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The generation of end group information from poly(styrene)s by means of matrix-assisted laser desorption/ionisation-collision induced dissociation

A.T. Jackson[a,*], A. Bunn[a], L.R. Hutchings[b], F.T. Kiff[b], R.W. Richards[b], J. Williams[c], M.R. Green[d], R.H. Bateman[d]

[a]ICI Research and Technology Centre, PO Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE, UK
[b]IRC in Polymer Science, Department of Chemistry, University of Durham, Durham DH1 3LE, UK
[c]Mass Spectrometry Research Unit, University of Wales, Swansea, Swansea SA2 8PP, UK
[d]Micromass, Floats Road, Wythenshawe, Manchester M23 9LZ, UK

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Abstract

Information on the masses of the end groups of four poly(styrene) polymers, with relatively low average molecular weights and polydispersities, has been obtained from matrix-assisted laser desorption/ionisation-collision induced dissociation (MALDI-CID) data. The masses of the end groups were calculated, using the equations shown, from the mass-to-charge ratios of two series of intense ion peaks that were observed at low mass-to-charge ratios in the MALDI-CID spectra. Certain mechanisms are proposed here to account for the formation of these ions and others that are observed in the spectra. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(styrene) polymers; Matrix-assisted laser desorption/ionisation-collision induced dissociation; Low molecular weight and polydispersity

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy remains the most potent single technique for the determination of end groups from synthetic polymers. Matrix-assisted laser desorption/ionisation-time of flight (MALDI-TOF) mass spectrometry [1,2] has been shown to be a powerful tool for the generation of end group information [3–8]. This is especially true when MALDI-TOF is employed in conjunction with NMR spectroscopy. The combined masses of the end groups of the polymer may be inferred by subtracting the mass of the cation (the oligomers are typically ionised by attachment of a cation such as sodium or silver ions, therefore forming species such as $[M + Na]^+$ or $[M + Ag]^+$) and a number of repeat units from the mass-to-charge ratio (*m*/*z*) of the intact oligomer ion peaks that are observed in the MALDI-TOF spectra [7]. The accuracy, to which the masses of the end groups may be calculated, is hence dependent on the error in the determination of the *m*/*z* of these adduct ions.

It has recently been shown that tandem mass spectrometry (MS/MS), especially when combined with MALDI, may be used to generate further information about the end groups of certain polymer systems [9–12]. Two intense series of ion peaks are observed in the spectra, from which the masses of the individual end groups of the polymer may be determined. This technique, termed MALDI-collision induced dissociation (CID), has been successfully used to determine the masses of end groups from poly(alkyl methacrylate) polymers [9,10] and, more recently, poly(styrene)s [12]. An individual oligomeric ion species is selected, from those generated from the polymer by MALDI, by means of a magnetic sector instrument. Fragmentation is induced by means of collisional activation in the collision region. An orthogonal acceleration-time of flight (oa-TOF) mass spectrometer is then used to determine the *m*/*z* of the fragment ions that are generated.

The MALDI-CID spectra from poly(styrene) standards (typically used in calibration for size exclusion chromatography), of narrow polydispersity and with molecular weights of up to 5000 Da, contained two intense series of ion peaks (denoted A and B), from the *m*/*z* of which the masses of the end groups could be determined [12]. The end groups of these standards were a butyl group and hydrogen. It was proposed that the masses of the end groups, from

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* Corresponding author. Tel.: + 44-1642-432147; fax: + 44-1642-432244.
E-mail address: tony_jackson@ici.com (A.T. Jackson).

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Table 1
Molecular weight and polydispersity of poly(styrene A), poly(styrene B), poly(styrene C) and poly(styrene D), as determined using size exclusion chromatography

Sample	Number average molecular weight (M_n)	Weight average molecular weight (M_w)	Polydispersity (M_w/M_n)
Poly(styrene) A	2600	2800	1.06
Poly(styrene) B	1600	1800	1.13
Poly(styrene) C	2400	2500	1.07
Poly(styrene) D	2800	2900	1.06

poly(styrene) polymers (1) with different initiator and terminating groups, could be inferred from the m/z of the two series of fragment ions using the equations shown below:

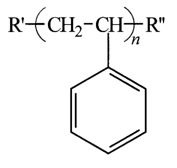
$$m/z(\mathrm{A}) = M(\mathrm{R}'') + 90 + 104n + M(\mathrm{Cat}) \quad (1)$$

$$m/z(\mathrm{B}) = M(\mathrm{R}') + 104 + 104n + M(\mathrm{Cat}) \quad (2)$$

where m/z(A) and m/z(B) are the mass-to-charge ratios of the ion peaks from the two series (denoted A and B, respectively). The mass of the cation is $M(\mathrm{Cat})$ and the masses of the end groups R″ and R′ are $M(\mathrm{R}'')$ and $M(\mathrm{R}')$, respectively [12]. Furthermore, it was proposed that these series of fragment ion peaks could be differentiated from others that are observed in the MALDI-CID spectra by the fact they are observed at low m/z and that:

$$m/z(\mathrm{precursor}) = m/z(\mathrm{A}) + m/z(\mathrm{B}) + 104n - M(\mathrm{Cat}) + 14 \quad (3)$$

where m/z(precursor) is the mass-to-charge ratio of the precursor ion.



