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Utilising matrix-assisted laser desorption/ionisation techniques for the generation of structural information from different end-group functionalised poly(methyl methacrylate)s

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ABSTRACT

End-group characterisation of three functionalised poly(methyl methacrylate) (PMMA) samples was performed by means of matrix-assisted laser desorption/ionisation-mass spectrometry (MALDI-MS). MALDI-time of flight (MALDI-TOF) data were employed to generate information about the initiators and chain-transfer agents used for the polymerisations. Further confirmation of the structural assignments was gleaned from MALDI-collision-induced dissociation (MALDI-CID) experiments. This latter technique is a powerful method for generating information on the masses of individual end groups.

1. Introduction

Polymer molecular weight, in free radical polymerisation, can be controlled with appropriate chain-transfer agents such as mercaptans [1]. In addition to controlling molecular weight, chain-transfer agents can also be employed to introduce a range of useful functionalities on the ends of polymer chains. The use of cobalt complexes in catalytic chain-transfer polymerisation (CCTP) [2,3] of methyl methacrylate (MMA), for example, is a relatively efficient means to introduce unsaturated terminating end groups on the PMMA molecule. PMMA with substituted alkylic end groups has also been prepared by an addition-fragmentation chain-transfer mechanism using 2,4-di-phenyl-4-methyl-1-pentene (i.e. α-methylstyrene dimer) (AMSD) [4].

Nuclear magnetic resonance (NMR) spectroscopy is the standard analytical technique for generating information on the backbone structure, and often end-group functionalisation, of soluble synthetic polymers [5]. Mass spectrometric characterisation of free radical and other polymers of alkyl methacrylates, typically with either matrix-assisted laser desorption/ionisation (MALDI) [6–25] or electrospray ionisation (ESI) [26–35], has been shown to be very useful in aiding the identification of end groups in these systems. The latter ionisation technique is particularly powerful when characterising polymers with labile end groups [24,27], but MALDI is still the standard methodology for end-group characterisation of acrylics (alongside NMR spectroscopy). This is mainly due to the simplicity of the spectra obtained with MALDI when compared to those from ESI (due to the presence of peaks from the multiply charged ions generated by the latter technique).

Further information on end-group structure from alkyl methacrylate polymers may be obtained using tandem mass spectrometry (MS/MS) techniques [19–21,24,36–40]. The advantage of these techniques over MALDI-time of flight (MALDI-TOF) mass spectrometry (MS) is their ability to calculate individual end-group masses from the MS/MS data. The combined masses of the end groups are typically obtained using MALDI-TOF or ESI-MS. MS/MS experiments with either MALDI (MALDI-collision-induced dissociation, MALDI-CID) or ESI (ESI-MS/MS) have been shown to be useful in aiding the identification of end groups from acrylic polymers [19–21,24,36–38,40,41].

This paper describes the characterisation of the end groups arising from the various possible chain-transfer mechanisms in the free radical polymerisation of MMA by means of both MALDI-TOF and MALDI-CID, in conjunction with NMR spectroscopy. Three different types of chain-transfer agent were employed in this study, namely bis(boron difluorodiphenylglyoximate) cobalt (II) (COBF)

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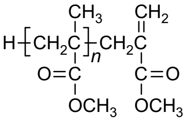
(to generate **1**), *n*-dodecylmercaptan (DDM) (to generate **2**) and AMSD (to generate **3**).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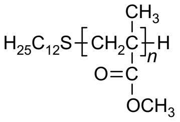
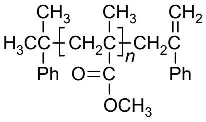
1


$H_{25}C_{12}S{-}[CH_2C(CH_3)(COOCH_3)]_n{-}H$

2


$H_3CC(CH_3)(Ph){-}[CH_2C(CH_3)(COOCH_3)]_n{-}CH_2C(=CH_2)Ph$

3

2. Experimental

2.1. Polymer synthesis

All PMMA samples were prepared by suspension polymerisation in demineralised water at 85 °C using 2,2′-azobis (isobutyronitrile) (AIBN) or 2,2′-azobis (2-methyl butanenitrile) (AMBN) as initiator. The resultant polymers were washed with copious amounts of water and dried in an air circulating oven at 70 °C. In the case of sample **3**, unreacted AMSD was then removed by dissolving the polymer in dichloromethane, precipitating in *n*-hexane and drying the recovered polymer in an air circulating oven at 70 °C. Table 1 details the amounts of chain-transfer agent and initiator employed. The molecular weight averages of the resultant PMMA samples were measured by gel-permeation chromatography (GPC) (in a chromatograph from Polymer Laboratories, Church Stretton, UK). The GPC data were acquired in chloroform at 23 °C using 2 × 10 μm mixed B columns (Polymer Laboratories) and an infra-red detector fixed at 1695 cm^{-1}, calibrated with linear PMMA standards.

2.2. Mass spectrometry

The time-lag focusing MALDI data were obtained using a Tof-Spec 2E (Waters MS Technologies, Manchester, UK) MALDI-TOF mass spectrometer, operated at an accelerating voltage of 20 kV in the reflectron mode of operation. A VSL-337i nitrogen laser (Laser Science Inc., Newton, MA, USA) was employed, operating at 337 nm with a pulse width of 4 ns and a maximum energy output of 180 mJ. Further instrumental details are described elsewhere [14,42].

