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Robust isocratic liquid chromatographic separation of functional poly(methyl methacrylate)

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Abstract

The separation of telechelic poly(methyl methacrylate) (PMMA) prepolymers based on the number of end-groups under critical liquid chromatography (LC) conditions has been studied using a bare-silica column, which can interact with polar functional groups. The critical solvent compositions for non-functional, mono-functional and bi-functional PMMAs were determined in normal-phase LC using mixtures of acetonitrile and dichloromethane (DCM) of varying composition as the mobile phase. The telechelic prepolymers were successfully separated according to hydroxyl (OH) functionality (with zero, one, or two OH groups, respectively) under the critical conditions, in which fast (5 min), base-line separations were obtained independent of molecular weight. Changing the column temperature, flow rate, and mobile-phase composition within a certain range did not affect the functionality separation. Therefore this isocratic LC separation method is quite robust. Evaporative light-scattering detector (ELSD) calibration curves were used for the quantitative analysis of functional PMMA prepolymers.

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1. Introduction

Functional (pre)polymers can be used as cross-linking components in coating formulations to create hard, durable films. For example, prepolymers containing two or more hydroxyl groups react with

tri-functional isocyanates to form a urethane network. The mechanical behaviour (e.g. strength, brittleness) of the network will be greatly affected by the length of the cross-linking segments, i.e. by the distance between hydroxy groups in the functional prepolymer. Therefore, the performance of a coating can be controlled by adjusting the number and positions of the functional groups. Superior performance of a coating can be anticipated if the cross-linking agent is a telechelic (bi-functional) polymer with a (very) narrow molecular-weight distribution (MWD). However, it is very difficult to produce such

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telechelic polymers by conventional polymerization methods.

Fortunately, the recent development of controlled/‘living’ radical polymerization has resulted in the synthesis of many well-defined architectures with predictable molecular weights [1,2]. The most important methodologies include nitroxide-mediated radical polymerization [3], atom-transfer radical polymerization (ATRP) [4], and lately reversible addition-fragmentation chain-transfer (RAFT) polymerization [5]. Among these, RAFT might arguably have the greatest commercial impact, because it only involves organic substances and because it works very well with most acrylic derivatives, including acrylic acid [2]. Therefore, this is the method of choice for the preparation of bi-functional telechelic acrylate polymers with a low polydispersity index.

The first functional group is incorporated into the polymer chain at the initiating chain end, using functionalized initiators and functionalized RAFT agents, which results in mono-functional polymers [6–8]. This is followed by an endcapping reaction to introduce another functional group. However, the efficiencies (yields) of these functionalization reactions are less than 100%, because of the side reactions inherent to growing radicals, such as termination by bimolecular combination or disproportionation. Moreover, chain transfer to solvent molecules or monomers will always occur. Finally, experience with macromolecular reactions has shown that the hydroxy-endcapping reaction does not proceed with full conversion [7].

The development and optimization of telechelic polymers require methods to determine the functionality-type distribution (FTD) and the molecular-weight distribution. This is a major challenge in the research on bi-functional telechelic polymers. The traditional analytical techniques, such as infrared absorption spectroscopy (IR), ultraviolet spectroscopy (UV), nuclear-magnetic-resonance spectroscopy (NMR), and specific OH titration, by which only the average functionality can be measured, are inadequate for this purpose. The same must still be said for modern mass-spectrometric techniques, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and electrospray ionization mass spectrometry (ESI-MS). These techniques provide good qualitative information, rather than quantitative results, due to variations in the ionization,

separation, and detection efficiencies. To reach the goals mentioned above, the telechelic polymers must be separated based on the number of end-groups.

LC under critical conditions (at which the retention time of a polymer is independent of the molecular weight) is a relatively new analytical method [9–15]. It can be used to separate polymers based on the number of functional groups into, for example, non-, mono-, and di-functional polymers [6,16–18]. However, the exact critical condition is not easy to obtain experimentally [19,20] and the critical conditions are rather sensitive to eluent composition [21], column packing [19,22], polymer nature [23,24], temperature [17,21,25], and even to pressure variations [17,23,24]. Critical conditions do not necessarily provide good functionality-based separations [9]. On a given critical system, the retention and separation of polymers with (for example) different end-groups may or may not be satisfactory. In this work, the critical solvent composition for poly(methyl methacrylate) (PMMA) was studied in normal-phase LC. A robust isocratic LC separation of hydroxy-functional PMMA was developed.

