



Study of the abnormal late co-elution phenomenon of low density polyethylene in size exclusion chromatography using high temperature size exclusion chromatography and high temperature asymmetrical flow field-flow fractionation

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ABSTRACT

The elution behaviour of linear and branched polyethylene samples in SEC was studied. For the branched samples an abnormal late co-elution of large and small macromolecules manifests itself as an abnormal re-increase of the molar mass and the radius of gyration values detected with multi angle light scattering at high elution volumes in SEC. The late co-elution of small and large macromolecules cannot be explained by the SEC mechanism alone. The influence of several experimental parameters on the late co-elution was studied. It was found that the type of SEC column and the flow rate have a significant influence. The late eluting part of the sample was fractionated and separated by HT-SEC- and HT-AF4-MALS. The different results of both methods have been discussed with the aim to find possible explanations for the late elution. The experiments indicate that especially large branched structures show an increased tendency for the phenomenon.

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1. Introduction

The molecular structure is excessively important for the application of polymer materials. Parameters like the degree of branching or the molar mass and their distribution, strongly influence the processability and morphology especially in the case of polyolefin materials [1–5]. For this reason, knowledge of the molecular parameters is essential for product development and quality control [6,7]. Currently, the most common way to analyze linear and branched polyolefins is the application of the high temperature size exclusion chromatography (HT-SEC) [8–15]. This analytical technique is based on the entropy-controlled separation of the polymer molecules according to their hydrodynamics volumes. This leads to an elution of nearly monodisperse molar mass fractions of polydisperse polymers in ideal case [16]. In combination with a multi-angle light scattering detector (MALS) the molar mass and the radius of gyration are accessible. In combination with a concentration detec-

tor, the molar mass distribution and the amount of long chain branching can be calculated [17,18]. An important requirement for a correct analysis is a continuous separation according to the entropy-controlled SEC mechanism and the absence of interactions between the molecules and the stationary phase. Unfortunately, the SEC separation is often disturbed for branched polymers with high molar mass and these macromolecules may co-elute through a SEC analysis together with small molecules. This leads to observation of an abnormal increase of the molar mass and radius of gyration at high elution volumes. This effect was described by several groups [16,19–27]. The phenomenon blocks the correct evaluation of the MMD as well as branching analysis. The following explanations were mostly proposed for the abnormal behaviour: partial entanglement in the porous packing for large macromolecules, limited diffusion of large chains in and out of the SEC pores, sieving in the inter-particle volume, adsorption, presence of small gel particles, molecular topology fractionation or the partial separation according to slalom chromatography.

In this study the late elution effect was investigated using LDPE samples. The influence of different SEC parameters on this effect was proved. New technologies like high temperature asymmetrical flow field-flow fractionation (HT-AF4) and coupling between HT-

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Table 1
Specific values of SEC columns used for separation of the PE-samples.

Column type	Packing material	Particle size (μm)	Dimensions (mm)	Average pore size (\AA) ^a
PL mixed B	Cross linked SDV	10	7.5 × 360	Mixed bed
PL Olexis	Cross linked SDV	13		Mixed bed
PSS 1	Cross linked SDV	20		1×10^7
PSS 2	Cross linked SDV	20		1×10^5
PSS 3	Cross linked SDV	20		1×10^3
MN 1	Porous silica	10		3×10^2
MN 2	Porous silica	7		1×10^3

^a Equivalent-length of a PS molecule.

SEC and HT-AF4 were used to get more detailed information about the influence of the chain-structure and the molar masses on the phenomenon.

2. Experimental

2.1. Instrumentation

A PL GPC 220 chromatograph from Polymer Laboratories (Church Stretton, England) was used as a platform for the AF2000 HT-AF4 system from Postnova Analytics. This system allows to perform either HT-SEC or HT-AF4 separations of polyolefins at a temperature of 145 °C in 1,2,4-trichlorobenzene (TCB). The connection between the flow paths was realized by three six-port valves from Valco Instruments (Waterbury, USA). For the most SEC separations two PL mixed B and two PL Olexis SDV-columns were used. In addition, different SDV columns from Polymer Standard Service (PSS, Mainz, Germany) and Silica columns from Macherey-Nagel (Düren, Germany) were used with regard to their influence on the late co-elution effect. The specific values of the columns are given in Table 1.