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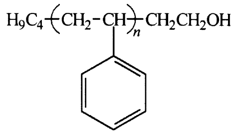
MALDI-CID data are presented in this article for four poly(styrene) polymers [poly(styrene) A, poly(styrene) B, poly(styrene) C and poly(styrene) D], with structures **2**–**5**. A variety of end groups have been introduced by using three different lithium initiators and/or capping the living polymer chains with one of three different terminating agents. The structures of these polymers were confirmed using data obtained by means of NMR spectroscopy. It is indicated how the masses of these end groups can be determined from the MALDI-CID spectra.



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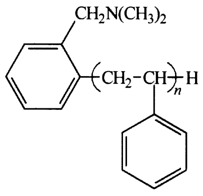

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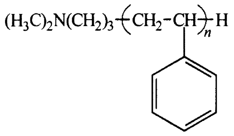

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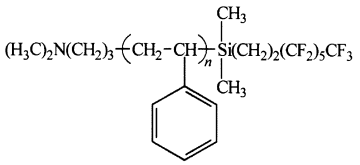

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2. Experimental

2.1. Polymer synthesis

Four poly(styrene) samples have been synthesised by anionic polymerisation using standard high vacuum techniques. Three different lithium initiators have been used along with three terminating agents to introduce a variety of end groups. Poly(styrene) A was initiated with *sec*-butyl lithium, polymerised in benzene and capped with ethylene oxide, which, when lithium is the counter-ion, results in the addition of a single ethylene oxide unit. Termination with methanol yields the alcohol end group. Poly(styrene) B was polymerised in 70/30 benzene/ether, initiated using *N*,*N*-dimethylbenzylaminolithium (synthesised according to the method of Schädler et al. [13]) and terminated with methanol. Poly(styrene) C and poly(styrene) D were prepared in the same experiment. Styrene was initiated by 3-(*N*,*N*-dimethylamino) propyllithium (synthesised according to the procedure of Hadjichristidis et al. [14]) and polymerised in benzene containing 1–2 ml THF. The living polymer was then divided into two, one half terminated with methanol to yield poly(styrene) C and the other half capped with 1H, 1H, 2H, 2H-perfluorooctyldimethylchlorosilane (Fluorochem) to yield poly(styrene) D. Molecular weights were obtained by size exclusion chromatography (SEC) using a conventional calibration of poly(styrene) standards and are shown in Table 1.

2.2. NMR spectroscopy

NMR spectra were recorded, for poly(styrene) A, poly(styrene) B, poly(styrene) C and poly(styrene) D, in a JEOL GSX 400 MHz NMR spectrometer, operating at 400 MHz and 100 MHz for ^{1}H and ^{13}C NMR spectroscopy, respectively. Three different solvents were used for ^{1}H NMR experiments, namely deutero-chloroform, deutero-dimethylsulphoxide and deutero-1,1,2,2-tetrachloroethane