2. Experimental

2.1. Chemicals

Dichloromethane (DCM), and acetonitrile (both HPLC grades), were from Rathburn Chemicals Ltd. (Walkerburn, Scotland). Poly(methyl methacrylate) standards were obtained from Polymer Laboratories (Church Stretton, UK). The molecular weight (M_n , M_p) and polydispersity index (PDI) values were supplied by the manufacturer. The polymers with one hydroxyl (OH) end-group were synthesized by reversible addition-fragmentation chain-transfer polymerization (named RAFT polymers) using a hydroxy-functional initiator and a hydroxy-functional RAFT chain-transfer agent [8]. A commercial telechelic PMMA (TEGO DIOL MD-1000X) with two OH groups was obtained from Tego Chemie Service (Essen, Germany). Since well-defined PMMA containing two OH groups is not easy to obtain, a sample VL57 (mainly containing two OH end-groups) was synthesised via end-group modification of a well-defined RAFT polymer with one OH end-group

[8]. The molecular weights and molecular-weight distributions were measured by SEC with a Waters (Milford, MA, USA) instrument equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 ml/min. A set of two linear columns (Mixed-C, Polymer Laboratories, 30 cm × 7.8 mm i.d., 40 °C) was used. The calibration curve was prepared with polystyrene (PS) standards, and the molecular weights were estimated based on the universal-calibration principle and Mark–Houwink parameters (PS, $K = 1.14 \times 10^{-4} \text{ dl g}^{-1}$ and $a = 0.716$; poly(methyl methacrylate), $K = 0.944 \times 10^{-4} \text{ dl g}^{-1}$ and $a = 0.719$) [26–28]. The effect of the hydroxyl end-groups on the Mark–Houwink parameters was neglected. All

the PMMA standards and samples used are summed in Table 1. All the samples were dissolved in DCM unless stated otherwise.

2.2. Equipment

A Waters (Milford) 2690 Alliance liquid chromatography (LC) system was used to perform the isocratic LC experiments. This HPLC instrument contained a built-in auto-injector with a sample loop allowing injection of variable sample volumes, and it was equipped with a Waters 996 PDA (photodiode-array detector) and a Sedex 55 evaporative light-scattering detector (ELSD) (temperature 62 °C, N₂ pressure 2.2 bar). The mobile phase was prepared in situ using the solvent-mixing capability of the instrument. The eluent composition is given in vol.%. The data collection and the data analysis were handled by Waters Millennium 3.2 software. The columns used (150 mm × 4.6 mm i.d.) were packed in-house with Hypersil Silica (3 μm particles; 100 Å pore size; Shandon, Runcorn, UK).

Also, an HPLC system consisting of a Shimadzu LC-10ADvp pump, a Rheodyne 7010 injector (Berkeley, CA, USA), and a Vorex ELSD II A (Burtonsville, MD, USA) was used. The columns were contained in a (Millipore) Waters temperature-control module.

3. Results and discussions

3.1. Critical composition of PMMA

Our objective is to establish robust isocratic LC conditions to separate PMMA samples based on the number of hydroxy end-groups, which means that the separation should not be very sensitive to small changes in solvent composition, flow rate, or column temperature. A bare-silica column, which can interact with polar functional groups, is thought to be a good choice. If one solvent causes the sample (i.e. the polymer backbone) to adsorb slightly, and the other solvent just causes the sample to desorb, then we expect the retention of the polymer not to be dramatically affected by the composition of the mobile phase. Dichloromethane is a good solvent, but a weak eluent for PMMA on a silica column [29]. It can be used as the injection solvent to avoid breakthrough problems