MALDI-CID experiments were performed in an AutoSpec 5000 orthogonal acceleration (oa)-TOF (Waters MS Technologies) tandem mass spectrometer equipped with a MALDI source. This hybrid sector-oa-TOF instrument has been described in more detail elsewhere [43,44]. The nitrogen laser ($\lambda = 337$ nm) was operated at a pulse rate of 10 Hz in the MALDI source. The laser energy per pulse was approximately 80 μJ in these experiments. The precursor ions, accelerated by a voltage of 2 kV, were selected by MS-1 [double focusing (EBE) mass spectrometer]. These ions were decelerated to an energy of 800 eV and focused into the collision cell. The precursor ion beam intensity was attenuated by approximately 70% using xenon as the collision gas. Ions exiting the collision cell were directed into the oa-TOF analyser (MS-2). The voltage pulse applied to the oa-TOF is automatically timed to coincide, because of the pulsed nature of the MALDI technique, with the time at which the packet of precursor and product ions are passing through the orthogonal acceleration chamber. The product ions are detected by the microchannel plate detector that has a total length of 150 mm. The full product ion spectrum was therefore recorded by MS-2. All data were processed by means of the OPUS software. The number of laser shots that were averaged to obtain a spectrum was approximately 5000 (which corresponds to an acquisition time of approximately 10 min).

All solutions were prepared at a concentration of 10 mg mL^{-1} for MALDI-TOF and MALDI-CID experiments. The matrix used was dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) which was obtained from Aldrich. Intense ion peaks were observed in the MALDI-TOF spectra from other PMMA polymers when this matrix was used [14]. The matrix and PMMA samples were dissolved in chloroform (Fisher) and mixed in a matrix-to-analyte ratio of 5:1. Fifty microlitres of this solution was mixed with 1 μL of a solution of sodium acetate (Sigma, Steinheim, Germany) in HPLC grade methanol (Aldrich), prior to deposition of approximately 0.5 μL on the sample plate. Sodiated oligomers of PMMA were previously shown to generate MALDI-CID spectra with high signal-to-noise values and, more importantly, fragment ion peaks from which end-group information can be inferred [38]. The signal-to-noise ratios, for the analogous structurally significant fragment ion peaks, were found to decrease when alkali metal cations (rubidium and caesium ions) with greater radii were employed in MALDI-CID experiments for this polymer.

2.3. Nuclear magnetic resonance (NMR) spectroscopy

Both ^1H and ^{13}C NMR spectra of PMMA polymers were acquired from deutero-chloroform solutions at an ambient temperature in a GSX 400 (JEOL, Welwyn, UK) spectrometer operating at 400.05 MHz for ^1H NMR (with the exception of ^1H NMR data from **3**, which were generated using 1,1,2,2-tetrachloroethane-d_2 as solvent). The principal parameters used were: 90° pulse width; acquisition time of 0.65 s; delay between pulses 1.7 s; 32,000 points were transformed and processed with 2.5 Hz exponential line broadening and approximately 16,000 scans were acquired to achieve reasonable signal-to-noise ratios.

3. Results and discussion

The use of COBF or AMSD as chain-transfer agents for methacrylate polymerisation is of interest because of the possibility of post-reacting the vinyl- or alkylic-ended polymer chains which are formed [2,3,45]. The synthesis of these functionalised polymers was fairly straightforward, but it was noted that the chain-transfer efficiency of each reagent varied quite considerably. Only minute amounts of COBF are required, for example, to control M_n to 3000 [10], whilst significant levels of AMSD must be employed to achieve comparable M_n control. This is consistent with published values for the chain-transfer constant (C_s) for these reagents in MMA polymerisations, e.g. C_s (COBF) is approximately 20,000 [3] and C_s (AMSD) is 0.13 [4,46,47]. This contrasts with a typical C_s of 0.67 for an alkyl mercaptan [48,49].

Understanding the structure and quantity of these unsaturated end groups of each polymer formed is clearly useful information to have when designing the final macromolecular structure, for example when utilising these reactive polymers as macromonomers in graft copolymer synthesis. Both ^1H- and ^{13}C NMR spectroscopies have been used to study the end groups of PMMA oligomers derived from COBF [50], but detailed structural information is difficult to obtain on the initiators used to generate these polymers using these techniques. Previous work on identifying the end groups of PMMA and other poly(alkyl methacrylates) by MALDI-TOF [6,7,9–19,24,28] and MALDI-CID [19–21,24,36–38] suggested that the use of these techniques might be appropriate to

Table 1
Recipe and molecular weight information for PMMA samples.