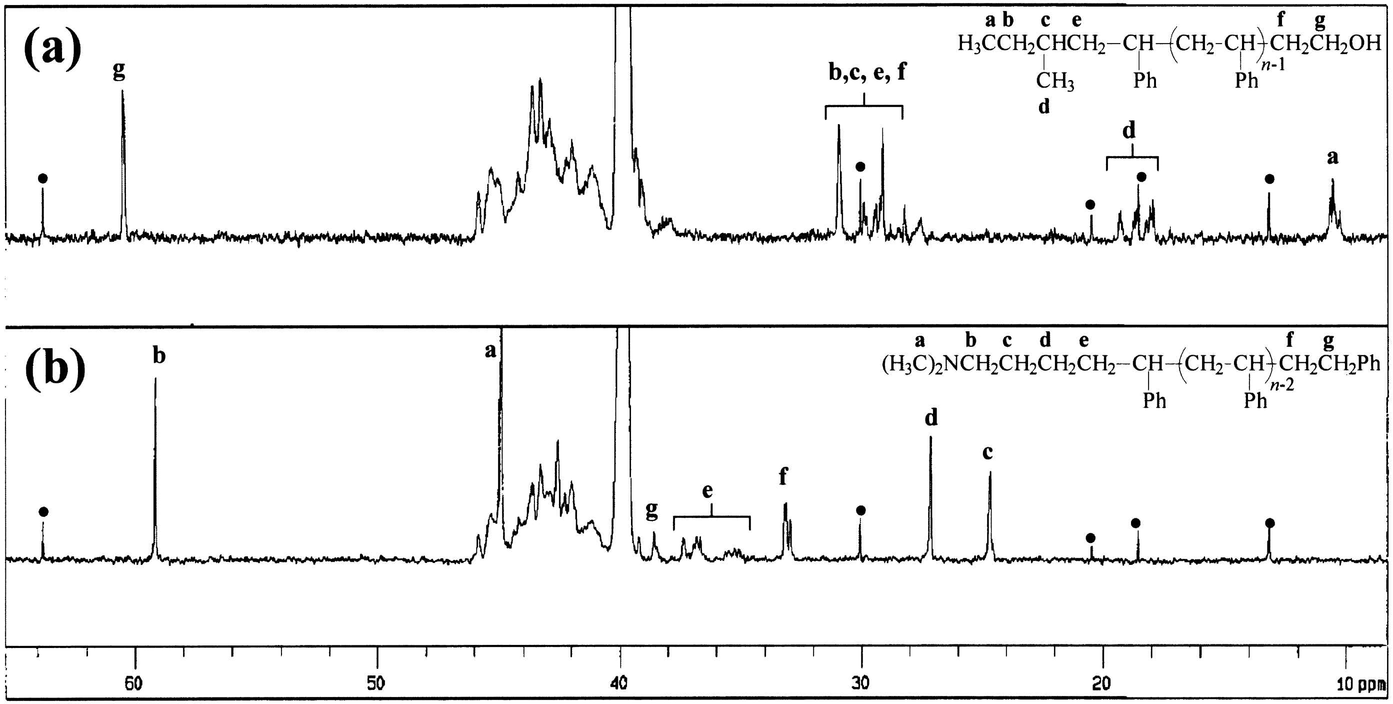


Fig. 1. Partial ^{13}C NMR spectra of: (a) poly(styrene) A; and (b) poly(styrene) C (taken in deutero-chloroform at 100 MHz frequency). The proposed assignments for peaks from end groups are also shown (● denotes butyl acetate as an impurity. Evidence for the presence of this compound was seen in the data from all four samples).

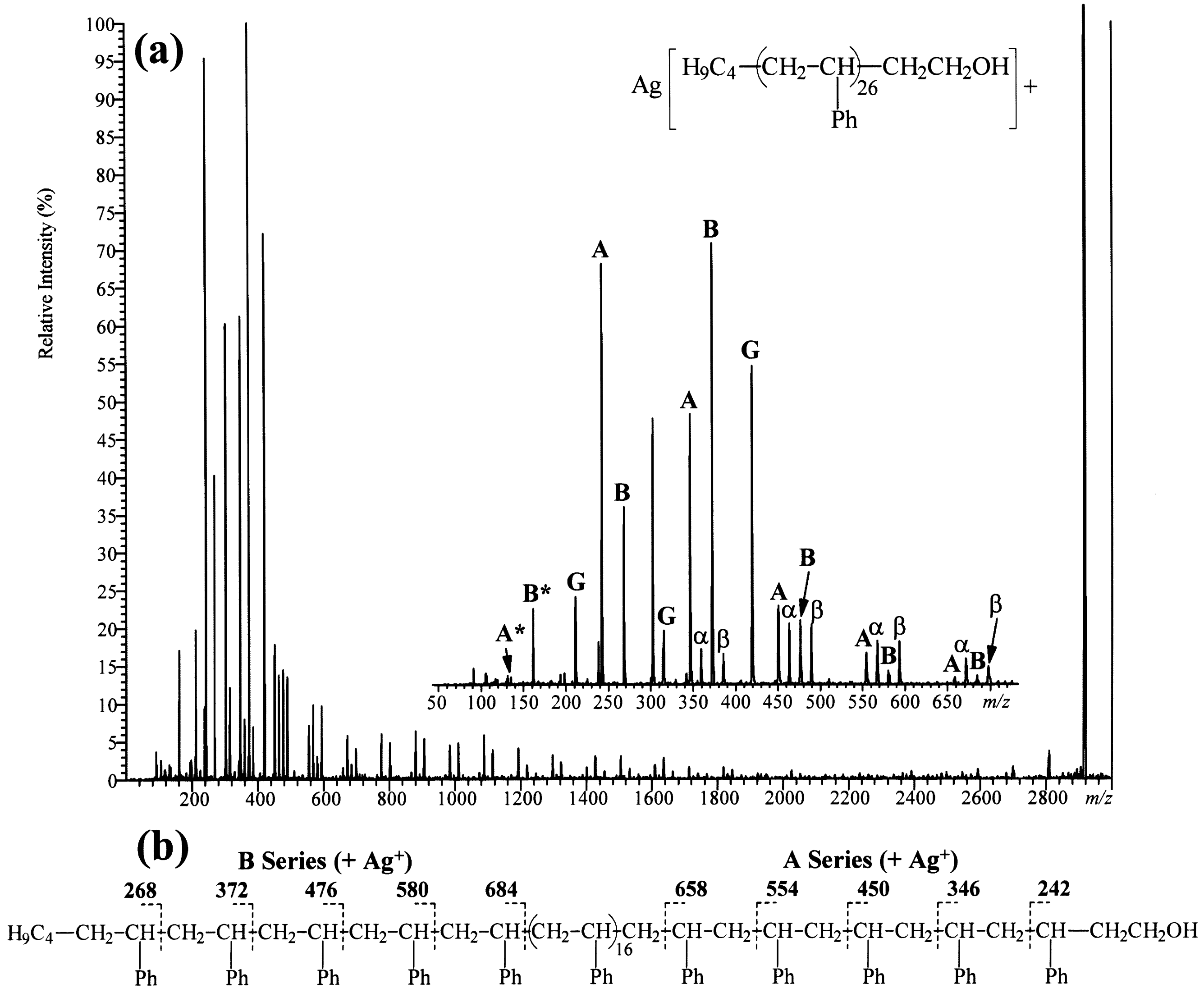
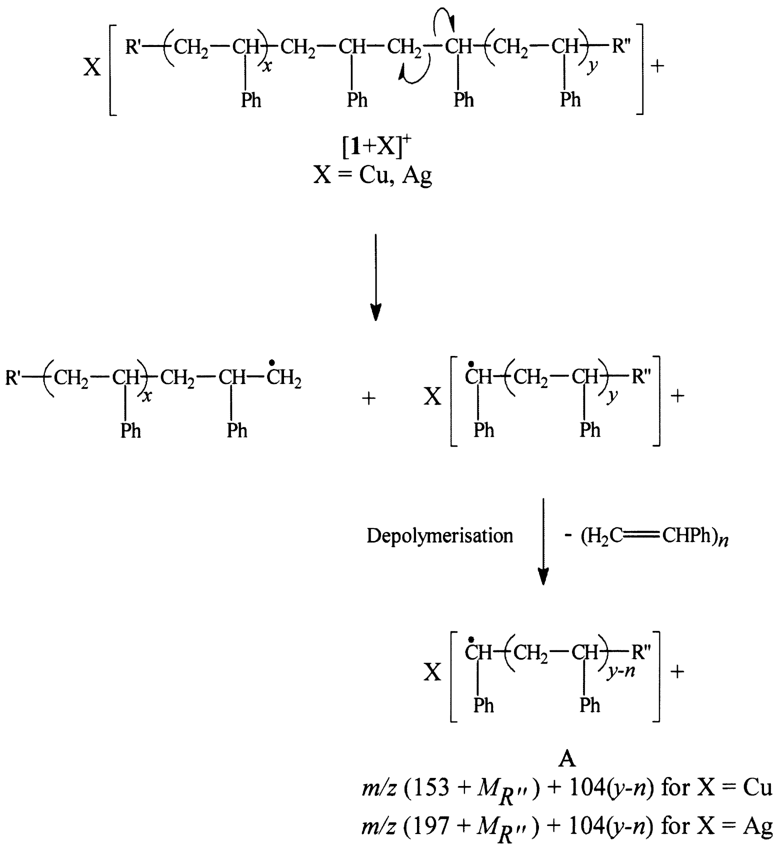


