens. This trend is independent of the chain length of the comonomer. It must be kept in mind that CRYSTAF cannot distinguish between inter- and intramolecular heterogeneity. The most probable explanation for the observed broadening is the compositional drift occurring in the reaction mixture during the copolymerisation. The copolymerisation parameters for the copolymerisation of ethylene and propene using *rac*Et[Ind]$_2$ZrCl$_2$/MAO (MAO: methylaluminoxane) are $r_\mathrm{1\,(ethylene)} = 2.57$ and $r_\mathrm{2\,(propene)} = 0.39$ [18,19]. These values indicate that ethylene is consumed at a higher rate than the comonomer. As a result of this, the ratio of comonomer/ethylene increases in the closed system during the reaction and the copolymer produced will be increasingly enriched in comonomer.

The samples were analysed using CRYSTAF. The traces for the copolymers containing 1-tetradecene and 1-octadecene are shown in Fig. 1. The same trend as observed for the CRYSTAF analysis is reflected in DSC (Fig. 2). With increasing comonomer content the melting and crystallisation temperatures drop as expected according to Eq. (1). Simultaneously, the crystallisation and melting peaks become flatter, the effect being more pronounced for the melt transition. These observations have been reported for ethylene/1-butene copolymers by Mathot et al. [20,21]

Tab. 1. Comonomer content in the feed stream and molecular characteristics of the produced copolymers

Sample code	Comonomer content in mol-%		$T_{c\ (CRYSTAF)}$ in °C	$T_{m\ (DSC)}$ in °C	$T_{c\ (DSC)}$ in °C	M_n	M_w / M_n
	in the feed	in polymer					
Polyethylene							
PE	0	0	86.3	134.5	115.6	54000	2.1
1-Decene							
ED1	1.66	0.57	84.5	130.0	113.2	35000	4.5
ED2	5.43	1.05	81.4	124.8	111.2	28000	6.3
ED3	9.89	1.79	78.8	121.3	107.9	31000	3.1
ED4	11.42	2.83	73.4	117.0	101.7	71000	1.8
ED5	17.47	3.57	72.5	116.5	96.4	70800	1.9
1-Tetradecene							
ET1	8.39	2.00	79.1	121.8	107.7	31000	2.2
ET2	5.25	2.05	81.9	123.5	109.4	58000	2.1
ET3	9.27	2.23	78.8	121.3	106.2	64000	1.9
ET4	14.04	2.83	73.2	117.5	102.5	54000	1.9
ET5	16.24	3.27	72.4	116.8	101.5	44000	2.2
ET6	18.38	4.56	62.8	110.3	92.6	59000	2.0
ET7	23.74	5.86	57.0	107.2	87.9	77000	1.7
1-Octadecene							
EO1	3.34	1.43	78.8	125.5	108.5	53000	2.1
EO2	6.94	1,50	76.5	125.5	89.0	48000	2,8
EO3	10.00	1.66	76.5	124.1	105.0	65000	2.2
EO4	6.99	1.77	78.9	121.8	105.7	87000	1.9
EO5	11.82	2.33	65.8	117.0	101.4	67000	1.8
EO6	16.56	3.55	63.7	111.5	101.4	80000	1.7
EO7	24.74	4.03	59.8	109.3	91.0	77000	1.8

It has been demonstrated previously using a Ziegler Natta based sample that the results from CRYSTAF and DSC agree well in a qualitative way [22]. This is confirmed by the overlay of the CRYSTAF and DSC curves by shifting along the temperature axis for an ethylene/1-octadecene copolymer (Fig 3).