Sample	CTA type	CTA amount (mol%)	Initiator type	Initiator amount (mol%)	M_w	M_n	PDI
1	COBF	7.9×10^{-4}	AMBN	0.39	6780	3000	2.26
2	DDM	1.58	AIBN	0.31	13,100	6750	1.94
3	AMSD	4.06	AIBN	0.87	15,700	7600	2.08

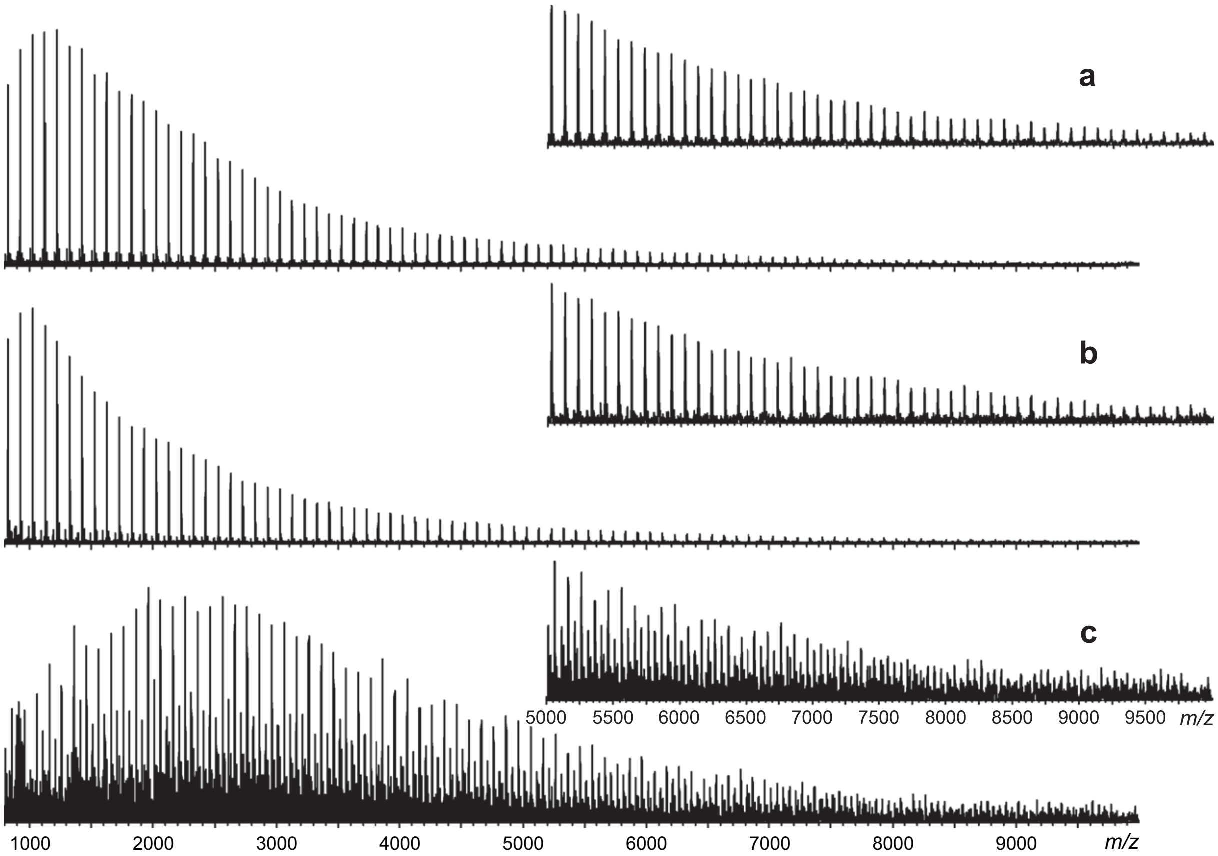


Fig. 1. MALDI-TOF spectra from PMMA polymers generated with: (a) COBF added for CCTP; (b) DDM as CTA and (c) AMSD as CTA. Expansions (*m*/*z* 5000–10000) of the spectra are also displayed.