Fig. 2. (a) MALDI-CID spectrum of $[M + {}^{107}Ag]^+$, *m/z* 2914.6, of the 26-mer of poly(styrene) A (inset—expansion of *m/z* 50–730). All fragments ions retain the cation (Ag^+) except where denoted by an asterisk. The A and B series are observed at *m/z* 242 + 104*n* and 268 + 104*n*, where *n* = 0–4. The G series is seen at *m/z* 211 + 104*n*, where *n* = 0–2. The α and β series are seen at *m/z* 255 + 104*n* and 281 + 104*n*, where *n* = 1–22. The C, D, E and F series are observed at *m/z* 267 + 104*n*, 179 + 104*n*, 205 + 104*n* and 345 + 104*n*, respectively, where *n* = 5–22. (b) Proposed fragmentation pathways of $[M + Ag]^+$, *m/z* 2914.6, of the 26-mer of poly(styrene) A showing how the A and B series may be used to infer the masses of the end groups of the polymer.

(TCE). Spectra taken in TCE gave the best discrimination of resonances from the polymer backbone and end groups. Number average molecular weights were, therefore, determined from these spectra. Deutero-chloroform was used as solvent for the ^{13}C NMR spectra and the data were generated from concentrated solutions in 10 mm (external diameter) NMR tubes. Sixteen thousand scans were typically accumulated in order to generate the ^{13}C NMR spectra, with a 90° pulse and a pulse repetition of 3 s. The spectra were taken without Nuclear Overhauser Enhancement and with ^{1}H NMR decoupling, and were processed with a 2.5 Hz exponential line-broadening and referenced to the resonance from the solvent (central resonance taken as 77 ppm). The majority of the resonances from end groups occurred in the 10–70 ppm region. Fig. 1 shows the ^{13}C NMR spectra from poly(styrene) A and poly(styrene) C, along with the proposed assignments. The data from all four samples indicate that the structures of these polymers are indeed those shown above (**2**, **3**, **4** and **5**). The ^{1}H NMR spectra (in TCE) were used to support the ^{13}C NMR evidence on end group type. The number average molecular weights (M_n) were measured from integrated areas of appropriate resonances and were shown to be close to the values determined by GPC and MALDI-TOF.

2.3. Mass spectrometry

MALDI-CID experiments were performed in an AutoSpec 5000 orthogonal acceleration (oa)-TOF (Micromass,



m/z $(153 + M_{R''}) + 104(y\text{-}n)$ for X = Cu

m/z $(197 + M_{R''}) + 104(y\text{-}n)$ for X = Ag

Scheme 1.

