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Molar mass determination of poly(octadecene-alt-maleic anhydride) copolymers by size exclusion chromatography and dilute solution viscometry

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Abstract

The number average molar mass M_n of poly(octadecene-alt-maleic anhydride) (PODMA) copolymers calculated from data obtained by size exclusion chromatography (SEC) using a polystyrene (PS) calibration was found to be inaccurate. The use of SEC combined with dilute solution viscometry enabled a method to be developed using an iterative approach, which does not require knowledge of the Mark–Houwink constants for PODMA samples. A new calibration curve was constructed as a plot of molar mass M_u for PODMA. True number-average molar masses M_n (true) calculated using the new calibration are approximately twice the apparent molar mass M_n (app) based on a PS calibration for higher molar mass samples (>10 000 g mol^{-1}). © 2002 Published by Elsevier Science Ltd.

Keywords: Maleic anhydride; α-Olefin; Alternating copolymers

1. Introduction

The combination of on-line molar mass M sensitive detectors such as light scattering (LS) and viscometry with a concentration detector such as a refractometer for separations of polymers by size exclusion chromatography (SEC) provides considerable potential for characterisation of molar mass distributions and for number and weight average molar masses, M_n and M_w, respectively [1]. In order to achieve reliability of results, practical procedures must be directed to optimising signal-to-noise output from detectors and to defining concentrations of polymer solutions consistent with detector response and with chromatographic conditions. For short chain polymers, the sensitivities of LS and viscometry detectors are much reduced, and so the accuracy of data for M_n and M_w by SEC with multi-detectors may be questionable [2]. For a polymer for which standards or reference materials are unavailable, one of several procedures based on the universal calibration approach can be considered [3], although a range of secondary problems, which might invalidate this approach, will have to be assessed. The universal calibration approach at a given elution time is defined by Eq. (1)

$$\log[\eta]_{st} \times M_{st} = \log[\eta]_u \times M_u \quad (1)$$

where $[\eta]$ is the intrinsic viscosity of a sample in the SEC eluent and st and u denote standards and unknown, respectively. Utilisation of this method allows the calculation of molar masses involving a SEC chromatogram and a calibration plot of log M_u versus elution time.

Copolymers of long alkyl chain α-olefins and maleic anhydride have short chain lengths [4], and studies of copolymerisations and properties require knowledge of M_n. A trial-and-error method originally proposed by Weiss and Cohn-Ginsberg [5], and developed by others [3], permits the determination of a Mark–Houwink (MH) equation between $[\eta]_u$ and M_u for a polymer from a universal calibration established with polystyrene (PS) standards. This method utilises values of $[\eta]$ for at least two polydispersed samples of that polymer measured off-line to the SEC instrument, in conjunction with SEC chromatograms for the same samples. A variation of this method in order to find a calibration curve for M_u for alternating copolymers of octadecene and maleic anhydride (PODMA) is presented here, without the need for constants in the MH equation.

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2. Experimental

2.1. Synthesis of PODMA

Commercial samples (MCD1 and MCD2) were supplied by Aldrich and SC Johnson, respectively. The following procedure was typical of that used for copolymerisations (MCD27, 44 and 66). The monomer and initiator concentrations were varied so as to produce samples of differing molar masses.

Maleic anhydride (4.90 g, 50 mmol, Aldrich, freshly recrystallised from toluene) was dissolved in dioxane (10 ml, Aldrich). Octadecene (12.63 g, 50 mmol, Aldrich) was added and the mixture decanted into a three-necked flask. Azo bis-*iso*-butyronitrile (0.0821 g, 0.5 mmol, Fluka, freshly recrystallised from methanol) was added. The vessel was evacuated by nitrogen sparge for 15 min before the nitrogen flow rate was reduced and the system was heated to 100 °C. Typically, the reaction ran for 12 h after which the solution was added dropwise to cold methanol (10 volumes). The PODMA sample was collected, reprecipitated from tetrahydrofuran (THF) into cold methanol (10 volumes) and dried under vacuum for 24 h at 60 °C. The copolymers were free-flowing pale yellow powders. Analysis was carried out by ^{1}H NMR ($CDCl_3$) and FTIR ($CHCl_3$) spectroscopies to elucidate the structure and composition. All the PODMA samples were found to have equimolar compositions irrespective of monomer feed. The normal linear methods developed by Fineman and Ross [6], and Kelen and Tudos [7] were used to calculate the values of the monomer reactivity ratios r_1 and r_2. The product $r_1 r_2$ was zero providing evidence for the strictly alternating structure of PODMA.