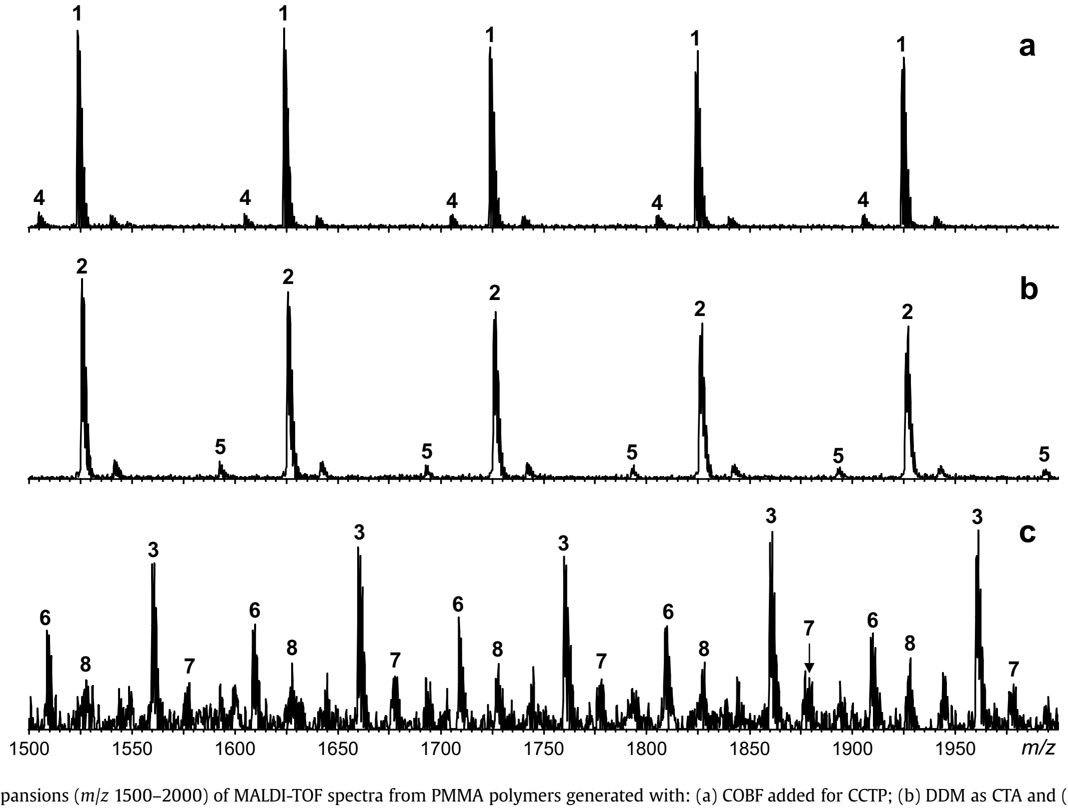


Fig. 2. Annotated expansions (*m*/*z* 1500–2000) of MALDI-TOF spectra from PMMA polymers generated with: (a) COBF added for CCTP; (b) DDM as CTA and (c) AMSD as CTA. See text for proposed structures corresponding to the annotation (**1**–**8**).

Table 2
Experimental and calculated mass-to-charge ratios for PMMA samples.

Proposed structure	Repeat units	Empirical formula	Calculated *m/z*	Experimental *m/z*
1	15	$C_{80}H_{128}O_{32}Na$	1623.8	1623.9
2	15	$C_{87}H_{146}O_{30}SNa$	1726.0	1725.9
3	15	$C_{93}H_{140}O_{30}Na$	1759.9	1760.0
4	15	$C_{85}H_{135}NO_{32}Na$	1704.9	1704.9
5	15	$C_{79}H_{127}NO_{30}Na$	1592.8	1592.7
6	15	$C_{88}H_{135}NO_{30}Na$	1708.9	1708.9

complement data from NMR spectroscopy for the polymers described here.

MALDI-TOF data have previously been employed to generate information on the end groups of PMMA polymers generated with COBF or similar cobalt complexes in CCTP, with unsaturated ends noted to be present [7,8,10,15,16]. Information on the initiator used was also gleaned in one example where high amounts of AMBN were added [7]. Characterisation of end groups of PMMA, generated by addition-fragmentation chain-transfer with hydroxyethyl methacrylate [9] and benzyl methacrylate [18] dimer, by means of MALDI-TOF has also been demonstrated.

The MALDI-TOF spectra from all three of the PMMA polymers are presented in Fig. 1. The spectra are typical to those obtained from free radical polymers and it is noted that the high molecular weight tail of oligomers is not detected, as may be expected from previous work [51]. The aim of the current study, however, was to generate information on the structure of the end groups of these samples, rather than average molecular weight values which can be obtained adequately for these systems using GPC (see Table 1). The data for all three samples indicate that the major components are those expected (i.e. **1**–**3**).

Expansions (*m/z* 1500–2000) of the MALDI-TOF spectra are displayed in Fig. 2 and are annotated with some of the proposed assignments for the peaks. The major series of peaks in all cases (separated by *m/z* 100 as expected for PMMA) is consistent with the presence of **1** (Fig. 2(a)), **2** (Fig. 2(b)) and **3** (Fig. 2(c)). Sodium acetate was added during sample preparation for MALDI-TOF experiments, resulting in peaks from sodiated oligomers ($[M+Na]^+$) being dominant in the spectra. It should be noted that there is also evidence for the presence of low intensity peaks from potassiated species (i.e. $[M+K]^+$) in these data. Peaks at *m/z* 1623.9 (Fig. 2(a)), *m/z* 1725.9 (Fig. 2(b)) and *m/z* 1760.0 (Fig. 2(c)), for example, are consistent with the expected structures for these PMMA polymers (i.e. **1**, **2** and **3** respectively). A comparison between the experimental and calculated mass-to-charge ratios for these oligomers is shown in Table 2 for reference.

Information on the initiators used to make these three polymers can also be gleaned from the MALDI-TOF data. This is where MALDI-TOF has significant advantages over NMR spectroscopy, as