Manchester, UK) tandem mass spectrometer equipped with a MALDI source. This hybrid sector-oa-TOF instrument has been described in more detail elsewhere [15,16]. 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 8 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 ranged from approximately 5000–15000 (which correspond to acquisition times of approximately 10–30 min).

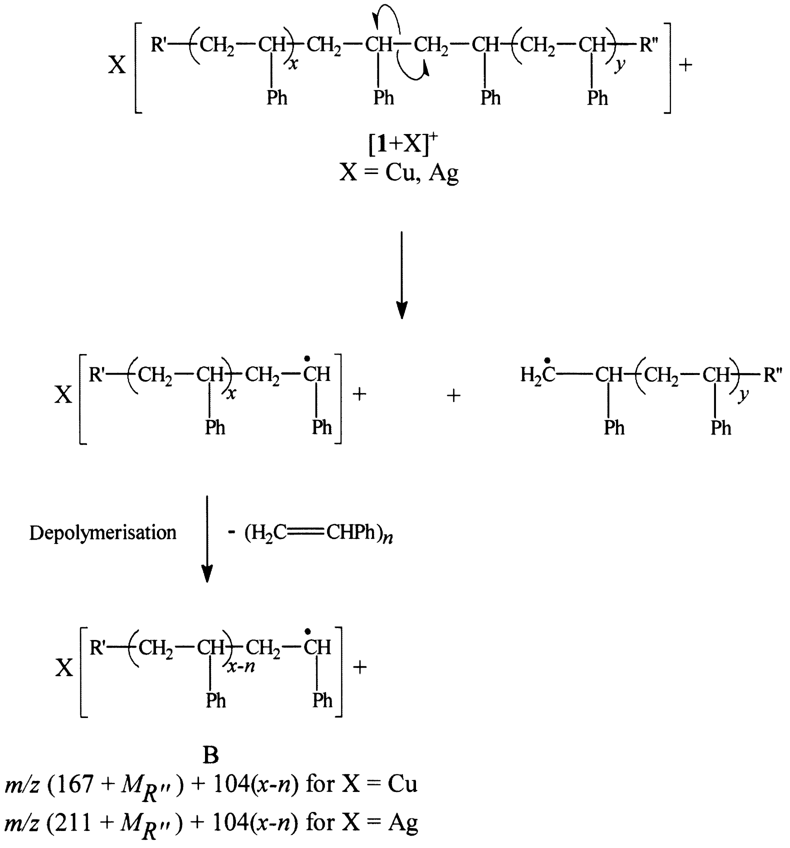
2.4. Sample preparation for mass spectrometry

Copper (II) nitrate, silver nitrate, *all-trans*-retinoic acid and anhydrous tetrahydrofuran were from Aldrich Chemical Company (Gillingham, UK). Analytical grade tetrahydrofuran was from Fisons Scientific Equipment (Loughborough, UK) and HPLC grade ethanol from BDH (Lutterworth, UK).

All solutions, except for that of silver nitrate in ethanol, were prepared at a concentration of 10 mg ml^{-1}. The polymer and matrix (*all-trans*-retinoic acid) were both dissolved in anhydrous tetrahydrofuran and mixed in a 1:20 ratio (v/v) for analysis of adducts of poly(styrene) with silver and copper ions. This solution was then mixed with copper (II) nitrate in tetrahydrofuran or saturated solution of silver nitrate in ethanol, in a 100:1 ratio (v/v), prior to deposition of approximately 0.5 μl on the sample stage. *All-trans*-retinoic acid was previously used to obtain spectra from narrow polydispersity poly(styrene) samples with average molecular weights of up to 1.5 MDa [17,18].

3. Results and discussion

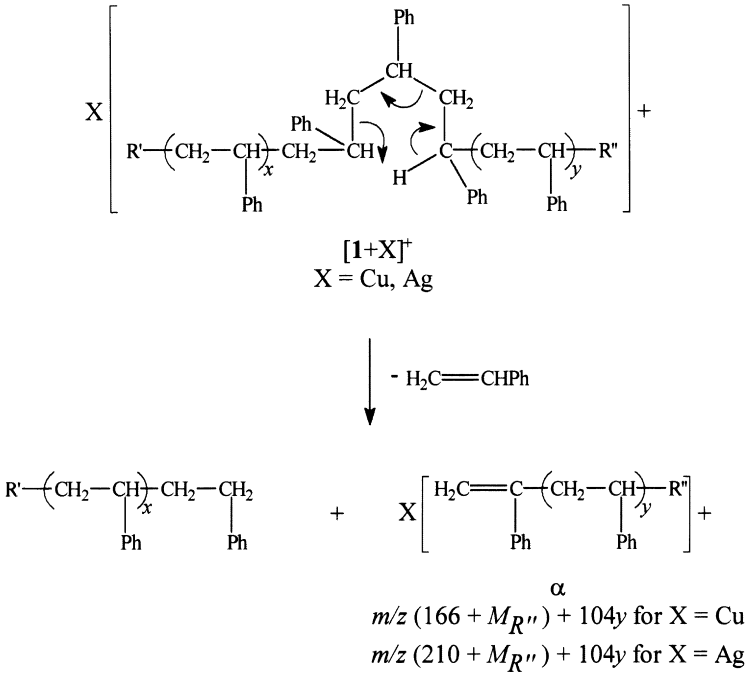
Poly(styrene) A is a narrow polydispersity polymer with a number average molecular weight (M_n) of 2600 (from SEC