Table 1
PMMA samples used in this study

Sample name	M_n	M_p	PDI	Intended number of OH end-groups
PMMA 1680 ^a	1327	1681	1.15	0
PMMA 2990 ^a	2756	2991	1.08	0
PMMA 3800 ^a	3437	3805	1.07	0
PMMA 6950 ^a	–	6950	1.05	0
PMMA 9200 ^a	8502	9198	1.06	0
PMMA 13930 ^a	12489	13934	1.06	0
PMMA 28300 ^a	26953	28304	1.04	0
PMMA–OH 3310 ^b	2425	3314	1.22	1
PMMA–OH 6680 ^b	4832	6679	1.25	1
PMMA–OH 13950 ^b	10934	13946	1.21	1
PMMA–OH 20740 ^b	17043	20744	1.16	1
MD-1000X	1490	2324	1.64	2
VL57 ^c	3577	5718	1.26	2
VL37A ^d	2587	3754	1.29	1
VL37B ^c	2853	3678	1.29	1
VL47B ^c	3312	5659	1.31	2

The molecular weight (M_n , M_p) and polydispersity index values were measured by SEC, except for PMMA standards supplied by the manufacturer.

^a PMMA standards were obtained from polymer laboratories.

^b Polymers with one OH group synthesised by reversible addition-fragmentation chain-transfer polymerization using a hydroxy-functional initiator and a hydroxy-functional RAFT chain-transfer agent.

^c Synthesized via end-group modification of well-defined RAFT polymers [8].

^d Synthesized by RAFT polymerization using a 2,2'-azobisisobutyronitrile (AIBN) initiator and a hydroxy-functional RAFT chain-transfer agent [8].

[29]. All the samples were dissolved in DCM in this work unless stated otherwise. Acetonitrile is a more-polar solvent, which can desorb PMMA from the silica column. Therefore these two solvents were used to make up the mobile phase.

The critical solvent composition for PMMA was determined using mixtures of acetonitrile and dichloromethane of varying composition. PMMA samples were used with different molecular weights and different numbers of end-groups, viz. PMMA standards with no OH groups, polymers with one OH group synthesised by reversible addition-fragmentation chain-transfer polymerization, and a commercial telechelic PMMA (MD-1000X) with two OH groups (see Table 1). Since well-defined PMMA containing two OH groups is not easy to obtain, sample VL57, synthesised via end-group modification of a well-defined RAFT polymer [8], was used as another bi-functional PMMA with a different molecular weight. The main fraction of VL57 contained two OH end-groups, but the product also contained a small fraction with only one OH end-group [8]. The observed retention times are shown in Figs. 1 and 2 (for sample VL57, only the retention time of the bi-functional fraction was recorded). Critical compositions for PMMAs with no OH groups, one OH group or two OH groups are found to be almost identical at about 43% acetonitrile in dichloromethane. The retention times of PMMA standards (molecular-weight range 1680–28,300) were almost constant when the mobile phase contained between about 42 and 55% acetonitrile in dichloromethane, as seen in Figs. 1A and 2A. From a combination of Fig. 1A and B we conclude that the mobile-phase compositions between 42–48% can be used to separate the low-molecular-weight PMMA samples based on number of hydroxy-functional end-groups.

Fig. 3 shows the representative ELSD chromatograms of PMMAs under conditions that yield base-line separation according to the number of OH end-groups. The two different PMMA standards (with no OH groups, molecular weights 3800 and 28,300) co-eluted. The RAFT polymers (with one OH end-group, molecular weights 3300 and 20,000) have identical retention times, but are clearly separated from the PMMA standards. The telechelic bi-functional sample is well separated from the mono-functional polymers. Thus, the low-molecular-weight PMMAs

