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ORIGINAL

Characterization of Low-Density Polyethylene in Dibutoxymethane by High-Temperature Gel Permeation Chromatography with Triple Detection

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Abstract The study presents the possibility to replace the 1,2,4-trichlorobenzene (TCB) for the analysis by gel permeation chromatography (GPC) of low-density polyethylenes (LDPE) with dibutoxymethane (DBM, butylal), a halogen free and less toxic solvent. The molecular weight distributions and the viscosity plots were measured for commercial LDPE samples solubilized in TCB, and DBM, using a GPC system with triple detection (light scattering, differential refractive index and viscometer). Similar results were obtained in both solvents for the molecular weight and long chain branching distributions of the analyzed resins, thus confirming the possibility to replace TCB with DBM for the analysis by high-temperature GPC of all types of polyolefins.

Keywords 3D-GPC · REACH · Dibutoxymethane · LDPE · Long chain branching (LCB)

Introduction

Gel permeation chromatography (GPC) has become the analytical method of choice over the past 30 years to evaluate the molecular weight distribution (MWD) of soluble polymers. For polyolefins, the ASTM D 6474 [1] recommends 1,2,4-trichlorobenzene (TCB) as chromatographic solvent due to its rather high boiling temperature (214 °C) allowing the solubility of these resins. Other advantages of using TCB are the relatively high d*n*/d*c* of dissolved polyolefins and good swelling of polystyrene-divinylbenzene packing of GPC columns.

Unfortunately, TCB has a quite high toxicity, causes skin irritation, and is labeled as very toxic to aquatic life with long lasting effects. For these concerns on the risks posed on human health and environment, REACH listed TCB in the Appendix XVII [2] regarding the restrictions on the manufacture, placing on the market and use of certain dangerous substances.

In our previous papers [3–5] we presented dibutoxymethane (DBM, butylal) as a possible alternative less toxic solvent for the analysis of linear polyethylenes (PE) and polypropylenes (PP) by GPC and by analytical temperature rising elution fractionation (ATREF). Essentially, we showed that for linear polyolefins the GPC peaks obtained in DBM with the differential refractive index detector have similar shapes and retention times as those obtained in TCB. When supplementary online detectors as viscometer and light scattering are available, the triple detection GPC in DBM provided accurate molecular weight values, without the necessity of performing a column calibration with polystyrene standards.

However, all investigated polyolefins were obtained with Ziegler–Natta or metallocene catalysts, which essentially yield resins with linear structures. On the other hand, the

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low-density polyethylene (LDPE) is obtained by radical polymerization and has a complex structure containing long and short chain branches. Based on the classical theory of Zimm and Stockmayer [6] on the dimensions of chains with branches and rings, Mirabella and Wild [7] clearly presented the practical method to evaluate the long chain branching (LCB) distribution by simultaneously measuring the concentration and the intrinsic viscosity of GPC eluting species. This method was implemented by the major providers of commercial high-temperature GPC instruments.

For these reasons, it was natural to unite our efforts, presented in this work, to evaluate the possibility to extend the applications of the triple detection GPC in DBM to commercial LDPE samples.

Experimental

Solvents

1,2,4-Trichlorobenzene (TCB Spectropure dry, Biosolve, Netherlands, CAS 120-82-1, refractive index of 1.571) and 1,1′-[methylenebis(oxy)]dibutane (dibutoxymethane, DBM, butylal ultra-pure grade, Lambiotte & Cie, Belgium, CAS 2568-90-3, refractive index of 1.405) were used for GPC analyses.

Samples

For this study we selected three commercial low-density polyethylenes (LDPE1, LDPE2, LDPE3) with melt flow rates (MFR) between 0.3 and 2.0 g/10 min and densities of 0.922–0.925 g cm^{-3}, which are commonly employed for blown film applications. The instrument calibration was done with a polystyrene PS 135k standard (Agilent Technologies) having a peak molecular weight of 135 kg mol^{-1} and a molar dispersity of 1.02. The column calibration was done in TCB with the commercially available Easivial PS-H (Red, Yellow and Green, Agilent Technologies), covering molecular weights from 162 to 6,870,000 g mol^{-1}. The long chain branching was calculated using as linear PE reference the HDPE SRM 1475a (denoted NIST 1475, molecular weight 52 kg mol^{-1}, molar dispersity 2.9, National Institute of Standards and Technology).