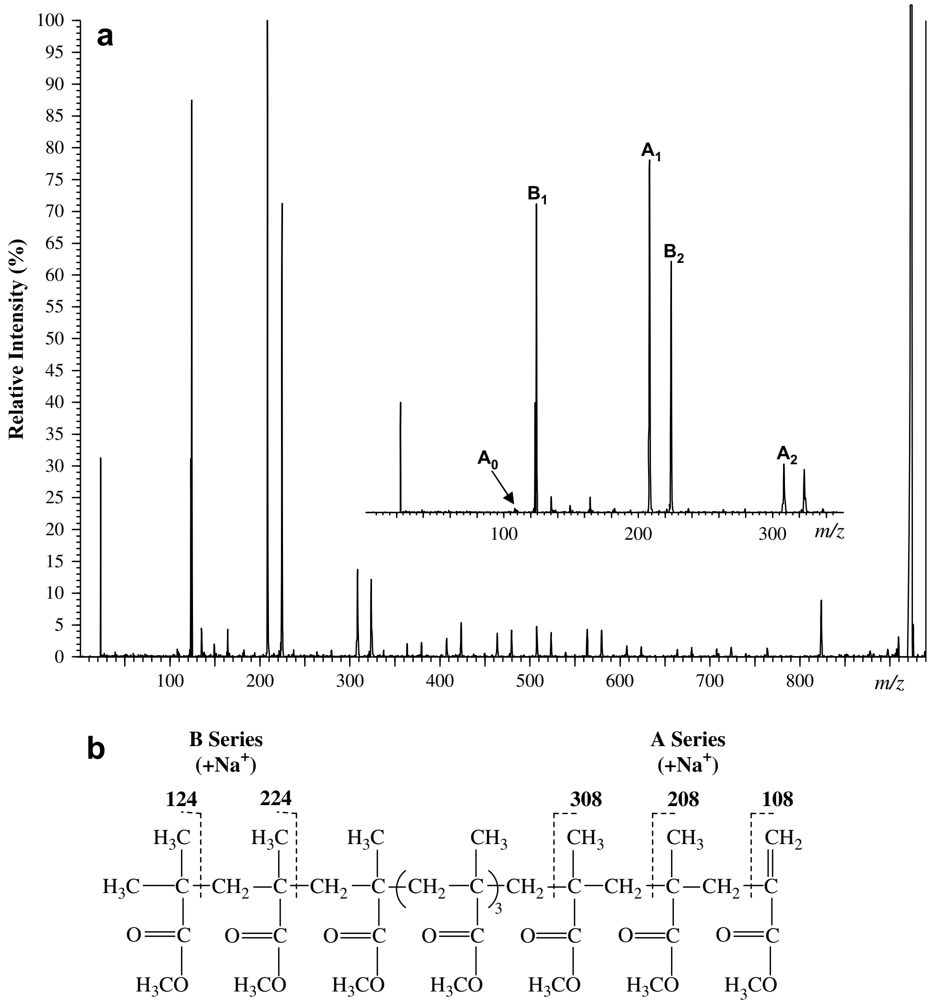
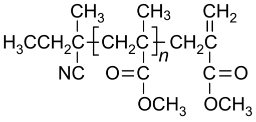
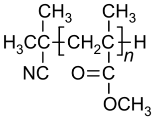


Fig. 3. (a) MALDI-CID spectrum from sodiated octamer ($[M+Na]^+$, *m/z* 923) of **1**. Inset is annotated expansion (*m/z* 0–350) of spectrum. (b) Proposed fragmentation scheme (**A*n*** and **B*n*** series) for sodiated octamer of **1**, indicating how end-group information may be inferred.

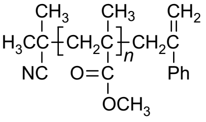
the latter technique has problems detecting these relatively minor components in the samples. A minor series of peaks, again separated by m/z 100 as expected for PMMA, in each of the three spectra can be used to generate information on the initiating systems used. These peaks are labelled **4**, **5**, and **6** in Fig. 2(a), Fig. 2(b) and Fig. 2(c) respectively. All of these components are proposed to contain a fragment of the azo-based initiator at the α-end of the polymer chain. Good agreement between experimental and calculated mass-to-charge ratios for these oligomers is again indicated by the data shown in Table 2. These data allow differentiation between the initiators employed, indicating that AIBN was used for two of the polymers (with AMSD and DDM as chain-transfer agents) and AMBN for the other (with COBF for CCTP), as expected from the polymer synthesis.


$H_3CCH_2C(CH_3)(NC){-}[CH_2C(CH_3)(C(=O)OCH_3)]_n{-}CH_2C(=CH_2)C(=O)OCH_3$

4

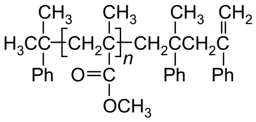

$H_3CC(CH_3)(NC){-}[CH_2C(CH_3)(C(=O)OCH_3)]_n{-}H$

5

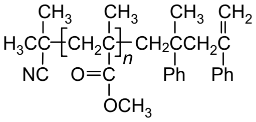

$H_3CC(CH_3)(NC){-}[CH_2C(CH_3)(C(=O)OCH_3)]_n{-}CH_2C(=CH_2)Ph$

6

The ^1H NMR data from the polymer made with AMSD as chain-transfer agent indicate that a second terminating end-group functionality is present at approximately 20% of the abundance of the expected unsaturated group (as in **3** and **6**). This end group is proposed to contain two units of α-methylstyrene at the terminating end of this PMMA. There is also evidence for the presence of this functionality in the MALDI-TOF data from the same polymer, with two types of oligomeric species matching this proposed end group. Peaks annotated in Fig. 2(c), which have fragments of AMSD (**7**) and the AMBN used as initiator (**8**), are consistent with the proposed structures from the NMR data. Furthermore, the combined peak intensity of peaks from **7** and **8** are approximately as expected, compared to peaks from **3** and **6**, from the levels proposed from NMR spectroscopy. The mechanism of formation of this additional terminating end-group functionality is presently not understood.