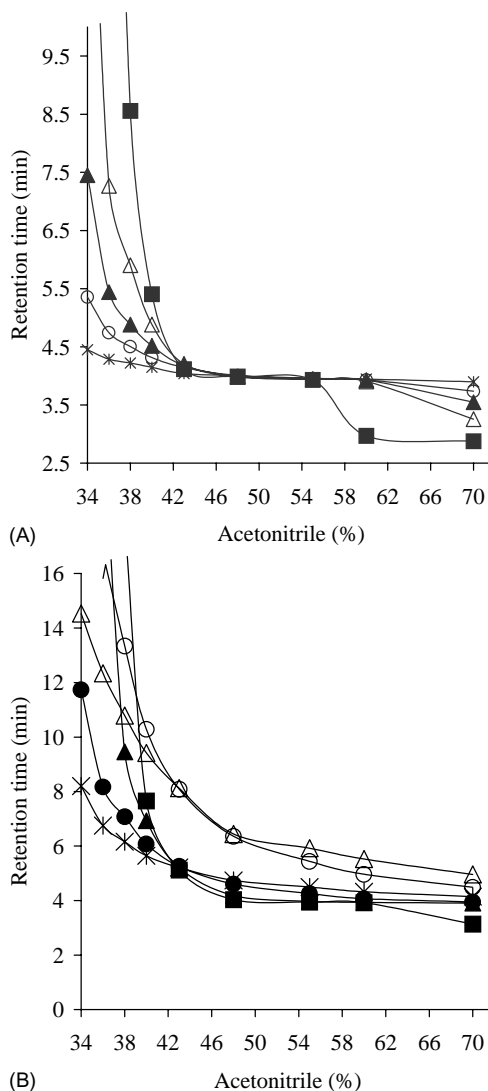


Fig. 1. (A) Dependence of retention time on the mobile-phase composition for PMMA standards with different molecular weights. Squares: PMMA 28,300; open triangles: PMMA 13,900; triangles: PMMA 6950; open circles: PMMA 3800; stars: PMMA 1680. (B) Dependence of retention time on the mobile-phase composition for PMMA-OH and HO-PMMA-OH samples with different molecular weights. Open circles: HO-PMMA-OH 5720 (VL57, see text); open triangles: MD-1000X; squares: PMMA-OH 20,740; triangles: PMMA-OH 13,950; circles: PMMA-OH 6680; stars: PMMA-OH 3310. ELSD detector, home-packed silica column (150 mm \times 4.6 mm i.d.; 3 μ m particles; 100 \AA pore size), flow rate 0.5 ml/min, column temperature 25 $^{\circ}$ C. Note: Data points with retention times larger than 10 min in (A) (15 min in (B)) were recorded and used to construct the curved lines. However, they are not shown in the figures.

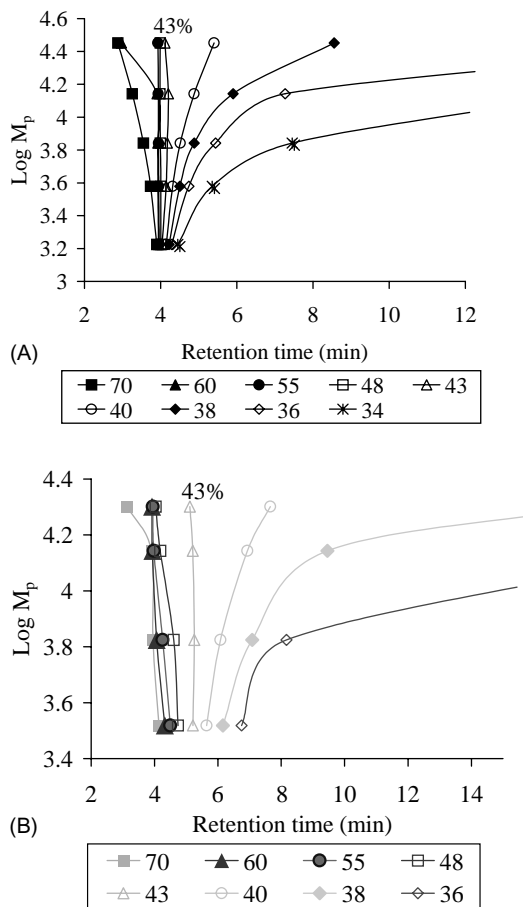


Fig. 2. (A) Calibration plots of $\log M_p$ vs. retention time for PMMA standards in different mobile phases. (B) Calibration plots of $\log M_p$ vs. retention time for PMMA samples with one OH end-group in different mobile phases (the values as indicated in the figure refer to the percentage of acetonitrile in DCM). LC conditions were the same in Fig. 1 (see note under Fig. 1).

were successfully separated according to the hydroxy functionality under the critical conditions.

