Journal of Chromatography A, 1407 (2015) 193–202

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Broadening of polymer chromatographic signals: Analysis, quantification and correction through effective diffusion coefficients

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ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form 25 June 2015
Accepted 27 June 2015
Available online 2 July 2015

Keywords:
Polydispersity index
Gel permeation chromatography
Multi angle light scattering
Diffusion

ABSTRACT

Average molecular weights and polydispersity indexes are some of the most important parameters considered in the polymer characterization. Usually, gel permeation chromatography (GPC) and multi angle light scattering (MALS) are used for this determination, but GPC values are overestimated due to the dispersion introduced by the column separation. Several procedures were proposed to correct such effect usually involving more complex calibration processes.

In this work, a new method of calculation has been considered including diffusion effects. An equation for the concentration profile due to diffusion effects along the GPC column was considered to be a Fickian function and polystyrene narrow standards were used to determine effective diffusion coefficients. The molecular weight distribution function of mono and poly disperse polymers was interpreted as a sum of several Fickian functions representing a sample formed by only few kind of polymer chains with specific molecular weight and diffusion coefficient.

Proposed model accurately fit the concentration profile along the whole elution time range as checked by the computed standard deviation. Molecular weights obtained by this new method are similar to those obtained by MALS or traditional GPC while polydispersity index values are intermediate between those obtained by the traditional GPC combined to Universal Calibration method and the MALS method.

Values for Pearson and Lin coefficients shows improvement in the correlation of polydispersity index values determined by GPC and MALS methods when diffusion coefficients and new methods are used.

1. Introduction

Average molecular weights are some of the most important parameters considered in the polymer characterization. Standard and routine methods allow determining reliable values for such different average values. Number, M_n, and mass, M_w, average weights are essential characterization properties and most common techniques for determining it are gel permeation chromatography (GPC) and multi angle light scattering (MALS). Both techniques report not only average values but the full distribution function in terms of molecular weight. However, only advanced characterization methods involve the use of the full distribution function and, very often, the only information about that distribution is reported trough the polydispersity index value, $PI = M_w/M_n$.

It is well known that separation carried out along the GPC column introduces additional dispersion [1,2] and PI values determined by GPC are usually higher than expected. Determination carried out by GPC-MALS is less affected because MALS is an absolute technique for molecular weight determination, however, because the calculation of M_n, MALS values for PI are usually underestimated [2]. The main reasons for the peak broadening are the diffusion phenomena along the column, capillaries, and detectors, which can be minimized, but not completely avoided. Additional broadening can be due to high sample loads, interaction of the sample with the column packing, and an imperfect chromatographic system. Void volumes between the connecting capillaries will lead to a dramatically decreased performance of the system [3].

Such dispersion effects are described for all the chromatographic techniques. Usually these effects are quantified through the Van Deemter equation [4] including terms of multiple paths, longitudinal diffusion and equilibration time. Effective diffusion coefficients dependent of several experimental factors are usually included. Darcy's law [5] is also widely used for the flow in porous media, a lot of work has been carried out and several forms were proposed.

Tung's integral equation is the most common approach for the study in polymeric systems, but there are some doubts about the applicability of this equation for complex polymers [6]. Additional

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http://dx.doi.org/10.1016/j.chroma.2015.06.068
0021-9673/

effects are found in the description of polymeric solutions. Several studies were carried out in order to describe effects of flow rate on radius of gyration for flexible polymers and consequently on the hydrodynamic radius, the GPC elution volume and finally on average molecular weight and polydispersity index [7–9].

Several procedures were proposed to correct such dispersion due to the column. Some authors describe the inclusion of a constant spreading factor that can be determined by polymer standards [1,10], but in some cases the instrumental spreading is dependent on the polymer concentration [11] or on the molecular weight [12]. An alternative procedure describes calibration methods that involve simultaneously the use of GPC and MALS techniques [13–15]. Other authors have studied different algorithm for band broadening correction in conventional SEC analysis with different detectors [16].

Some of these studies conclude that neglecting the spreading effect for GPC would not introduce much error in molecular weight calculation nor in scaling relationship between radius of gyration and molecular weight. Consequently, only effect on polydispersity index is expected.

In this work, a different approach was considered. Equation for the concentration profile due to diffusion effects along the GPC column was considered to be a Fickian function. Narrow standards were used to calibrate the GPC–VIS (GPC–Viscometer) technique according to Universal Calibration method and to determine effective diffusion coefficients. Such coefficients were assumed to be dependent only on the molecular weight and a general correlation was proposed. The molecular weight distribution function was interpreted as a sum of several Fickian functions representing a sample formed by polymer chains with only few given sizes as determined by specific molecular weight and effective diffusion coefficient. Contribution of each Fickian function is proportional to the content of the corresponding polymer size. The new description reports values for the molecular weight as well as for the polydispersity index. That computed values are compared to that obtained by GPC with the usual Universal Calibration method and to that obtained by MALS method.