GPC Apparatus and Method

All GPC data were recorded using an Agilent PL-GPC 220 High-Temperature GPC System equipped with light scattering (LS), differential refractive index (DRI) and viscometer (VS) detectors. The PE samples were dissolved to obtain concentrations of 2 mg mL^{-1} in TCB and DBM at 160 °C. The injection volume was 200 μL and the chromatographic separation was performed using 3 PLgel 10 μm Mixed-B (300 × 7.5 mm) columns at a flow rate of 1 mL min^{-1} and a temperature of 160 °C. For the analysis of PE in TCB, due to its negative d*n*/d*c*, an inversed polarity of DRI detector was selected. Agilent GPC/SEC software (v2.1) was used for data interpretation. Apart from applying different offsets, all chromatograms are presented without smoothing or drift corrections.

Results and Discussion

Figures 1 and 2 show comparisons of raw chromatograms of two LDPE samples (LDPE1 and LDPE2), having the same MFR (0.3 g/10 min) but produced by different

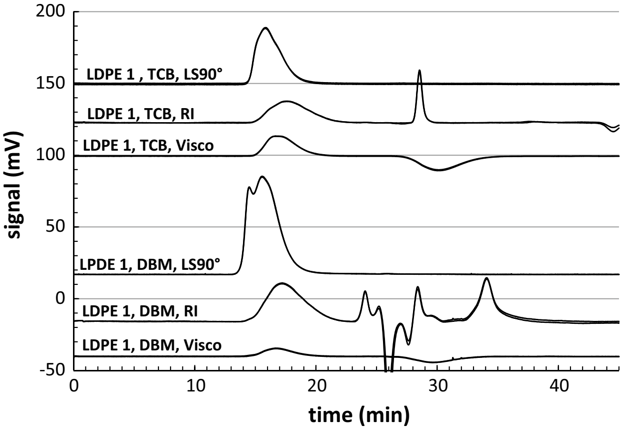

Fig. 1 Comparison of chromatograms obtained with light scattering, differential refractive index and viscometer detectors for solutions of LDPE 1 with the same concentration in TCB and DBM. Each chromatogram is an overlay of two injections

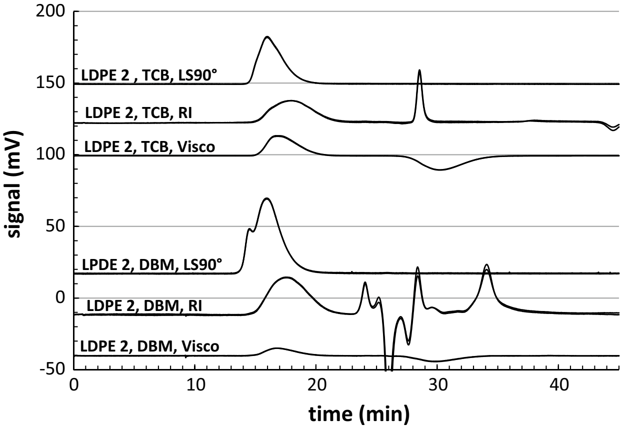

Fig. 2 Comparison of chromatograms obtained with light scattering, differential refractive index and viscometer detectors for solutions of LDPE 2 with the same concentration in TCB and DBM. Each chromatogram is an overlay of two injections

companies. These chromatograms were obtained with LS, DRI and VS on-line detectors in TCB and DBM, respectively. Several important observations are to be made:

