

Analysis Method

Investigation of sample preparation for high temperature gel permeation chromatography using a low solvent consumption method

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ABSTRACT

The study explored the optimum conditions for sample preparation of polyolefins for high temperature gel permeation chromatography (GPC) recommended by ASTM D 6474, and the potential for reducing solvent consumption by using columns with reduced internal diameter. A polypropylene sample with high crystallinity and high molecular weight was selected, because this is one of the most difficult polyolefins to analyze by GPC. Sequences of injections covering 20 h showed that, at 160 °C, 2 h is enough to dissolve this sample, and that the antioxidant concentration is the critical parameter in obtaining reproducible GPC results. By using one column with an internal diameter (ID) of 4.6 mm and a flow rate of 0.3 mL/min, instead of the classical set of 3 columns of 7.5 mm ID and a flow rate of 1 mL/min, the solvent consumption can be reduced to about 10%.

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1. Introduction

Gel permeation chromatography (GPC) has become a well-established analytical method over the last thirty years to evaluate the molecular weight distribution (MWD) of soluble polymers. For linear polyethylene (PE) and polypropylene (PP) resins, a GPC method was standardized in 1999 by ASTM D 6474 [1], which was then amended in 2012 [2]. Although the procedure recommends that 250 ppm of an antioxidant should be added to the chromatographic solvent, typically 1,2,4-trichlorobenzene (TCB), this addition is often overlooked. Therefore, inter-laboratory tests comparing the molecular weight distribution (MWD) of polyolefins are often not consistent. A good example is the study done by International Union of Pure and Applied Chemistry (IUPAC) [3] in which a major source of error was recognized to be the thermoxidative instability of the sample: “to dissolve the sample, high temperatures, extended dissolution times and sample agitation are required, and the polyolefins may degrade under these severe conditions. Therefore, quite divergent results can be expected if the sample preparation is not done properly, i.e. when too long dissolution times and too high dissolution temperatures are used” [3]. In

the IUPAC study, for the polypropylene (PP) sample, weight average molecular weights (M_w) between 122,500 and 242,780 were reported by different laboratories. Recommendations on dealing with PP sample preparation for GPC can be found in reviews discussing the polyolefin fractionation [4,5]: adding the antioxidant, using the dual temperature zone autosamplers, purging the vial with nitrogen, or using solvents (decalin) allowing lower dissolution temperatures. The GPC analysis of PP in cyclohexane at 70 °C after prior dissolution in decalin at 140 °C was also presented as a possible solution to avoid the PP degradation, although the obtained chromatograms are more difficult to convert in MWD due to the very high peak of decalin and high differences in Mark-Houwink-Sakurada parameters between the polystyrene standards and PP [6]. We found only one paper evaluating the PP degradation as a function of dissolution time in TCB at 145 °C [7], but the recommended window for sample analysis was between 35 and 50 h after starting the dissolution, due to aggregate formation at this relatively low temperature. To protect the polymer chain during this long dissolution time, two additives were used with a total concentration of 2000 ppm.

In order to investigate the influence of sample preparation on GPC results for polyolefins, we conducted a study on a PP sample with high crystallinity and relatively high molecular weight, which is one of the most difficult polyolefins to analyze. The GPC analyses

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were performed using a 4.6 mm ID column which allows us to generate reliable results whilst reducing solvent consumption.

2. Experimental

2.1. Solvent

1,2,4-trichlorobenzene (TCB Spectropure dry, Biosolve, Netherlands, CAS 120-82-1) was used for GPC and analytical temperature rising elution fractionation (TREF) analyses. To allow us to investigate the influence of the antioxidant added to solvent for the GPC analyses, the TCB was prepared with different concentrations of 2,6-Di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT, CAS 128-37-0).

2.2. Samples

A high crystallinity PP standard (PP 450k, $M_w = 445,000$, $\bar{D} = 6.6$, American Polymer Standards Corp., US), was analyzed by triple detection GPC. Commercially available EasiVials from Agilent Technologies LDA UK Ltd, containing polystyrene (PS) standard mixtures used for column calibration are described in Table 1.

2.3. GPC apparatus and method

All GPC analyses were performed on an Agilent PL-GPC 220 High Temperature GPC System equipped with light scattering (LS), differential refractive index (DRI) and viscometer detectors. The PP sample was dissolved at a concentration of 0.5 mg/mL in TCB at 160 °C. The dissolution time prior to first injection was 1 h, during which the vial was gently shaken. The injection volume was 100 μ L and the chromatographic separation was performed using 1 Poly-Pore (250 \times 4.6 mm) column at a flow rate of 0.3 mL/min and a temperature of 160 °C. Apart from applying different offsets, all chromatograms are presented without smoothing or drift corrections.