Mengerink et al. described that the critical composition for polyamide varies when the column temperature or the flow rate changes [17]. Other authors [19,23] also reported that the critical composition is very sensitive to the column temperature and the pressure drop. We investigated the effects of temperature and flow rate (pressure drop changes when flow rate varies) on our critical composition. No effect was observed in our experiments when the flow rate changes from 0.1 to 1.0 ml/min. The same critical

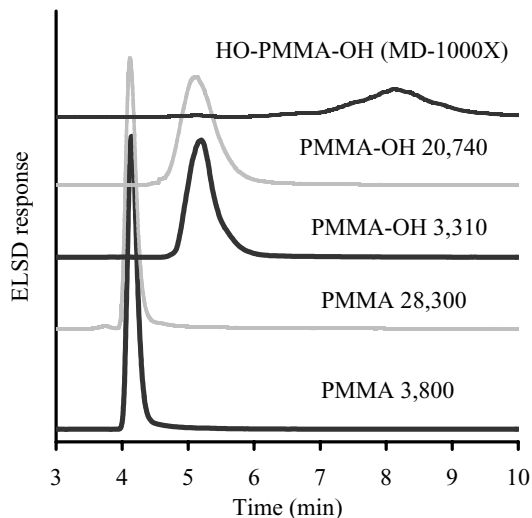


Fig. 3. Representative OH-based separations (chromatograms) of PMMA functional polymers at 25 °C. Detector ELSD, mobile phase 43% acetonitrile in DCM, flow rate 0.5 ml/min, injection volume 10 μ l, sample concentration 1 mg/ml in DCM, home-packed silica column (150 mm \times 4.6 mm i.d.; 3 μ m particles; 100 Å pore size).

composition, 43% acetonitrile in dichloromethane, was obtained when the flow rate used was 0.1, 0.5, or 1.0 ml/min. The temperature had very little effect on the retention of the PMMA standards between 25 and 50 °C. Because sample VL37B contained fractions with zero, one, and two OH end-groups [30], it was selected as a sample material in the following discussion. As shown in Fig. 4, the base-line separations of sample VL37B according to the hydroxy functionality were not affected when the column temperature changed from 25 to 50 °C, although the retention times of mono-functional and bi-functional polymers somewhat decreased when the temperature increased.

The effect of the mobile-phase composition is illustrated in Fig. 5. Only one tailing peak was obtained when 70% acetonitrile in dichloromethane was used as mobile phase. Two ill-resolved peaks were observed when the acetonitrile concentration decreased to 60%. Three barely discernible peaks were obtained at 55%. The separation of these three peaks was improved at 50% acetonitrile in dichloromethane. Base-line separations of sample VL37B based on hydroxy functionality were achieved when the mobile-phase

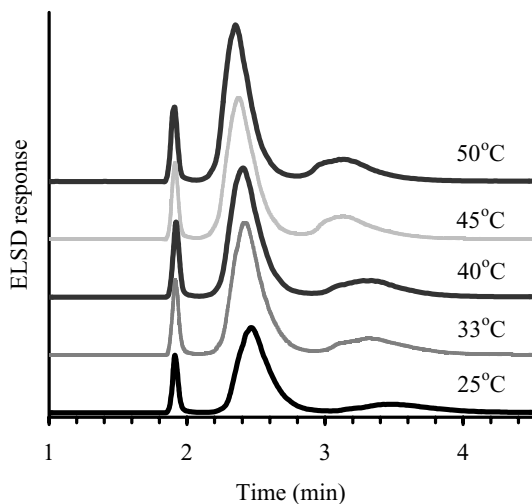


Fig. 4. Effect of the temperature on the separation of a PMMA functional polymer (VL37B). Detector ELSD, mobile phase 45% acetonitrile in DCM, flow rate 1.0 ml/min, injection volume 20 μ l, sample concentration 5 mg/ml in DCM, column as in Fig. 3.