- The overlays of chromatograms recorded for two separate injections show the excellent reproducibility achieved for both solvents, which is a powerful proof of the good quality and stability of the method (complete dissolution of samples, constant injection volume, no variation in the solvent composition, no degradation of the samples, etc.)
- For each sample, similar peak elution times are observed in TCB and in DBM. Therefore, for instruments having only a concentration detector, relative molecular weights can be measured based on a calibration with PS standards and Mark-Houwink constants in TCB provided by literature [1].
- For the same concentration, the peak intensities in LS and DRI detectors are higher in DBM than in TCB, because the dn/dc of LDPE is higher in DBM compared to TCB.
- Again for the same concentration, the peak intensities recorded by the viscometer are lower in DBM than in TCB. This is mainly because the intensity of the signal is proportional with the pressure generated in viscometer by the solvent viscosity, which in the case of DBM is about 50 % lower as compared to TCB.
- Although the two LDPE have the same MFR values, we observed important differences between the shapes of the LS peaks in DBM as compared with the LS peaks in TCB, showing only minor differences at low elution times. Apart from the obvious explanation based on a higher value of dn/dc in DBM as compared with TCB, we suspect that this difference in the LS traces is also produced by the lower viscosity of DBM, which at 160 °C is about half of the viscosity of TCB [4]. Essentially, a low-viscosity solvent will yield a lower shear of the polymer chains passing through the columns, and therefore a lower degradation of the high molecular chains. Therefore, using butylal, the high molecular fraction will arrive less damaged at LS detector, thus producing a first shoulder in the LS peak. Because the high molecular fraction is less damaged in butylal, this shoulder will have a higher intensity in DBM as compared with the one observed in TCB.

As a final point for this preliminary qualitative discussion, Fig. 3 shows a comparison of raw chromatograms of LDPE 2 (MFR 0.3 g/10 min) and LDPE 3 (MFR 2.0 g/10 min) obtained with LS, DRI and VS on-line detectors in DBM. A more important shoulder in the LS peak towards low elution times, corresponding to high molecular weights, is obtained for LDPE 2 as compared with LDPE 3, attesting that the GPC in DBM can discriminate between LDPE samples having different MFR values.

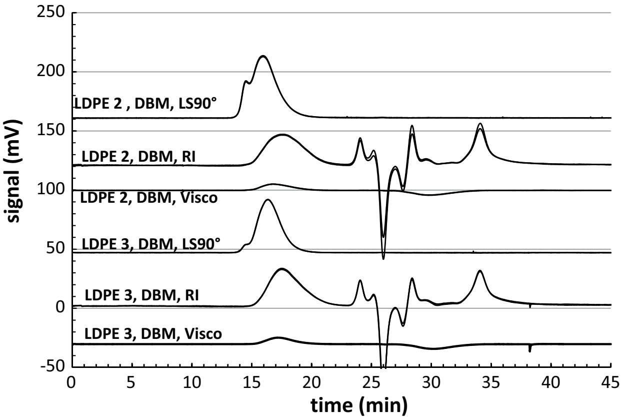

Fig. 3 Comparison of chromatograms obtained in DBM with light scattering, differential refractive index and viscometer detectors for LDPE 2 (MFI of 0.3 g/10 min) and LDPE 3 (MFI 2.0 g/10 min). Each chromatogram is an overlay of two injections

For these qualitative observations, in the following paragraphs we give quantitative relationships.

Conventional Calibration Using Only a Concentration Detector

The calibration curve was verified by analyzing the NIST 1475 reference. Its molecular weight distribution was calculated with the Mark-Houwink-Sakurada parameters provided for polyethylene and polystyrene by ASTM D 6474 [1].

As presented in Table 1, an excellent correlation with the reference values provided by NIST was obtained for the average molecular weights of NIST 1475 measured in TCB. For DBM, we confirm our previous studies in which higher average molecular weights were obtained than those measured in TCB [3, 4]. Therefore, applying the calibration and Mark-Houwink parameters evaluated in TCB for the chromatograms recorded in DBM gives biased molecular weights and can be used only for comparative studies. Nevertheless, the method for DBM can be easily corrected by slightly modifying the free term of the calibration curve to provide comparable results with those in TCB.

Table 1 Average molecular weights (g mol^{-1}) for NIST 1475 measured in TCB and DBM using conventional GPC method with ASTM D 6474 parameters, as compared with the values provided by NIST

	NIST	GPC in TCB	GPC in DBM
M_n	18310 ± 360	18,200	23,500
M_w	52000 ± 2000	54,000	70,700
M_z	138000 ± 3700	135,200	172,000

Table 2 Calculated average molecular weights (M_{n}, M_{w}) in g mol^{-1} and molar mass dispersity ($Đ_{\mathrm{M}}$) measured in TCB and DBM using conventional GPC method