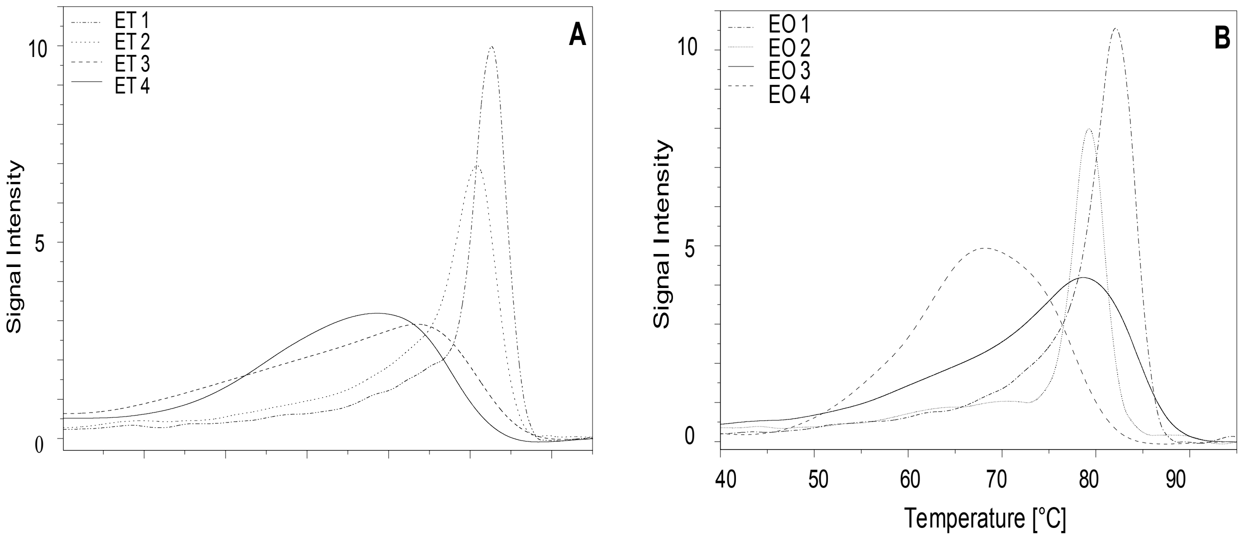

Fig. 1. CRYSTAF curves of ethylene/1-tetradecene (A) and ethylene/1-octadecene (B) copolymer samples with varying amounts of comonomer

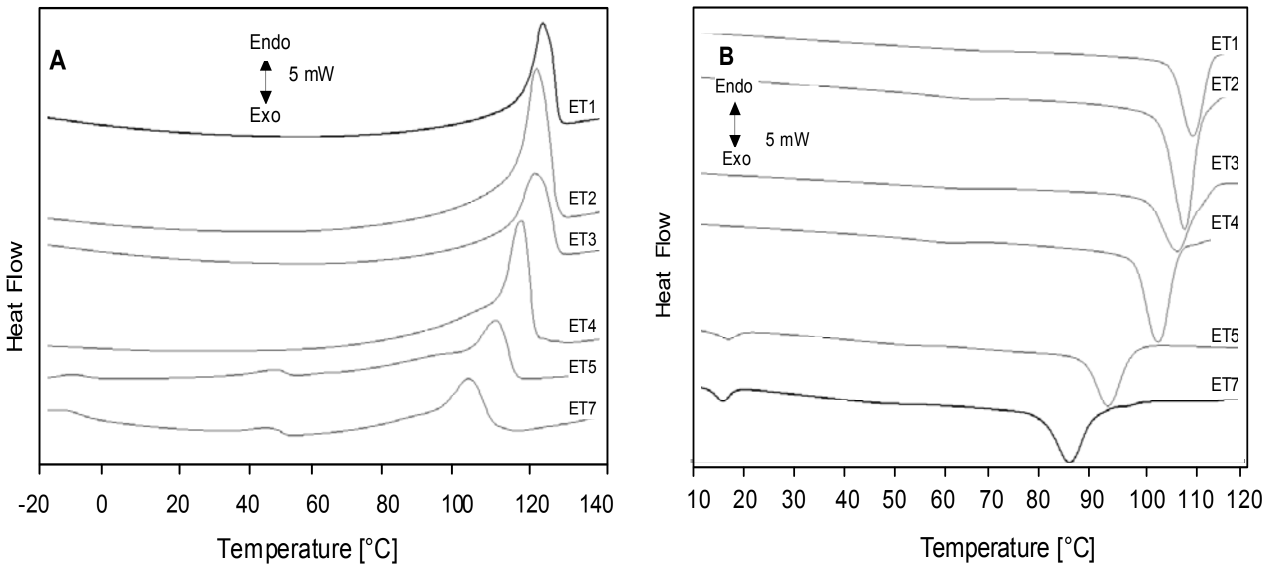

Fig. 2. DSC heating (A) curves (2nd heating cycle, heating rate 10°C/min) and cooling (B) curves (cooling rate 10°C/min) of ethylene/1-tetradecene copolymer samples with varying 1-tetradecene content (increasing from top to bottom)