2.2. Size exclusion chromatography

SEC was performed on a Polymer Laboratories instrument (PL-GPC 110) equipped with a refractive index detector. A set of two Polymer Laboratories columns (PLgel 5μm MIXED-D 300 × 7.5 mm) was used. The eluent was a mixed system (v/v) of THF (90%, Aldrich)/acetic acid (10%, Aldrich) and was used at a flow rate of 1.0 ml min^{-1} The analysis was carried out at 40 °C. Calibration was carried out using 10 different PS standards with narrow distributions and molar masses ranging from 580 to 325 000 g mol^{-1}. The data were processed using a RM 575 computer operating Caliber GPC software from Polymer Laboratories.

2.3. Dilute solution viscometry

Intrinsic viscosity measurements were carried out using an Ubbelohde capillary viscometer having an internal diameter of 0.53 mm and a length of 10 cm. The flow times were automatically recorded by a viscometer timer (Schotte Gerate AVS 310). The solvent and temperature were the same as those used for the SEC analysis. Corrections for kinetic energy could be ignored as the flow times were relatively long ($t_0 \sim 100$ s). The samples were dissolved in 15 ml of solvent, filtered and then added to the viscometer reservoir. Dilutions were carried out by adding fresh solvent to the viscometer and allowing 10 min for the solution to reach thermal equilibrium. The range of relative viscosities (η_r) for each experiment was between 1.2 and 2.0. The data were plotted using the Huggins equation with the intrinsic viscosity $[\eta]$ (dl g^{-1}) determined by extrapolation to infinite dilution.

3. Results and discussion

THF is the solvent of choice for a number of polymer separations by SEC [2]. The use of THF for the separation of PODMA, however, does not provide good chromatographic resolution. Over a period of time, the chromatogram is shifted to longer elution times and the polydispersity of the sample is broadened. Tacx et al. [8] reported similar observations during the analysis of styrene–maleic anhydride (SMA) copolymers. Both LS and viscometry indicated no enhancement of molar mass or intrinsic viscosity and so intermolecular aggregation was not considered to be a reasonable explanation for this behaviour. It is suggested that a mixed exclusion/adsorption mechanism contributes to adsorption of SMA and PODMA onto the column packing. As PS does not exhibit such anomalies, it is assumed that the polar anhydride rings are responsible. Copolymers containing anhydride groups may also contain a number of dicarboxylic acid groups due to ring opening hydrolysis. This reaction is facilitated by THF that may contain low levels of water. The adsorption of SMA and PODMA can be suppressed by the addition of an acid. The addition of

Table 1
Intrinsic viscosity and molar mass results for PODMA using PS and PODMA calibrations

Sample	Measured intrinsic viscosity $[\eta]_{exp}$	Calculated intrinsic viscosity $[\eta]_{calc}$	Apparent number average molar mass, M_n (app)	True number average molar mass, M_n (true)
MCD2	0.0574	0.066	4000	3900
MCD27	0.0664	0.0672	6200	15 600
MCD44	0.0737	0.0734	12 700	29 700
MCD1	0.0976	0.0998	14 400	37 100
MCD66	0.1278	0.1284	23 400	56 300

acetic acid to THF (10:90) stabilises the anhydride ring and competes for the adsorption sites present on the column packing. Use of the modified mobile phase allows a size exclusion mechanism to operate without any interference.

In order to construct a universal calibration curve for PS, the MH constants for PS under the experimental conditions need to be utilised. Because of the modified mobile phase, MH constants were not available and so were determined by experiment. Values of $[\eta]$ for a number of PS standards were measured and a double logarithmic plot used to evaluate these constants. The following MH relationship was derived (Eq. (2)):