Scheme 2.

data). Polymerisation was initiated with butyl lithium and terminated by ethylene oxide. Intense ion peaks, corresponding to the $[\mathbf{2} + \mathrm{Ag}]^+$ species, were observed in the MALDI-TOF spectrum of this polymer from the 15-mer to the 46-mer (data not shown). The $[\mathbf{2} + \mathrm{Ag}]^+$ ion from the 26-mer was chosen for further study as it generated the most intense peak in the MALDI-TOF data. The MALDI-CID spectrum of the $[\mathbf{2} + {}^{107}\mathrm{Ag}]^+$ ion, with a *m/z* ratio of 2914.6, from the 26-mer of poly(styrene) A is shown in Fig. 2(a). Most of the fragment ions are proposed to retain the cation (Ag^+), except for some peaks of lower intensity that are seen at lower mass-to-charge ratios (less than *m/z* 200). It is interesting to compare the MALDI-CID data from this polymer with that from the poly(styrene) standards that were previously studied [12], as one end group (butyl) is the same. It would therefore be expected, from Eqs. (1) and (2), that the B series of ion peaks would be seen at the same mass-to-charge ratios in Fig. 2(a) as in the spectrum from the standard [12], but that the ion peaks of the A series would be shifted by a *m/z* ratio of $44 + 104n$, as poly(styrene) A is terminated by ethylene oxide rather than hydrogen. This shift in *m/z* for the peaks of the A series is indeed seen in the spectrum [Fig. 2(a)], with the peaks of the B series observed at the same values as from the standard. Fig. 2(b) indicates how the mass-to-charge ratios of the ion peaks of the A and B series may be used to infer the masses of the end groups of poly(styrene) A. Subtraction of the mass of the cation (107 u) and part or whole of the mass of a number of repeat units [see Eqs. (1) and (2)] allows the masses of the end groups to be correctly calculated [the mass of R' is 57 u and R'' is 45 u for species **2** of poly(styrene) A]. The mass of end group R' may be derived from any member of the B series of ion peaks using Eq. (2). An example is the ion peak at *m/z* 372, which gives a mass for R' of 57 u, where $n = 1$ and $M(\mathrm{Cat})$ is 107 u (for ${}^{107}\mathrm{Ag}^+$). Similarly, for end group R'', it may be calculated, from the peak of the A series seen at *m/z* 346, from Eq. (1) that the mass of this end group is 45 u where $n = 1$ and $M(\mathrm{Cat})$ is again 107 u.

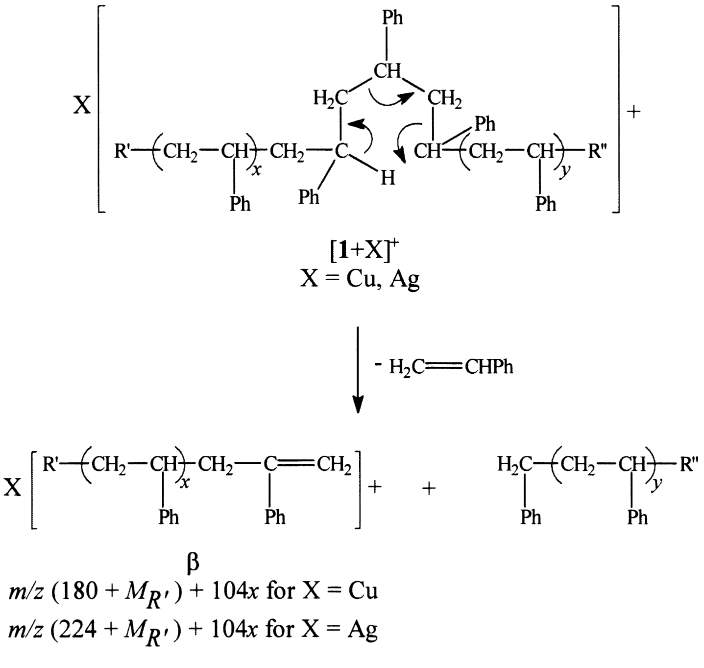
The proposed structures of ion peaks of the A and B series were shown in a recent article [11]. These ions are thought to be distonic radical cations, where the site of the radical is a secondary carbon of the polymer backbone. The ions are possibly formed by means of the mechanisms shown in Schemes 1 and 2 [proposed mechanisms for generation of the A and B series, respectively, from poly(styrene)]. Random, direct radical cleavage of the polymer backbone is the first step in this mechanism. This is followed by depolymerisation to form the ions of the A and B series. The difference in mechanism for formation of the A and B series is the initial cleavage site and the end of the polymer chain that interacts with the cation after fragmentation occurs. This mechanism is analogous to that proposed for



Scheme 3.

the formation of intense fragment ion peaks that were observed in the MALDI-CID spectra of poly(alkyl methacrylate) polymers [11].