Plotting the melting temperature, the crystallisation temperature recorded by DSC and the crystallisation temperature recorded by CRYSTAF against the amount of comonomer for the three series in a common figure leads to three parallel lines. The results for three series of copolymers of ethylene/1-olefins (1-decene, 1-tetradecene and 1-octadecene) synthesized in this study are shown in Fig. 4.

At a constant cooling rate the peak melting and crystallisation temperatures from DSC solely depend on the amount of comonomer and are independent of the nature thereof. Furthermore, the amount of comonomer has an equally depressant effect on the melting and crystallisation temperature from DSC. In an analogue way the crystallisation from solution can be approximated by a straight-line relationship. A close comparison of the three curves reveals that the slope of the CRYSTAF curve is somewhat steeper than for values from DSC. The reason is that the copolymers containing 1-octadecene display a stronger depression of the crystallisation temperature. The same phenomenon is found again when superposing the melting temperature, $T_{m\ (DSC)}$, and the crystallisation temperature, $T_{c\ (CRYSTAF)}$. This is shown in Fig. 5 by cancelling the temperature difference from supercooling through the solvent for the polyethylene sample, thereby aligning the temperature points of the polyethylene as measured by CRYSTAF and DSC on top of each other.

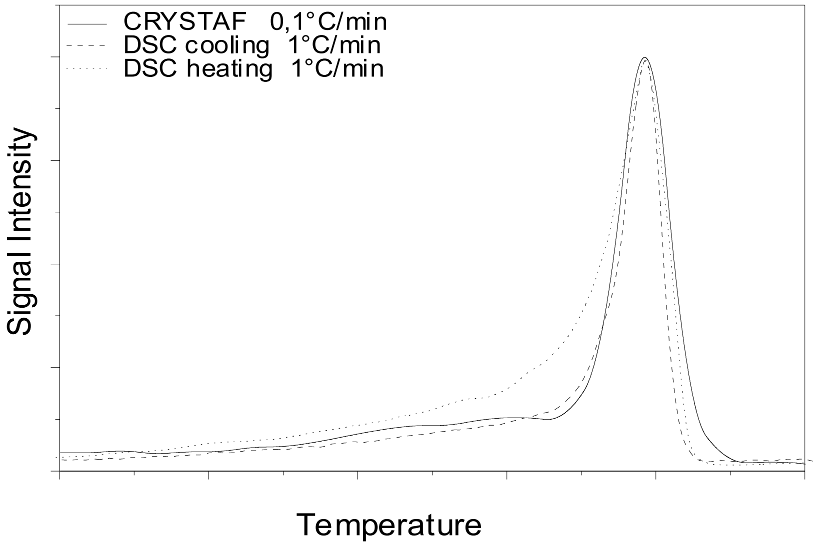

Fig. 3. Superposition of the cooling and heating curves from CRYSTAF and DSC for ethylene/1-octadecene sample EO2