$H_3CC(CH_3)(Ph){-}[CH_2C(CH_3)(C(=O)OCH_3)]_n{-}CH_2C(CH_3)(Ph)CH_2C(=CH_2)Ph$

7


$H_3CC(CH_3)(NC){-}[CH_2C(CH_3)(C(=O)OCH_3)]_n{-}CH_2C(CH_3)(Ph)CH_2C(=CH_2)Ph$

8

MALDI-TOF is a very powerful method for end-group characterisation of polymers, especially for confirming the identity of structural features of synthesised samples. The combined masses of the end groups can be calculated from the peaks in the spectra (by subtracting the masses of a number of repeat units of the polymer, plus the mass of the cation used in the experiment, from the m/z of the ions detected). More information on individual end-group masses can be obtained for many polymer systems, including PMMA [37], using MS/MS experiments. This can be very useful

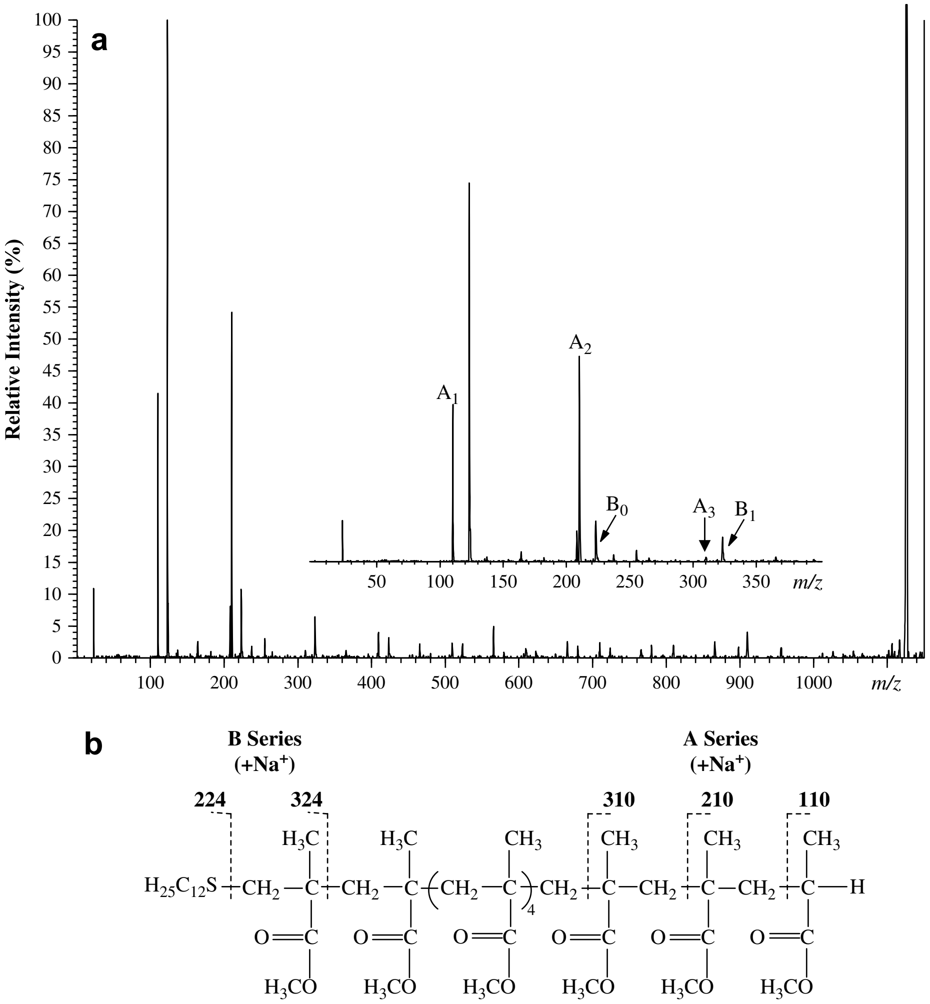


Fig. 4. (a) MALDI-CID spectrum from sodiated nonamer ($[M+Na]^+$, m/z 1125) of 2. Inset is annotated expansion (m/z 0–400) of spectrum. (b) Proposed fragmentation scheme ($\mathbf{A}_n$ and $\mathbf{B}_n$ series) for sodiated nonamer of **2**, indicating how end-group information may be inferred.

when trying to identify unknown end-group structures, as has been shown previously [19,24]. Individual oligomers are studied in these MS/MS experiments, so that many different structures in a polymer system can be analysed separately if required.

The MALDI-CID spectrum obtained from the sodiated octamer of **1** (*m*/*z* 923) is shown in Fig. 3(a). This spectrum has an appearance similar to that noted previously for PMMA polymers [19,24,36–38], with fragment ion peaks at low mass-to-charge ratios dominating. Two series, each separated by *m*/*z* 100 (mass of the repeat unit of the polymer) are annotated in the expansion (*m*/*z* 0–350) of the MALDI-CID spectrum shown in Fig. 3(a). These two series of peaks may be used to generate information on the masses of the individual initiating (α) and terminating (ω) end groups, as proposed previously [37]. One series (labelled as $\mathbf{A}_n$ in the expansion of the MALDI-CID spectrum shown in Fig. 3(a)) can be used to calculate the mass of the ω-end unit and the other series ($\mathbf{B}_n$ in Fig. 3(a)) may be employed for the mass of the α-end group. A fragment ion scheme for these two series of peaks is shown in Fig. 3(b), indicating how the end-group masses can be inferred from their mass-to-charge ratios. Equations that allowed the end-group masses to be calculated from the mass-to-charge ratios of these peaks were previously described [37]. Subtracting the mass of the cation (23 for Na^+) and a portion of a monomer unit (86 Da) from one of the ions of the $\mathbf{A}_n$ series ($\mathbf{A}_1$ at *m*/*z* 208) gives a ω-end-group mass of 99 Da for **1**. Furthermore, subtracting the mass of the cation and a whole monomer unit (100 Da) from one of the ions of the $\mathbf{B}_n$ series ($\mathbf{B}_1$ at *m*/*z* 124) leads to the mass of the α-end group of **1** being 1 Da.