The abundant ion at *m/z* 302 [the peak is not labelled in Fig. 2(a)] is proposed to be generated by loss of ethylene oxide from the ion of the A series at *m/z* 346. Less intense ion peaks, that are expected to be formed by a similar pathway, are observed at *m/z* 198 and 406. Another intense series of ion peaks, also separated by a *m/z* that is equivalent to the mass of the repeat unit of **2** (104 u), is labelled G in the expansion of the MALDI-CID spectrum shown in Fig. 2(a). The peaks from the G series are observed at lower mass-to-charge ratios (less than *m/z* 500) in the MALDI-CID data from $[\mathbf{2} + \mathrm{Ag}]^+$. These ions were previously proposed to be generated by at least two consecutive hydrogen rearrangement reactions from the precursor ion [12], so that the resulting fragments do not contain either of the end groups of the poly(styrene) polymer. A possible structure



Scheme 4.

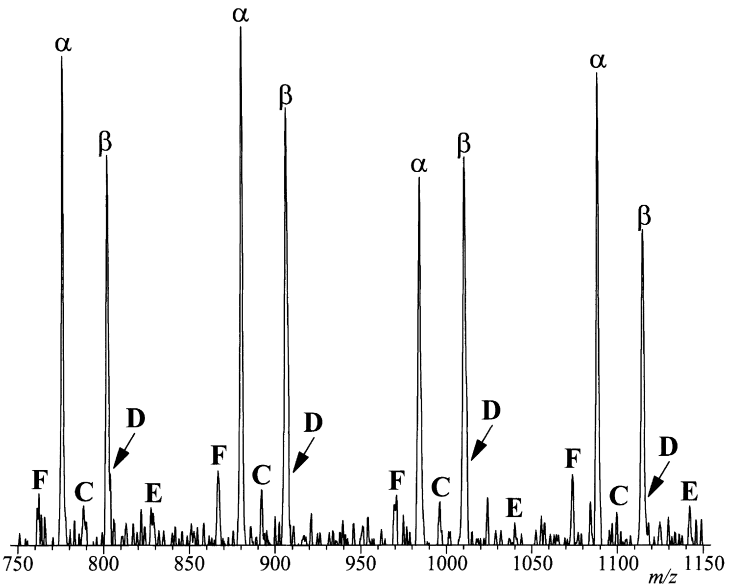
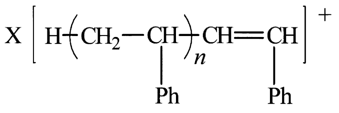


Fig. 3. Expansion (*m*/*z* 750–1150) of the MALDI-CID spectrum of $[M + Ag]^+$, *m*/*z* 2914.6, of the 26-mer of poly(styrene) A (see Fig. 2 for description of annotation).

for the ions of the G series is shown below.



$$X\left[H\left(CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}\right)_n CH{=}\underset{\displaystyle Ph}{\underset{|}{CH}}\right]^+$$