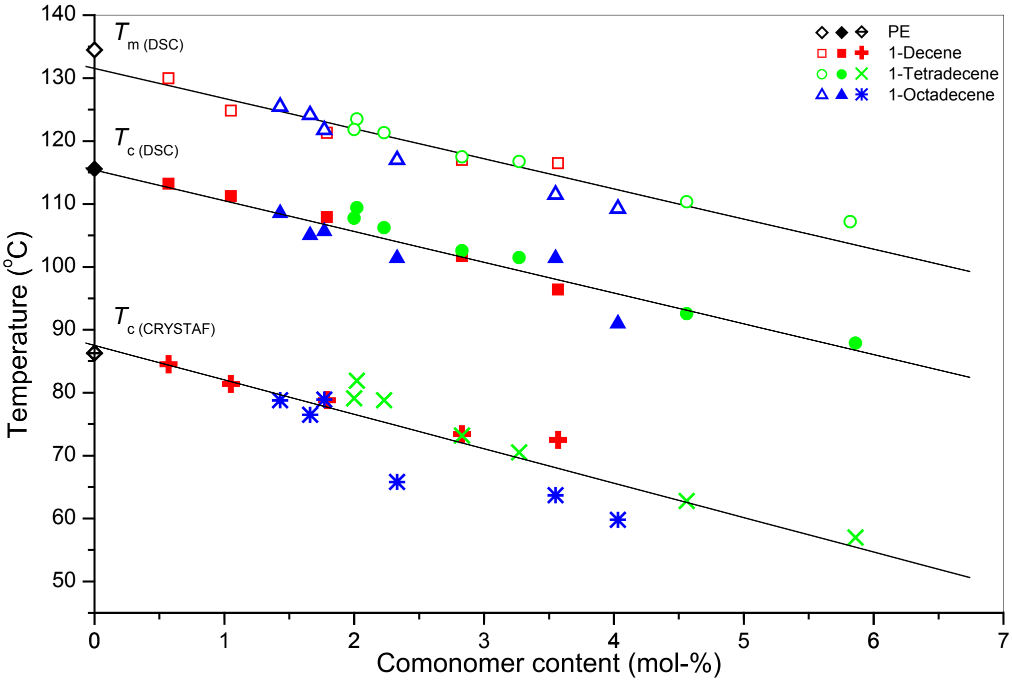

Fig. 4. Crystallisation (from DSC and CRYSTAF) and melting temperatures from DSC for copolymers of ethylene and 1-olefins as a function of the comonomer content

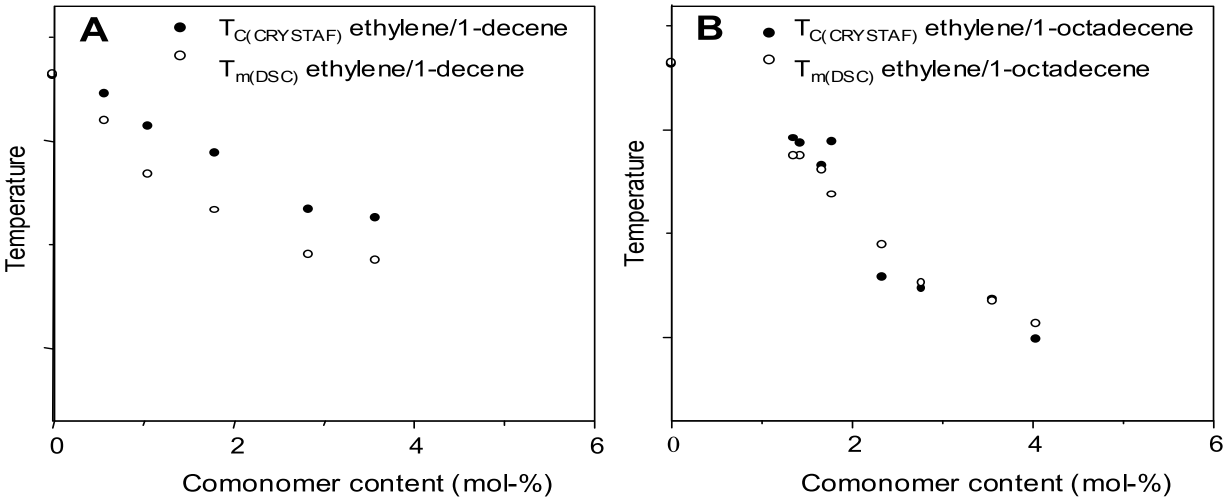

Fig. 5. Superposition of $T_{c\ (CRYSTAF)}$ and $T_{m\ (DSC)}$ for copolymers of ethylene with 1-decene (A) and 1-octadecene (B) as a function of the comonomer content

As seen in Fig. 5 the difference between both temperatures decreases as the length of the side chain is increased from 8 to 16 carbon atoms. A similar observation has been reported by us for syndiotactic copolymers of propene and higher 1-olefins [7]. It has been known that side chain crystallisation is likely to occur from melt for poly(1-olefin)s containing branches with a larger number of methylene units [23,24]. As a result it can be speculated that interaction between the side chains prevents the crystallisable sequences of the main chain from crystallisation and thus leads to an additional depression of the crystallisation temperature. In order to investigate the distribution of the comonomer along the molecular weight axis the copolymers were analysed by coupled SEC-FTIR using the LC-transform technique (Fig. 6).