The PL mixed B or PL Olexis columns have been applied for the HT-SEC separations because these columns are very frequently used for standard analysis of polyolefins in many laboratories all over the world. The broad size range, the linearity of the calibration curves and the good filtration, which leads to low noise in the light scattering signal, may be the reasons for it. The lower particle size of approximately 10–13 μm compared e.g. to mixed A columns may lead to pronounced shear stress which is also a source of error in addition to the late elution phenomenon. The columns were chosen for comparison of SEC and FFF with the aim to show the real extent of error which can be produced during a routine SEC-MALS analysis.

A HT-AF4 channel obtained from Postnova Analytics was used for the HT-AF4 measurements. The channel has the outer dimensions of 295 × 30 × 60 mm and the internal channel cavity was 275 mm in length with a 350 μm thickness. The channel contains an integrated inert membrane with a nominal pore size of approximately 10 nm. The detection was realized with a HT-MALS Heleos II (Wyatt, Santa Barbara, USA) and with an infrared detector, model IR4, from Polymer Char (Valencia, Spain). The HT-IR4 detector was used for concentration detection. If it is not specially mentioned, the samples were analyzed with a detector flow rate of 0.5 mL/min in SEC and AF4 mode.

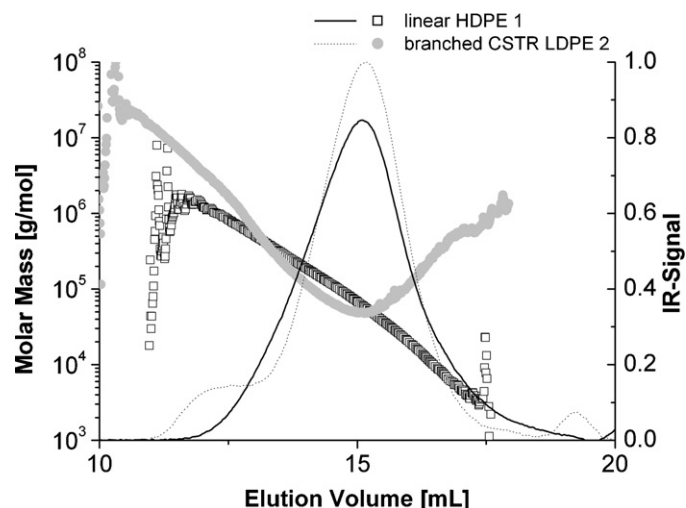


Fig. 1. Elugram of the mostly linear sample HDPE 1 and the branched sample CSTR-LDPE 2 obtained after SEC separation using two PL mixed B columns. The corresponding molar masses were calculated using MALS + IR detection.

2.2. Materials and methods

The HDPE samples 1 and 2 have been obtained from Dow Chemical Company (Terneuzen, Netherlands). The sample HDPE 1 was synthesized by Ziegler Polymerization and HDPE 2 was the reference material NIST NSRM 1496, which contains mainly linear macromolecules. The sample CSTR LDPE 2 is highly branched and was produced by free radical polymerization in a continuously stirred tank reactor (CSTR) under high pressure of approximately 2000 bar and temperatures up to 245 °C. The details of synthesis and rheological data have been reported in Ref. [21].

The PE samples were dissolved for 4 h in 1,2,4-trichlorobenzene (TCB, obtained from Acros, Geel, Belgium) at 160 °C with a concentration of 2 mg/mL. The TCB was stabilized with 1 mg butylated-hydroxytoluene (BHT, obtained from Merck, Hohenbrunn, Germany) per 1 mL of TCB to avoid thermal-oxidative degradation during sample preparation and analysis. In addition, the solvent was flushed with argon gas. No shaking or stirring was applied on the sample to ensure the absence of shear forces in the concentrated polymer solution. A good homogenization was realized by gentle rotation of the vials with the polymer solution inside. The injection volume was 200 μL for all separations. The fractionation of sample LDPE 2 was done during the SEC separation process. The outlet of the columns was collected between an elution volume of 15 and 20 mL for 50 times. All solutions were merged and the polymer was precipitated by adding an excess of methanol (Merck, Hohenbrunn, Germany). After precipitation the solvent and precipitant were removed by filtration and the polymer was dried for 5 h at 50 °C. Prior re-injection the fractionated polymer was re-dissolved with the standard procedure described above. The mass and radius values were calculated from MALS-data using a second order Berry equation.

3. Results and discussion

The SEC elugram of a linear HDPE and a branched LDPE is displayed in Fig. 1.

The molar mass of HDPE 1 is continuously decreasing with the elution volume. For the LDPE sample the course of the molar mass runs comparably until an elution volume of approximately 14 mL is reached. At this point values of the molar mass start to increase. This effect is well known for branched polymers of different nature [16,19–27]. A typical explanation for this behaviour, which was

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