2.4. Analytical TREF apparatus and method

The analyses were performed on a TREF-CRYSTAF model 300 instrument (Polymer Char, Valencia, Spain). The elution step was performed with an Intelligent Pump Series 300 (IP300, Flom corporation, Tokyo, Japan). The concentrations of the eluted polymer fractions were measured with the built-in infrared detector. Firstly, 300 μ L of the hot solution was injected at 160 °C in the TREF column (100 mm length, 1/4 inch ID, Polymer Char, Valencia, Spain). The column filled with solution was initially fast cooled (1 °C/min) to 130 °C, and then was further cooled to 30 °C at a rate of 0.1 °C/min. After this cooling step, the polymer was eluted from the column, through the TREF process using a flow rate of 0.5 mL/min and a heating rate of 1 °C/min.

3. Results and discussion

The analytical TREF offers a convenient way to evaluate the dissolution temperature of a polyolefin in a certain solvent. As a first step of the TREF technique, a polymer solution is injected at 160 °C into a column, and then slowly cooled to room temperature. In the second step the column is heated under a constant flow of solvent so that, as soon as the polymer is dissolved at a certain temperature, it is eluted from the column and a peak is recorded in the infrared detector.

Fig. 1 shows that the dissolution temperature for the PP 450k sample must be higher than 125 °C. However, this temperature corresponds to a precipitated solution, because the polymer was

Table 1

Average molecular weights (M_n , M_w) and molar mass dispersity (\bar{D}_M) for PS standards (batch 0006231262).

EasiVial	Code	M_n	M_w	\bar{D}_M	Peak MW	Mass (mg)
PS Red	PS 6870k	5,670,000	6,200,000	1.09	6,870,000	0.8
	PS 465k	446,500	464,600	1.04	465,600	1.6
	PS 18k	17,890	18,500	1.03	18,340	2.4
	PS 1390	1300	1370	1.05	1390	3.2
PS Yellow	PS 3242k	2,730,000	2,950,000	1.08	3,242,000	0.8
	PS 225k	218,600	224,200	1.03	224,900	1.6
	PS 10k	9580	9850	1.03	9970	2.4
	PS 580	540	605	1.12	580	3.2
PS Green	PS 1214k	1,140,000	1,183,000	1.04	1,214,000	0.8
	PS 70k	66,150	68,200	1.03	69,950	1.6
	PS 4800	4560	4730	1.04	4830	2.4
	PS 162	–	–	1.0	162	3.2

previously dissolved at a higher temperature and then re-crystallized by cooling the hot solution in the column. Hence, the correct temperature of dissolution and analysis is typically about 30 °C higher than the TREF temperature, in this case about 160 °C.

Another important piece of information provided by the TREF chromatogram in Fig. 1 is that, for a precipitated PP solution, the dissolution is instantaneous for temperatures higher than 130 °C. Therefore, to avoid sample degradation in the auto-sampler carousel, it is better to keep the solution at a lower temperature and to heat it to injection temperature a few minutes prior to injection. This is possible when an auto-sampler with dual temperature zones is available, for which we recommend in the case of PP temperatures of 120 and 160 °C.

Once the optimum temperature for dissolution was determined, we prepared a series of solutions of the PP 450k sample in TCB containing different concentrations of BHT. These solutions were placed in the dual zone carousel and injected as a sequence over 20 h.

In Fig. 2 the chromatograms recorded with the LS and DRI detectors for the solutions of PP 450k without antioxidant are shown. Because in GPC the elution times of high molecular weight fractions are shorter than the elution times corresponding to low molecular weight fractions, the peaks moving to longer elution volumes suggest polymer degradation. Peak areas from the LS detector are proportional to the injected concentration and the molecular weight of the polymer so, for solutions with the same concentration, a decrease of the LS peak areas confirms that the polymer has degraded.

In Fig. 3, the chromatograms recorded with the LS and DRI detectors for the solutions of PP 450k containing 500 ppm BHT show

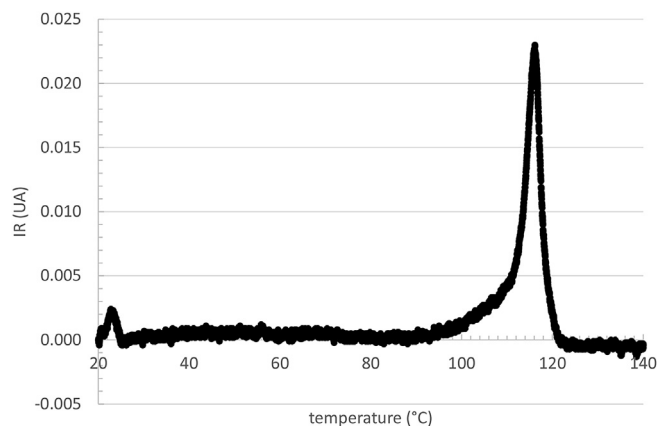


Fig. 1. Analytical TREF chromatogram obtained in TCB for PP 450k.

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