Fig. 6a shows the so-called Gram Schmidt plot and the chemigrams. (These are - for reasons of clarity - not shown in Fig. 6b-e.) The Gram Schmidt plot is a sum over all absorptions and corresponds with the sample concentration. Chemigrams can be generated to show the intensity of a particular absorption along the molecular weight axis. The bands centred around 1379 cm^{-1} (CH_3) and 1460 cm^{-1} (CH_2) can be used for a quantitative determination of the composition [25]. While the concentration of CH_3 reflects the comonomer concentration, the concentration of CH_2 is equivalent to the total concentration. The quotient of the chemigrams at 1379 cm^{-1} and 1460 cm^{-1} reflects then the ratio of methyl groups to methylene groups. Particularly interesting is the fact that in all samples the methyl groups are not homogeneously distributed, which means that intermolecular inhomogeneity occurs (Fig. 6). Although an exact quantification of the methyl concentration is affected by the reproducibility of the deposition on the germanium carrier, a slightly increased accumulation of the comonomer to the high end of the molecular weight distribution can be observed. Metallocene catalysts are claimed to produce copolymers with a narrow chemical composition distribution. However, intermolecular compositional inhomogeneity of metallocene-made ethylene copolymers has been found recently. Hsie et al. used cross fractionation which combines a solvent gradient fractionation and a temperature gradient fractionation step and found inhomogeneity of the comonomer distribution in Zr-based ethylene/1-hexene copolymers [26]. Fu et al. proved the occurrence of intermolecular heterogeneity for metallocene-made ethylene/1-hexene samples by multiple step isothermal crystallisation experiments [27].