2. Experimental

2.1. Materials

Samples used as reference in this work were those usually involved as standards in the GPC Universal Calibration. Two series of polystyrene (PS) samples covering a wide average molecular weight range (from 1.1 to 3742 kg mol^{-1}) from Polymer Laboratories were used. Their polydispersity indexes are in the range of 1.00–1.07, and they can be considered monodisperse samples. In this work, these samples will be named as PS followed by the M_w value.

Pure *n*-paraffin samples with the molecular weight ranging from 0.2 to 0.7 kg mol^{-1} and supplied by Supelco were also analysed in order to cover a lower molecular weight range.

Polydisperse standard materials, linear polyethylene NIST1475a and polystyrene NIST706a, were supplied by National Institute of Standards and Technology used to check the procedure developed in this work.

Samples with higher polydispersity indexes have been synthesized following a procedure developed in our laboratories and previously reported for ethylene/propylene copolymers [17]. The supported metallocene catalysts used was rac-dimethyl-silylbis(2-methylindenyl)zirconium dichloride (Boulder Scientific Company) and the cocatalyst was triisobuthylaluminium (TIBA, 1 M in toluene, supplied by Witco). Copolymerization reactions were carried out during 30 min in a 1-L Büchi® stirred glass reactor at 70 °C, 5 bar with an Al/Zr molar ratio of 400, *n*-heptane was used as solvent that was saturated with an ethylene/propylene gas mixture previously to the copolymerization reaction. Monomers were fed continuously during reaction through calibrated gas flow-meters.

The overall composition of the copolymers was carried out with a 13C nuclear magnetic resonance analysis in a NMR BRUKER AVANCE III 500 spectrometer. The polymers were solved in 1,2,4-trichlorobenzene at 100 °C with 1,2-dichlorobenzene-d4 as deuterated reference. NMR analyses were carried at 500 MHz, with 1024 total number of scans and 10 s of delay time. All the copolymers were analysed according to the method of the triad distribution with the assignment of chemical shifts previously reported by Randall [18] and Kakugo [19]. These samples will be named as EP (ethylene/propylene) followed by a number according to ethylene molar percent.

2.2. GPC and MALS characterization

GPC–vis–MALS equipment was a gel permeation chromatograph (GPC, Waters Alliance 2000) equipped with refractive index and viscometer detectors combined with a multi-angle light scattering (MALS, DAWN EOS Wyatt Technology).

The GPC separation was carried out by using two columns PLgel 10 μm MIXED-B, 300x7.5 mm and one PLgel 10 μm 10E6 Å, 300 × 7.5 mm, the temperature was set at 145 °C, and the flow rate was 1 mL min^{-1}. The solvent was 1,2,4-trichlorobenzene (TCB) with 400 mg L^{-1} Irganox 1010 added in order to stabilize the polymer against oxidative degradation. The software used was EMPOWER LOGIN 2002, from WATERS.

The MALS detector is equipped with a laser at 690 nm and 17 multi angle detectors. Temperature was also set at 145 °C. The DAWN EOS photometer system was calibrated with toluene, the detectors were normalized with a standard monodisperse PS (M_w = 30 kg mol^{-1}) which was also used to determine inter-detector volume [20]. The differential refractive index increments d*n*/d*c* of the polymers and copolymers were determined following a procedure previously described [21]. Constant d*n*/d*c* values of 0.053 mL g^{-1} and 0.101 mL g^{-1} were used for PS and EP polymers, respectively. d*n*/d*c* values for EP copolymers were considered composition independent according to previous work [21]. The software used was ASTRA V 5.1.9.1, from Wyatt Technology.

3. Diffusion model and data analysis

3.1. GPC-diffusion model: Monodisperse polymers

Fig. 1 displays simplified geometry of the system, a slice (with section A and thickness d*x*) of solution of j-component with concentration c_{0j} placed at the coordinate x_{0j} experiments a diffusion process because the concentration gradient. In this work, mathematical functions obtained from the Fick law for one dimension displacement were considered to model diffusion

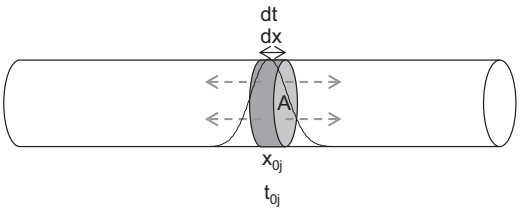

Fig. 1. The diffusion process occurring from a concentrated slice placed at the position x_{0j} (being detected at elution time t_{0j}).