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Short Communication: Analysis Method

Polyolefin characterization in dibutoxymethane by high temperature gel permeation chromatography with a new evaporative light scattering detector

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ABSTRACT

A new evaporative light scattering detector (ELSD) for the analysis of polyolefins by high temperature gel permeation chromatography (GPC) was recently introduced by Agilent Technologies. For the first time, we investigated the possibility to use this detector to measure the molecular weight distributions (MWD) of different types of polyolefins (polypropylene, linear and low-density polyethylene) in dibutoxymethane (DBM, butylal). These samples were previously characterized by GPC in trichlorobenzene (TCB) with a differential refractive index (DRI) detector in an interlaboratory study conducted by the International Union of Pure and Applied Chemistry (IUPAC) [1], and in a recent publication by GPC with the new ELSD in TCB [2]. The signal to noise of ELSD using DBM is about 10 times lower than that for TCB. However, the ELSD signal power exponent for DBM was measured as 1.35, which is much closer to unity than the value of 1.61 for TCB. After applying the required corrections to linearize the response of the ELSD signal as a function of concentration, similar average molecular weights to those measured in the interlaboratory study using DRI, were obtained for the analyzed resins.

1. Introduction

This study is a combination of two projects: the first one aims to evaluate non-hazardous solvents for the gel permeation chromatography (GPC) analysis of polyolefins, and the second one to evaluate the possibility of using the recently introduced high temperature evaporative light scattering detector (ELSD) by Agilent Technologies to accurately evaluate the molecular weight distribution (MWD) of polymers.

In our previous papers [3–6] we presented dibutoxymethane (DBM, butylal) as an alternative, less toxic solvent, for the GPC analysis of polypropylenes and linear and branched polyethylenes, with a differential refractive index (DRI) detector.

In our parallel project on ELSD applications [2,7], we showed that recent advances in nebulizer technology of the ELSD allow the evaporation of trichlorobenzene (TCB), at much lower temperatures than previous instruments, thus avoiding the sample loss in the lower molecular weight region. Therefore, the new ELSD opens the possibility to correctly evaluate the MWD of polymers by GPC, after linearizing the ELSD signal intensity as a function of concentration, based on a power law function:

$$\textit{ELSD signal intensity} = k_{ELSD} * \textit{concentration}^{a_{ELSD}}$$

In order to find the exponent parameter governing the non-linearity of the ELSD signal, we developed a new method which takes into account, not only the peak area, but each point of the ELSD chromatogram [7]. This exponent parameter was found to be 1.61 for the analysis in TCB of polyolefin and polystyrene samples.

In this study, we evaluate the suitability of a high temperature GPC with an ELSD method performed in DBM, by comparing the previously measured average molecular weights in TCB of different resins, covering typical applications of polyolefins, with those measured in DBM using an ELSD.

2. Experimental

2.1. Solvent

1,1'-[methylenebis (oxy)]dibutane (dibutoxymethane, DBM, butylal ultra-pure grade, Lambiotte & Cie, Belgium, CAS 2568-90-3, refractive index of 1.405).

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2.2. Samples

Six polyolefins samples: polypropylene homopolymer (PP), impact propylene-ethylene copolymer (PP_PE), linear low density polyethylene with 1-butene as comonomer (LLDPE_C4), linear low density polyethylene with 1-hexene as comonomer (LLDPE_C6), low density polyethylene (LDPE_1) and low density polyethylene with a broad distribution (LDPE_2), for which the MWD were previously reported [1,2], were analyzed by high temperature GPC with ELSD. The column calibration was done with EasiVials from Agilent Technologies as described in Ref. [2]. A narrow polystyrene standard (PS 135k, $M_w = 135000$ g/mol, $Đ_M = 1.02$, Agilent Technologies, UK) was used to evaluate the ELSD signal power exponent for DBM.

2.3. GPC apparatus and method

All GPC data were recorded using an Agilent PL-GPC 220 High Temperature GPC System equipped with light scattering (LS) and ELSD. The samples were dissolved to obtain concentrations of 1 mg/mL in DBM at 160 °C using the procedure detailed in our previous paper in order to avoid the polymer degradation [8]. The injection volume was 200 μL and the chromatographic separation was performed using 2 PLgel 10 μm Mixed-B (300 × 7.5 mm) columns at a flow rate of 1 mL/min and a temperature of 160 °C.

Due to the fact that DBM has a lower boiling point compared to TCB, the ELSD parameters for DBM were set at the following values:

- Transfer line temperature: 160 °C
- Nebulizer gas flow: 0.6 SLM
- Nebulizer temperature: 110 °C
- Evaporator temperature: 110 °C

During the preliminary tests with the ELSD using DBM we found a higher noise than the one measured with TCB, therefore the LED power was reduced to 5%.

Agilent GPC software (v1.2) was used to calculate the MWD using the uncorrected ELSD traces and to export the ELSD chromatograms as Excel files. These chromatograms were corrected for non-linearity using Excel templates.