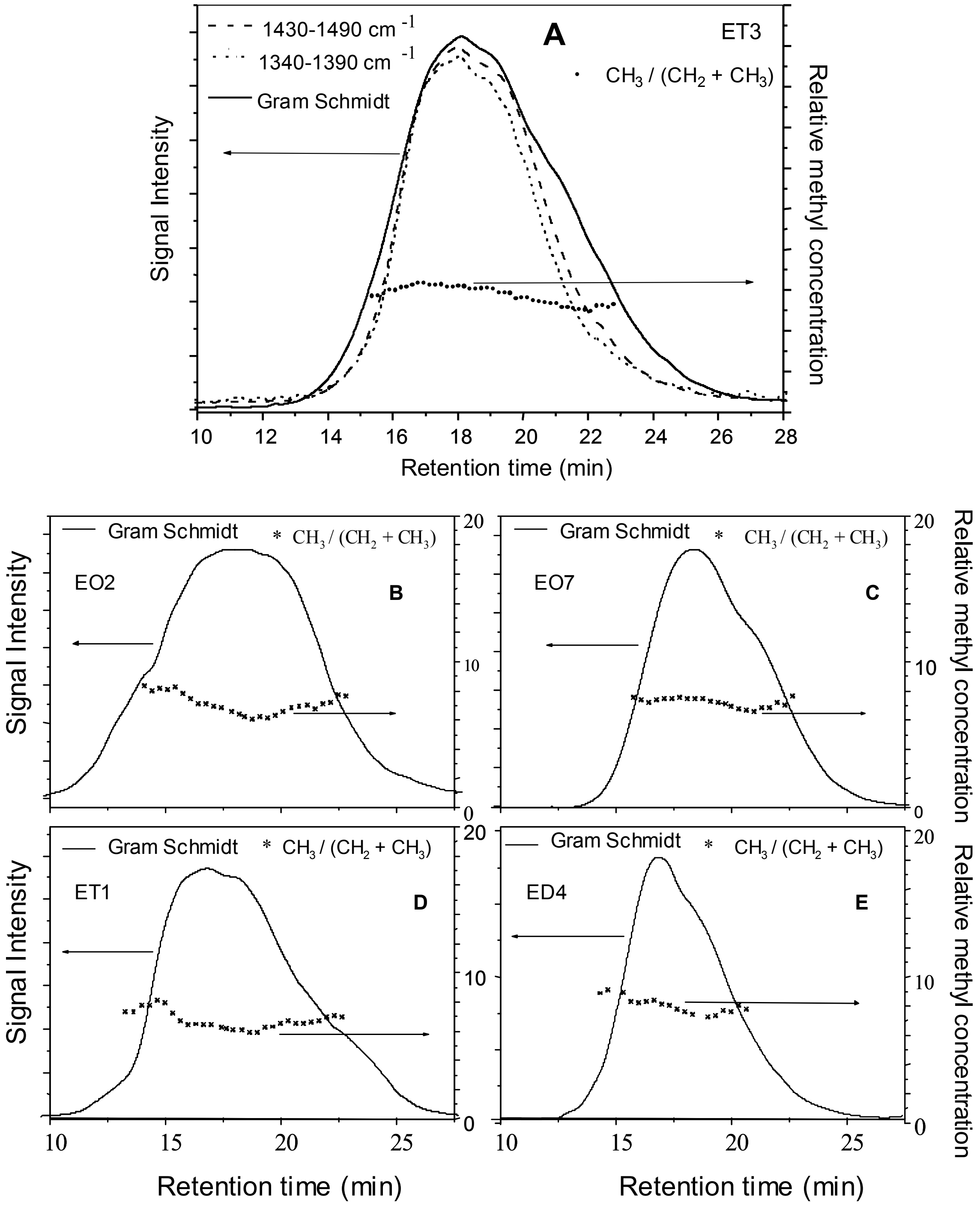

Fig. 6. SEC-FTIR analysis of copolymers of ethylene with 1-decene (a), 1-tetradecene (d, e) and 1-octadecene (b, c)

Conclusion

It can be concluded that both techniques, CRYSTAF and hyphenated SEC-FTIR, are necessary to analyse the chemical heterogeneity of ethylene copolymers. CRYSTAF is particularly suitable to reveal the compositional heterogeneity of materials which are formed under compositional drift in the reaction mixture.

Experimental part

Polymer synthesis

All experiments were performed under inert gas atmosphere. Copolymerisation experiments were carried out in batch mode using a 350 ml stainless steel autoclave at room temperature and a reaction time of 2 h. The reactor was equipped with a glass inlet and a magnetic stirrer. The catalyst, *rac*Et[Ind]$_2$ZrCl$_2$, was obtained from Sigma Aldrich. Ethylene was supplied by Fedgas and used as received. The 1-olefins were purchased from Sigma Aldrich and distilled from calcium hydride prior to use. Reaction conditions: [Zr] / [Al] = 1 : 6000; $T = 25°C$; $p_{\text{ethylene}} = 30$ bar.

Polymer characterisation

The comonomer content of the copolymers was calculated from ^{13}C NMR spectroscopy measured in 1,2,4-trichlorobenzene/C_6D_6 (9:1) at 100°C at 75.42 MHz on a Varian VXR-300 NMR spectrometer. The molar masses of the polymers were determined using a Waters 150C chromatograph at 140°C with Waters Styragel columns (HT 2 - 6). The solvent used was 1,2,4-trichlorobenzene at a flow rate of 1 ml/min. The thermal properties were determined with a Pyris 1 differential scanning calorimeter from Perkin Elmer. 5 mg of the polymer were used. Two heating and one cooling cycles were performed at a cooling and heating rate of 1°C/min. A CRYSTAF model 200 from Polymer Char S.A. (Valencia, Spain) was used for fractionation. 20 mg of the sample were dissolved in 30 ml 1,2,4-trichlorobenzene. The temperature gradient was 0.1°C/min. An LC-transform Model 300 from LabConnections coupled to a Waters 150C chromatograph was used for the SEC-FTIR analysis. The stage temperature was 160°C, the temperature of the nozzle was 125°C and the transfer line 150°C. The rotating speed of the germanium disc was 10°/min.

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