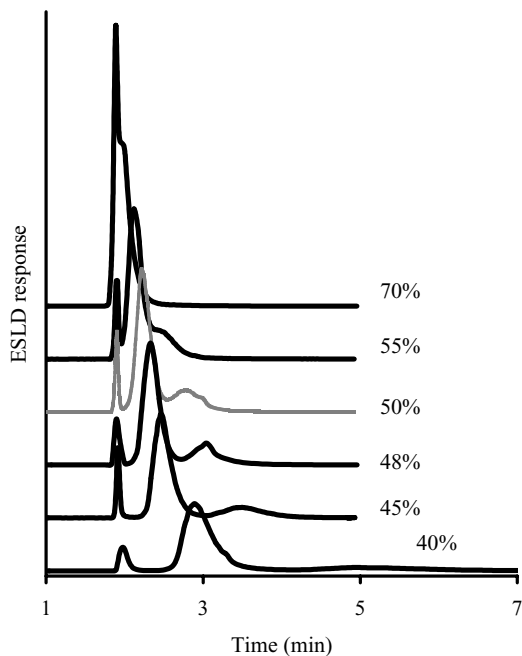


Fig. 5. Effect of mobile-phase composition effect on the separation of a PMMA functional polymer (VL37B). Detector ELSD, flow rate 1.0 ml/min, injection volume 20 μ l, sample concentration 5 mg/ml in DCM at 25 $^{\circ}$ C, column as in Fig. 3.

composition was between 48 and 40% of acetonitrile in dichloromethane. This is a substantial range in composition. Therefore, these “critical” conditions are quite robust. When the mobile-phase composition was below 40% acetonitrile in dichloromethane, bi-functional PMMA polymers were strongly retained on the column and molecular-weight (adsorption) effects became apparent.

3.2. Quantitative aspects

We have already shown that the isocratic separations of PMMA functional prepolymers based on hydroxy end-groups are quite robust with respect to fluctuations in the LC conditions, such as variations in temperature, mobile-phase composition, and flow rate. The OH base-line separations (the structures of the RAFT polymers and the derivatives) were confirmed by off-line MALDI-TOF-MS and on-line LC-ESI-MS [30]. However, mass spectrometry is not suitable for quantitative analysis due to discrimination in the ionization efficiency. The problem of quantitative analysis arises not only in MS, but also in all chromatographic techniques [31], since many of the typical HPLC detectors are not very relevant for the analysis of PMMA samples. For example, lack of suitable chromophores in PMMA prohibits the use of UV and fluorescence detectors in practice. Refraction-index (RI) detectors are not sufficiently sensitive and are easily interfered by the sample solvent and fluctuations in the mobile-phase composition due to the great difference in refractive index between the two mobile-phase solvents (acetonitrile, $n_D^{20} = 1.344$, and dichloromethane, $n_D^{20} = 1.424$).

In recent years, evaporative light-scattering detection has become increasing popular in HPLC, due to its “universal” applicability for all non-volatile analytes [32]. However, quantitative analysis using an ELSD is not easily achieved [22,31,32], because its response depends on operating parameters (mobile phase, gas pressure, temperature) as well as on the nature of the polymer (monomeric unit, molecular weight, end-groups). Moreover, the response of such an instrument is generally not linear with concentration, but it can be expressed by an exponential relation [6,20,31]. Calibration curves should be established carefully. An exponential calibration curve, such as in

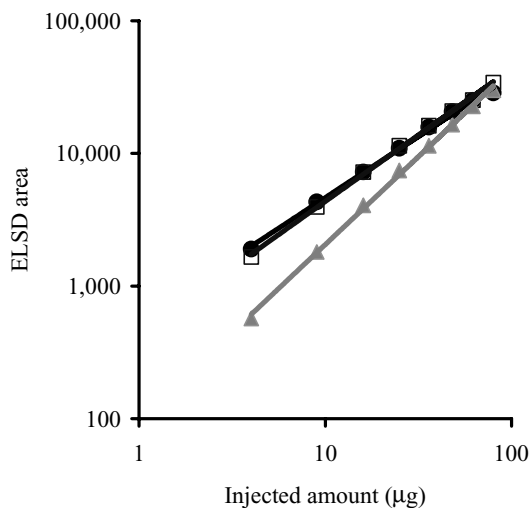


Fig. 6. ELSD calibration curves (logarithmic scale) for PMMAs with different end-groups. Circles: PMMA 2900; open squares: PMMA-OH 3310; triangles: MD-1000X. Mobile phase 42% acetonitrile in DCM, flow rate 0.5 ml/min at 25 °C, column as in Fig. 3.