3. Results and discussion

In order to accurately evaluate the power exponent, a_{ELSD}, GPC analyses were perfomed on PS 135k using the ELSD and the light scattering detector in series. The chromatograms obtained for different injected concentrations of the PS 135k standard are shown in Fig. 1. For a particular compound, the peak area of the LS chromatogram is a linear function of the injected concentration. This linearity, presented in Fig. 2, was used to verify the accuracy of the injected concentration values. Excellent linear correlation through zero was obtained between the LS peak area and the injected concentration, with R-squared of 0.9996. The slope of the plot in DBM is about 16 times higher than in TCB [7], thus confirming our previous results [3–6] that the dn/dc of polystyrene in DBM is about 4 times higher than in TCB.

Once the values of the injected concentrations were verified, Excel templates were prepared to evaluate the peak area of the corrected ELSD signal, performing the following operations:

- For each point of the ELSD chromatogram the following correction was applied:

$$\text{corrected ELSD} = (\text{ELSD}_{\text{signal}} - \text{BASELINE})\hat{}(1/a_{\text{ELSD}})$$

- For each corrected chromatogram, the peak area was calculated based on the peak start and end retention times.

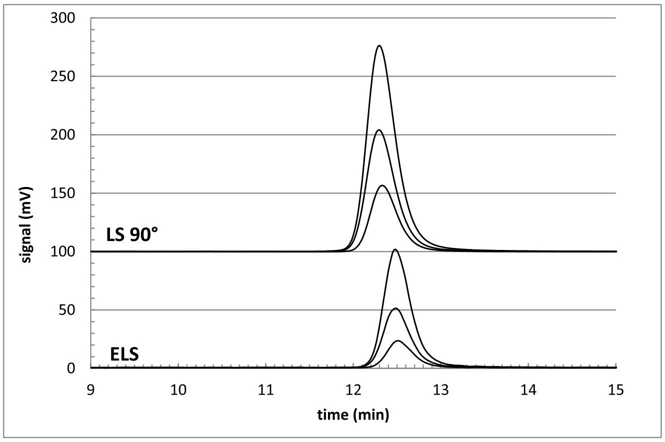

Fig. 1. Overlay of GPC chromatograms obtained with evaporative light scattering (ELS) and light scattering (LS90°) detectors for solutions of PS 135k having the following concentrations in DBM: 0.15, 0.30, and 0.50 mg/mL.

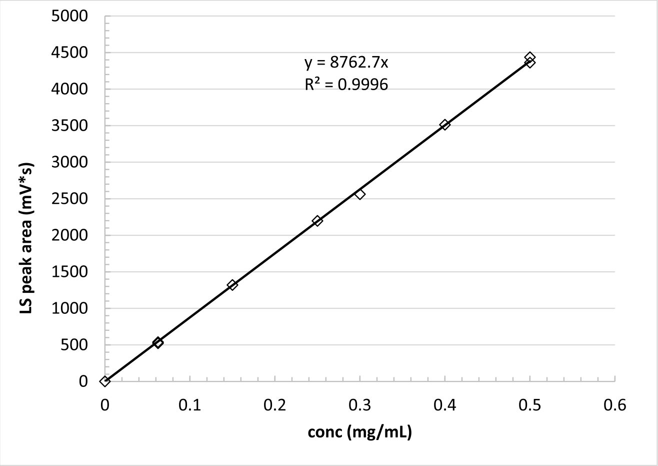

Fig. 2. Linear correlation of the light scattering (LS 90°) peak areas in function of the injected concentrations of PS 135k in DBM.

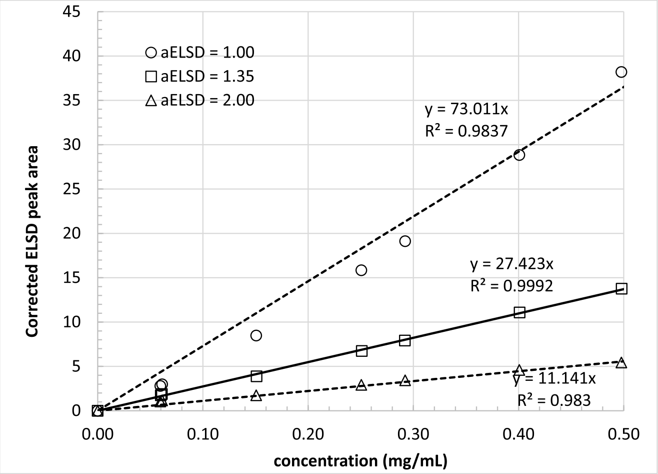

Fig. 3. Correlations of the evaporative light scattering (ELS) peak areas in function of the injected concentrations of PS 135k, for different values of a_{ELSD}.

The correlation between the ELSD peak area and the concentration depends on the selected a_{ELSD} parameter, as presented in Fig. 3. Obviously, the ELSD signal is not a linear function of the concentration, the correlation for $a_{ELSD} = 1$ having a low R-squared of 0.9837. By increasing the a_{ELSD} value, the correlations improve, the R-squared