Sample	TCB			DBM		
	M_{n}	M_{w}	$Đ_{\mathrm{M}}$	M_{n}	M_{w}	$Đ_{\mathrm{M}}$
LDPE 1 (1)	21,100	112,000	5.3	27,000	152,000	5.6
LDPE 1 (2)	19,400	111,900	5.8	27,900	150,700	5.4
LDPE 2 (1)	20,200	99,600	4.9	25,200	122,700	4.9
LDPE 2 (2)	19,900	97,700	4.9	26,300	122,200	4.6
LDPE 3 (1)	18,400	77,000	4.2	24,100	99,600	4.1
LDPE 3 (2)	18,800	77,300	4.1	24,900	98,800	4.0

Table 3 Calculated average molecular weights (M_{n}, M_{w}) in g mol^{-1} and molar mass dispersity ($Đ_{\mathrm{M}}$) measured in TCB and DBM using triple detection GPC method

Sample	TCB			DBM		
	M_{n}	M_{w}	$Đ_{\mathrm{M}}$	M_{n}	M_{w}	$Đ_{\mathrm{M}}$
NIST 1475	20,000	52,500	2.6	21,100	55,100	2.6
LDPE 1 (1)	27,800	179,800	6.5	29,800	187,300	6.3
LDPE 1 (2)	29,300	183,700	6.3	30,500	177,400	5.8
LDPE 2 (1)	27,200	151,600	5.6	27,100	148,900	5.5
LDPE 2 (2)	26,500	148,200	5.6	29,600	151,300	5.1
LDPE 3 (1)	21,800	116,300	5.3	23,400	117,500	5.0
LDPE 3 (2)	20,000	111,200	5.6	24,000	115,900	4.8

Although it is obvious that the parameters for linear PE from the ASTM D 6474 will not provide the accurate results for molecular weight distributions of LDPE, for laboratories having high-temperature GPC with only a concentration detector, we present in Table 2 a comparison of the average molecular weights evaluated in both solvents.

Similar tendencies are obtained in both solvents, the calculated average molecular weights in DBM being about 20–40 % higher than those measured in TCB. Therefore, applying the conventional method in DBM allows a direct comparison of the samples and could be helpful in solving problems related to polymer degradation or in assessing batch-to-batch differences for quality measurements.

Table 4 Mark Houwink Sakurada parameters of PE samples evaluated by triple detection GPC in TCB and DBM at 160 °C

Sample	K_{TCB} [(10^{-5}) dL/g]	α_{TCB}	K_{DBM} [(10^{-5}) dL/g]	$\alpha_{,\mathrm{DBM}}$
PE NIST 1475	45.7	0.71	63.1	0.64
LDPE 1 (1)	204	0.53	334	0.45
LDPE 1 (2)	201	0.53	265	0.47
LDPE 2 (1)	153	0.56	228	0.48
LDPE 2 (2)	155	0.56	234	0.48
LDPE 3 (1)	237	0.52	434	0.42
LDPE 3 (2)	245	0.52	376	0.43

Triple Detection Method

Although conventional GPC can be in many cases enough in providing the necessary data for relative comparison of the molecular weight distributions of the samples, by adding online LS and VS detectors it is possible to directly measure true molecular weights and to evaluate the long chain branching distributions. Details for instrument calibration by injecting a PS standard with a molecular weight between 100 and 200 kg mol^{-1} were given in our previous works [3–5].

A comparison between the calculated average molecular weights for the PE samples analyzed in TCB and DBM is given in Table 3. As in previous studies, a good agreement with the expected NIST values was obtained for the linear reference PE sample. Further, an excellent correlation was observed for average molecular weights obtained in TCB and the respective values in DBM (differences of ±10 %) for LDPE samples.

The triple detection procedure also allows measuring the viscosity, and hence the Mark-Houwink parameters for PE samples. The results are summarized in Table 4. For both solvents, a clear distinction is observed between the linear PE alpha values (0.71 in TCB and 0.64 in DBM), and the branched LDPE having much lower alpha values (between 0.51 and 0.56 in TCB, and between 0.42 and 0.48 in DBM).