The MALDI-CID spectrum from the sodiated nonamer of **2** ($[\mathrm{M}+\mathrm{Na}]^+$ with *m*/*z* 1125) is displayed in Fig. 4(a), along with an annotated expansion (*m*/*z* 0–400). Low *m*/*z* peaks again dominate the fragment ion spectrum, but there are some differences from that previously noted for other PMMA polymers (*vide supra* and [19,24,36,38]). Peaks from the $\mathbf{A}_n$ series ($\mathbf{A}_1$ at *m*/*z* 110, $\mathbf{A}_2$ at *m*/*z* 210 and $\mathbf{A}_3$ at *m*/*z* 310) indicate that the terminating unit of the polymer is as expected, as shown by the fragmentation scheme in Fig. 4(b). Subtraction of the mass of a portion of the monomer and the cation (as above and described previously [37]) from the *m*/*z* of $\mathbf{A}_1$ indicates that the mass of the terminating end group is 1 Da, as for **2**. There is no second dominant series of peaks in the MALDI-CID spectrum, however, that can clearly be assigned to the $\mathbf{B}_n$ series and enable the mass of the α-end group to be calculated. Utilising the equation previously published that describes the link between the *m*/*z* of the precursor ion, and peaks of both the $\mathbf{A}_n$ series and $\mathbf{B}_n$ series [37], it can be calculated where the latter peaks would be expected to be observed in the MS/MS spectrum. The results of this calculation indicate that peaks of the $\mathbf{B}_n$ series would be expected at *m*/*z* $24+100n$, where *n* is a number of repeat units of the monomer. There are possibly peaks at very low intensity at *m*/*z* 224 and 324 in the spectrum in Fig. 4(a) that could be assigned to $\mathbf{B}_0$ and $\mathbf{B}_1$ respectively, as shown in the fragmentation scheme in Fig. 4(b). Another option for the structure of the α-end group, from the results of the calculation described above, would be a hydride (or the typical α-end functionality of polymers made by group-transfer polymerisation). The typical fragment ion pattern for these options

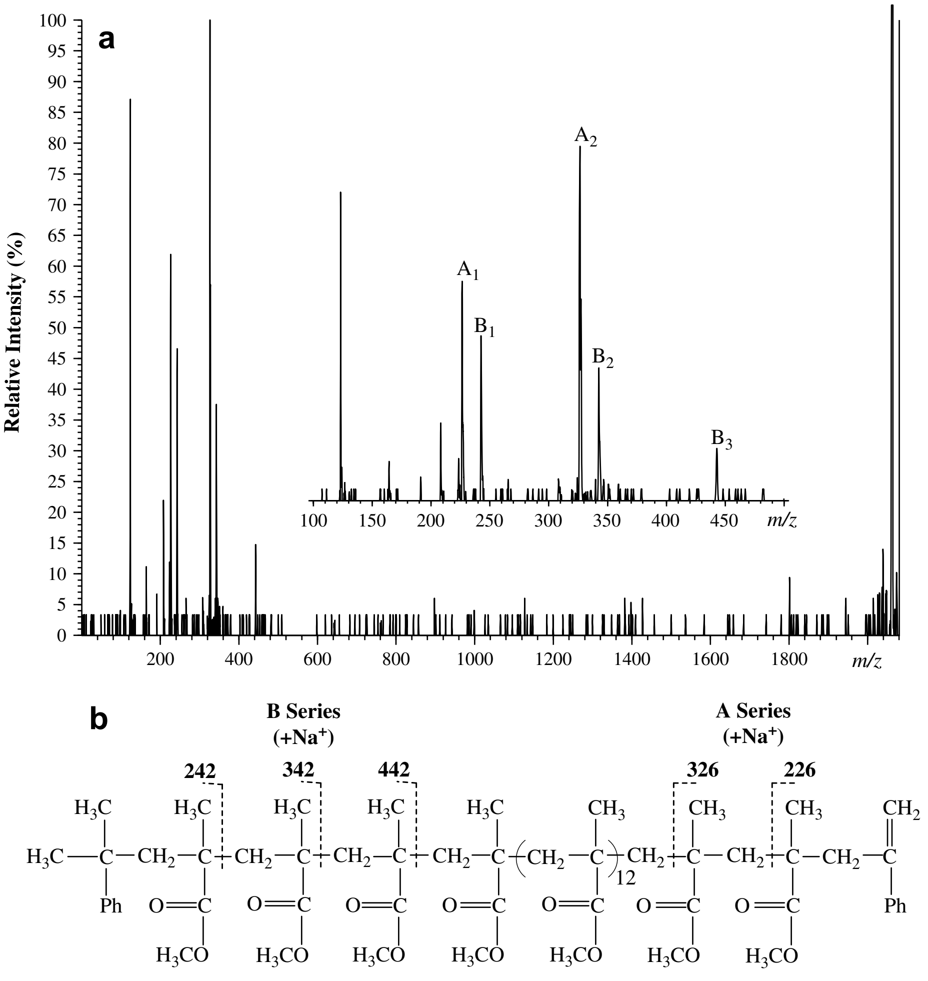


Fig. 5. (a) MALDI-CID spectrum from sodiated octadecamer ($[\mathrm{M}+\mathrm{Na}]^+$, *m*/*z* 2060) of **3**. Inset is annotated expansion (*m*/*z* 100–500) of spectrum. (b) Proposed fragmentation scheme ($\mathbf{A}_n$ and $\mathbf{B}_n$ series) for sodiated octadecamer of **3**, indicating how end-group information may be inferred.