Eq. (1), is often used [31]:

$$A = a \times m_i^b \quad (1)$$

where A is the ELSD response area, m_i is the injected sample amount, and a and b are constants. The values of a and b can easily be determined from a logarithmic plot, in which the exponent b is obtained from the slope and the constant a from the intercept of the regression line. Fig. 6 shows ELSD calibration curves of PMMAs with different end-groups and very similar molecular weights. The values of a and b are shown in Table 2. It can be seen from Fig. 6 and Table 2 that the OH end-groups had a significant influence on the ELSD response. An exponent b of 0.999 indicates a good linear ELSD response for PMMA samples with one OH end-group. The

Table 2
End-group effect on ELSD calibration curves, LC conditions as in Fig. 6

Sample	a	b	R^2
PMMA 2900	556.7	0.921	0.9973
PMMA-OH 3310	436.1	0.999	0.9984
HO-PMMA-OH (MD-1000X)	97.5	1.324	0.9985

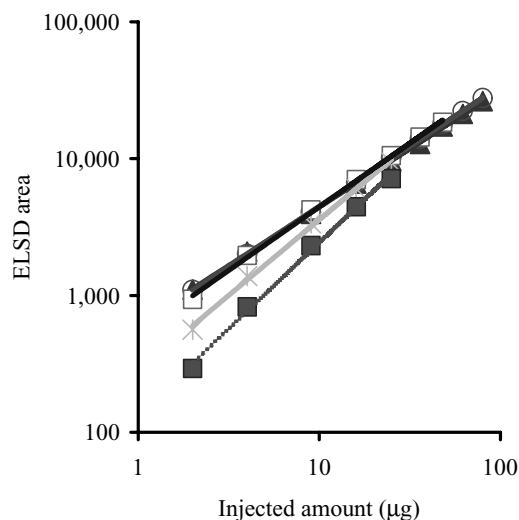


Fig. 7. Effect of mobile-phase flow rate on ELSD calibration curve (logarithmic scale) for PMMA standard ($M_p = 9200$). Triangles: 0.1 ml/min; open circles: 0.3 ml/min; open squares: 0.5 ml/min; stars: 0.75 ml/min; squares: 1.0 ml/min. Mobile phase 42% acetonitrile in DCM, temperature 25 °C, column as in Fig. 3.

mobile-phase flow rate was found to have a clear effect on the ELSD response as shown in Fig. 7 and in Table 3. The molecular weights of PMMA standards were found to have only a minor effect on ELSD calibration in our study (molecular-weight range investigated from 1680 to 28,300, results not shown). This is in agreement with the results reported in the literature [31,33–35]. The calibration curves in Fig. 6 could therefore be used for the quantitative analysis of functional PMMA prepolymers under the specified LC conditions (42% acetonitrile in dichloromethane at 0.5 ml/min). Some representative results are shown in Table 4.

Table 3
Flow rate effect on ELSD calibration curve (PMMA 9200), LC conditions as in Fig. 7

Flow rate (ml/min)	a	b	R^2
0.1	619.0	0.854	0.9996
0.3	594.2	0.879	0.9999
0.5	522.3	0.930	0.9988
0.75	280.3	1.106	0.9972
1.0	133.8	1.261	0.9960

Table 4
Quantitative analysis of hydroxy-functional PMMAs by LC-ELSD

Sample	Non-functional (%)	Mono-functional (%)	Bi-functional (%)
VL37A	10	90	0
VL37B	6	83	11
VL47A (PMMA–OH 3310)	0	100	0
VL47B	0	13	87
VL57	0	12	88

Isocratic conditions and column as in Fig. 6. Sample volume 20 μ l for all injections (samples as indicated in Table 1).

4. Conclusions

The critical solvent compositions for non-functional, mono-functional and bi-functional hydroxy PMMAs were determined in normal-phase LC using mixtures of acetonitrile and dichloromethane of varying composition. The low-molecular-weight PMMAs were successfully separated according to hydroxy functionality (zero, one, or two OH groups, respectively) at the critical conditions. Fast (5 min), base-line separations were obtained independent of molecular weight. The separations were shown to be quite robust, as changing the column temperature, flow rate, and mobile-phase composition within reasonable ranges did not affect the resolution.

Under appropriate conditions, reliable ELSD calibration curves could be obtained and these were used for the quantitative analysis of hydroxy-functional PMMA prepolymers at the robust critical condition of 42% acetonitrile in dichloromethane at 0.5 ml/min.

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