Finally, based on the classical theory of Zimm and Stockmayer [6], it is possible to estimate the number of long chain branches in function of molecular weight for LDPE samples. The obtained LCB distributions (number of long branches corresponding to 1000C in function of

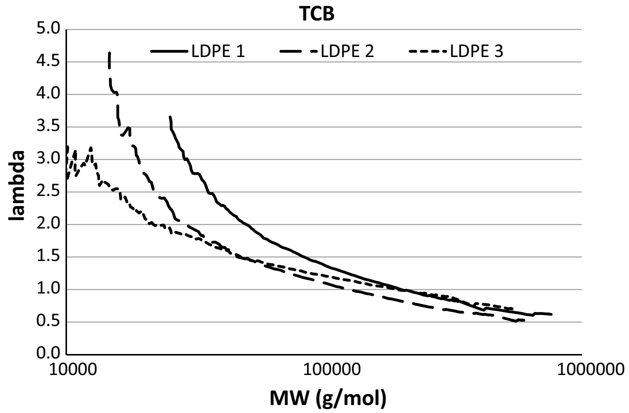

Fig. 4 Long chain branching distributions for LDPE samples measured in TCB. A value of $E = 0.7$ for the exponent and the Random Branched—Ternary Weight Average model were used in software calculation of lambda (number of LCB for 1000C)

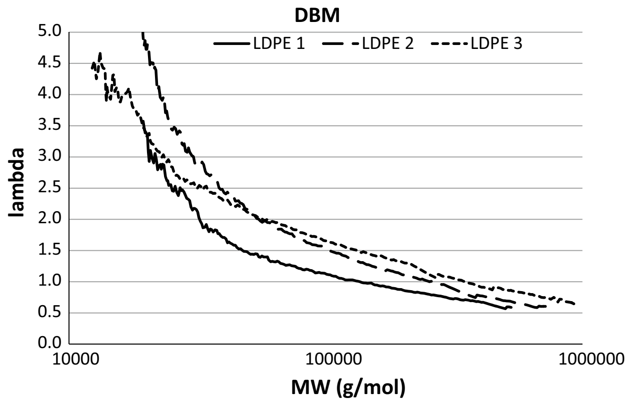

Fig. 5 Long chain branching distributions for LDPE samples measured in DBM. A value of $E = 0.7$ for the exponent and the Random Branched—Ternary Weight Average model were used in software calculation of lambda (number of LCB for 1000C)

molecular weight) for LDPE samples using NIST 1475 as linear reference are given for TCB in Fig. 4, and for DBM in Fig. 5. The important result is that the obtained values are similar for both solvents, between 0.5 and 3 LCB for 1000C, which are in good agreement with the values reported in literature for this type of LDPE in the investigated domain of molecular weights [7]. This completes our previously obtained results for linear polyethylenes and polypropylenes, showing the possibility to use a less toxic solvent for the GPC analysis of all types of polyolefins.

Conclusions

This work concludes our previous papers presenting DBM (butylal) as a possible less toxic alternative to traditionally employed TCB, as solvent for the high-temperature GPC analyses of all types of polyolefins.

The excellent correlations between the GPC results obtained in TCB and in DBM for linear polyethylenes, homo- and co-polymers of polypropylene, are completed for linear low densities polyethylenes, which have complex structures containing short and long chain branches.

The fact that DBM is practically a theta solvent for PS, making it difficult to perform the conventional calibration of the GPC with PS standards, can be circumvented for instruments with only a concentration detector by generating a calibration in TCB prior to switching to DBM. A more elegant solution however, is provided by instruments with triple detection, where it is not necessary to perform the column calibration with PS standards. For these instruments, DBM has a supplementary advantage over TCB because the dn/dc of PS is about four times higher in DBM as compared to TCB, thus improving accuracy of the calibration of differential refractive index and light scattering detectors.

From the academic perspective, the similar absolute value (about 0.1 mL g^{-1}) and sign difference of dn/dc between polyolefin solutions in TCB (negative) and DBM (positive) opens the possibility of new applications regarding the evaluation of the distribution of co-monomers as maleic anhydride and vinyl acetate in the main polyolefin chain. Actually, it is obvious that for certain compositions of TCB/DBM mixtures the dn/dc of the main olefin chain will be zero, so only the co-monomer signal will be recorded in the differential refractive index trace.

Finally, it is our hope that this paper will trigger the implementation of more environmentally friendly policies by polyolefin manufacturers, who routinely use high-temperature GPC for research and quality control measurements, and therefore are the main consumers of analytical grade TCB, a major source of chlorinated waste solvents.

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Compliance with Ethical Standards

Conflict of interest The authors declares that they have no conflict of interest.

Ethical statement This article does not contain any studies with human participants or animals performed by any of the authors.

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