$$[\eta]_{ps} = 1.52 \times 10^{-4} M^{0.71} \quad (2)$$

Our proposed variation of the method of Weiss and Cohn-Ginsberg [5] starts with a plot of $\log[\eta]$ versus peak elution time for PODMA samples with apparent molar masses in the range 4–24 kg mol^{-1}. These apparent number average molar masses M_n (app) which were determined by a PS calibration are given in Table 1. Values of $[\eta]_{exp}$ determined experimentally by solution viscometry are also given in Table 1. This initial plot together with SEC chromatograms for PODMA samples permitted the calculation of $[\eta]_{calc}$ for all PODMA samples. The PODMA samples characterised by SEC have polydispersities in the range 1.6–2.0, which are typical of conventional radical polymerisation and for which exponential molar mass distributions are generated [9]. It follows from earlier calibration studies [10] that the value of M corresponding to the peak position of a chromatogram should be close to the viscosity–average molar mass M_v. The iteration method requires matching $[\eta]_{exp}$ and $[\eta]_{calc}$ for all PODMA samples by a series of calculations involving SEC chromatograms and trial-and-error placements of the plot of $\log[\eta]$ versus elution time. The resulting quadratic function is shown in Fig. 1 and values of $[\eta]_{calc}$ are compared with $[\eta]_{exp}$ in Table 1. The iteration method involves extrapolation of the plot beyond experimental data points as illustrated for the tails of the chromatogram for sample MCD44 in Fig. 1. However, only for the sample of lowest M, there is a problem in matching $[\eta]_{calc}$ and $[\eta]_{exp}$.

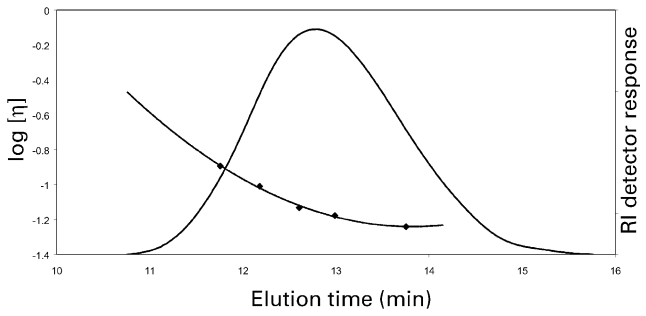

Fig. 1. SEC calibration curve for PODMA samples based on intrinsic viscosity and chromatogram for sample MCD44.

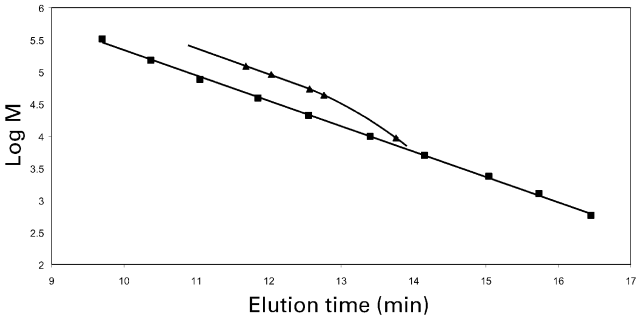

Fig. 2. SEC calibration curves for PODMA. (■) PS calibration; (▲) calibration based on SEC/$[\eta]$ analysis for PODMA.

A major aim was to establish a SEC calibration M_u for PODMA samples in THF/acetic acid (90/10) at 40 °C. The derivation of Eq. (2) enables a universal calibration to be determined with Eq. (1) from which a calibration for M_u can be calculated since the dependence of $[\eta]_u$ on elution time is available from Fig. 1. The resulting calibration for PODMA is displayed in Fig. 2, demonstrating linearity in the region of high M with a similar slope to the calibration for PS, indicating that the MH exponents for the two polymers in THF/acetic acid (90:10) are quite similar. The downturn in the plot for PODMA at low M is consistent with the observation that the MH exponent should fall to 0.5 for short chains in good solvents, which has been demonstrated experimentally for several polymers [11–13]. Our method avoids the stipulation by Weiss and Cohn-Ginsberg [5] who determined fixed results for MH constants.

The described method allows the calculation of the true number average molar mass M_n (true) for PODMA based on the M_u calibration displayed in Fig. 2. For PODMA samples of high molar mass (>10 000 g mol^{-1}), values of M_n in Table 1 obtained with the constructed calibration are approximately twice the apparent molar mass results based on a PS calibration. For the lowest molar mass PODMA sample (<10 000 g mol^{-1}) which is positioned in the downturn of the calibration (at higher elution times), similar values of M_n (true) and M_n (app) are obtained.

4. Conclusions

An iterative method for the calculation of average molar masses of PODMA has been demonstrated. The technique utilises SEC elution times in conjunction with dilute solution viscometry, measured off-line to the SEC instrument. This method does not require knowledge of the MH constants for the unknown copolymer. The values of M_n (true) of the PODMA samples were calculated and in all but the lowest molar mass sample, the M_n (true) was at least twice the M_n (app). The lowest molar mass PODMA sample had an M_n (true) that was very similar to M_n (app).

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