[36,38–40], however, is very different to that seen in Fig. 4(a), indicating that these can be ruled out as likely end-group structures.

It was recently proposed that differing fragmentation for poly(styrene) made with a mercaptan as CTA, when compared to those made by anionic polymerisation with butyl groups at the α-end of the chain, could be explained by losses of part or the whole of the thio-ether unit as a consequence of the low energies required to break the carbon-to-sulphur bond [52]. MS/MS results from another alkyl methacrylate polymer, poly(2-hydroxyethyl methacrylate), made with DDM as CTA were analogous to that seen for PMMA [unpublished data].

Further confirmatory evidence for the presence of the thio-ether on the α-end group of **2** can be obtained from other series of peaks seen in the MALDI-CID spectrum shown in Fig. 4(a). Four minor series of peaks are typically noted to be present in MS/MS spectra of alkyl methacrylates that can be used to generate information about end-group masses [37,40] and sequences of copolymers [20,21]. Two of each series retain the α- or ω-end groups of the polymer, with the $\mathbf{C}_{\boldsymbol{n}}$ series and $\mathbf{F}_{\boldsymbol{n}}$ series containing the initiating species and the $\mathbf{D}_{\boldsymbol{n}}$ series and $\mathbf{E}_{\boldsymbol{n}}$ series retaining the terminating group. These four series are indeed noted to be present (not annotated in Fig. 4(a)) in the MALDI-CID spectrum from **2** (for example, $\mathbf{C}_2$ at m/z 423, $\mathbf{D}_4$ at m/z 365, $\mathbf{E}_4$ at m/z 409 and $\mathbf{F}_2$ at m/z 379). A similar phenomenon, with regard to the very low intensity for the $\mathbf{B}_{\boldsymbol{n}}$ series and typical signal intensity for the $\mathbf{C}_{\boldsymbol{n}}$ series and $\mathbf{F}_{\boldsymbol{n}}$ series (all retaining the α-end group), was also noted for a polymer of 2-hydroxyethyl methacrylate made with DDM as CTA [unpublished data]. This indicates that this pattern (and mass-to-charge ratios for the $\mathbf{C}_{\boldsymbol{n}}$ series and $\mathbf{F}_{\boldsymbol{n}}$ series) for these three series is an indicator for the presence of DDM as CTA.

A low intensity fragment ion spectrum was obtained from the sodiated octadecamer of **3** ($[\mathrm{M}+\mathrm{Na}]^+$ at m/z 2060), as shown in Fig. 5(a). The low signal-to-noise of the fragment ion peaks is a consequence of the low abundance of the precursor ion selected (it was noted that there was a low signal for this polymer in the MALDI-TOF experiment). These data, however, still allow information about the end groups to be gleaned. An annotated expansion (m/z 100–500) of the MALDI-CID spectrum is also displayed in Fig. 5(a) and a proposed fragmentation scheme is shown in Fig. 5(b). Peaks from the $\mathbf{B}_{\boldsymbol{n}}$ series ($\mathbf{B}_1$ at m/z 242, $\mathbf{B}_2$ at m/z 342 and $\mathbf{B}_3$ at m/z 442) and $\mathbf{A}_{\boldsymbol{n}}$ series ($\mathbf{A}_1$ at m/z 226 and $\mathbf{A}_2$ at m/z 326) allow the masses of the end groups to be calculated as described previously [37]. Subtraction of the mass of the cation and a monomer unit from the m/z of $\mathbf{B}_1$ indicates that the mass of the α-end group is 119 Da, which is correct for the saturated portion of AMSD in the proposed structure for **3**. The mass of the terminating end group is calculated as being 117 Da, by subtracting the mass of the cation and a repeat unit from the m/z of $\mathbf{A}_1$ (m/z 226). This equates to the expected unsaturated portion of AMSD that was used as the CTA in the generation of this sample.

The MALDI-CID data from **1**, **2** and **3** complement that from NMR spectroscopy and MALDI-TOF. These MS/MS data, for example, provide further evidence for the presence of a portion of the AMSD on both the α- and ω-end groups of the polymer chain in **3**. This is where the ability to generate information about masses of individual end groups can be very useful in structural identification from alkyl methacrylate polymers, often additional to that obtained by NMR spectroscopy and MALDI-TOF. This was also recently shown when studying PMMA generated by ATRP [19,24].

4. Conclusions

This work has shown that the use of the MALDI-TOF and MALDI-CID techniques can provide useful end-group information on various functionalised poly(methyl methacrylate)s. As well as confirming previous end-group studies of major components using NMR spectroscopy, this work has also shown the existence of various other end-group types in the polymers studied. The identification of the initiators used to make these polymers is typically possible from MALDI-TOF data, but is normally not gleaned from the respective NMR spectroscopic results.

The ability to generate the masses of individual end groups is a major advantage of the MALDI-CID experiments. The combination of NMR spectroscopy, MALDI-TOF and MALDI-CID mass spectrometry is a very powerful combination for the end-group characterisation of PMMA polymers.

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