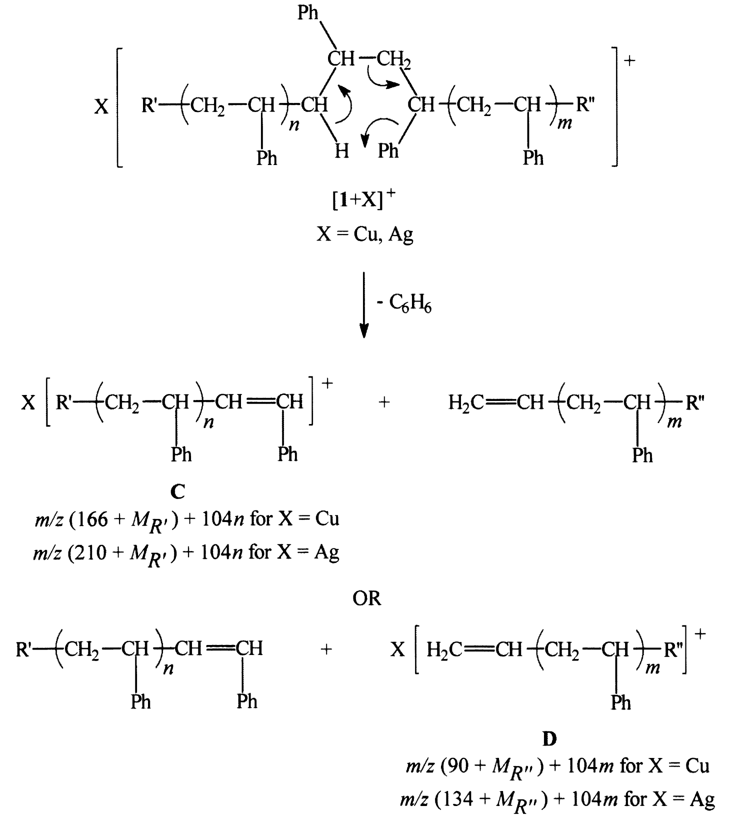
G

m/*z* 167+104*n* for X = Cu
m/*z* 211+104*n* for X = Ag

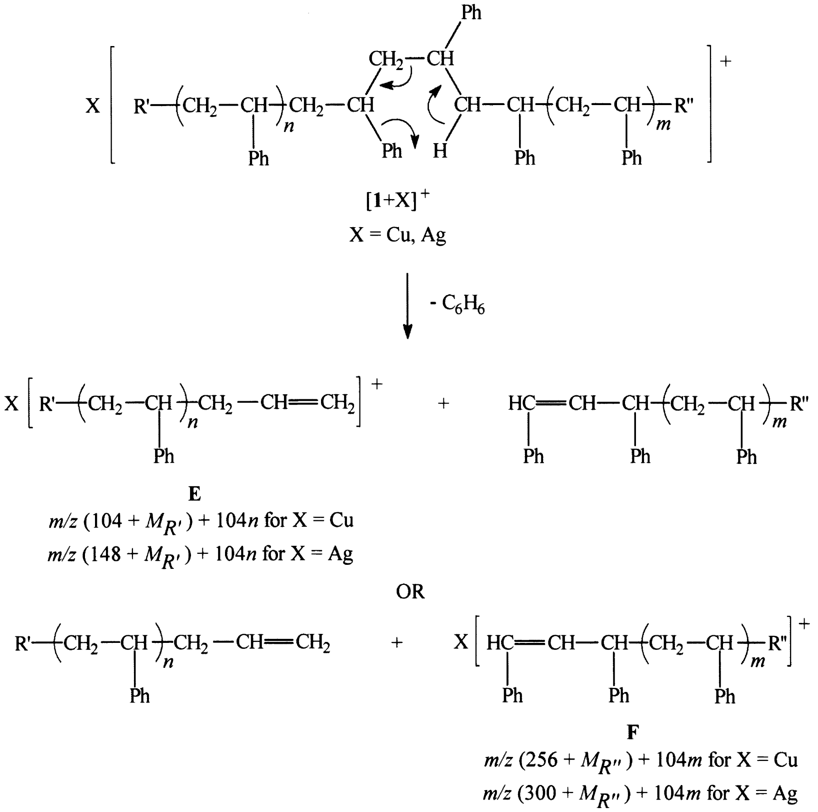
Two other relatively less intense series of ion peaks, where each successive peak in both of the series are separated by *m*/*z* 104, are labelled α and β in the expansion of the MALDI-CID spectrum which is shown in Fig. 2(a). The ion peaks of these series are observed, both in Fig. 2(a) and in data shown previously [12], at successively lower relative intensities with increasing mass-to-charge ratio. The proposed mechanisms of formation for the ions of these two series are shown in Schemes 3 and 4 [proposed mechanisms for generation of the α and β series, respectively, from poly(styrene)]. Both of these mechanisms involve 1,5-hydrogen rearrangement reactions with concurrent loss of styrene and the portion of the oligomer with a saturated chain end, with charge retention (Ag^+ from $[\mathbf{2} + Ag]^+$ of poly(styrene) A) at the moiety of the oligomer with an unsaturated chain end. No fragment ion peaks are seen in the spectrum that are consistent with retention of the cation at fragments with two saturated chain ends. This is possibly a consequence of the increased delocalisation of electrons in the fragments with an unsaturated chain end, which means that the affinity of these species with the silver ion is greater. Decomposition of molecular ions ($M^{+\cdot}$) of poly(styrene) oligomers, formed in a field desorption ion source, results in the generation of fragment ions that have both unsaturated and saturated chain ends [19–22]. These ions were proposed as formed by mechanisms that are similar to those shown in Schemes 1 and 2 [22].

The β series of ion peaks are observed at the same mass-to-charge ratios as in the MALDI-CID data from the poly(styrene) standards [12]. This is because these fragment ions are generated with retention of the cation at the portion of the oligomer that contains the butyl end group. This end group is the same for both the poly(styrene) standards and 2. The ion peaks of the α series are shifted by *m*/*z* 44 in the data shown in Fig. 2(a), as a consequence of the change in end group from hydrogen [poly(styrene) standard] to that formed by termination with ethylene oxide (2). Furthermore, the G and α series of ion peaks are observed at the same mass-to-charge ratios in the MALDI-CID spectra from the poly(styrene) standards [12]. These two series of ion peaks are differentiated by *m*/*z*, however, in the MALDI-CID data from $[\mathbf{2} + Ag]^+$ [Fig. 2(a)]. This indicates that the ions of the G and α series are formed by different mechanisms, as was proposed previously [12].

An expansion (from *m*/*z* 750–1150) of the MALDI-CID spectrum, from the $[M + Ag]^+$ ion of the 26-mer of poly(styrene) A, is shown in Fig. 3. Four other sequences of peaks of low signal-to-noise ratios are observed in this region of the spectrum, in addition to the relatively intense ion peaks from the α and β series. These peaks are labelled C, D, E and F and the proposed mechanisms of formation of the ions from these series are shown in Scheme 5 [proposed mechanism for generation of the C and D series from poly(styrene)] and Scheme 6 [proposed mechanism for generation of the E and F series from poly(styrene)]. These hydrogen rearrangement mechanisms are analogous to those put forth to account for the generation of these ions from poly(styrene) standards [12]. The ion peaks of these



Scheme 5.



Scheme 6.

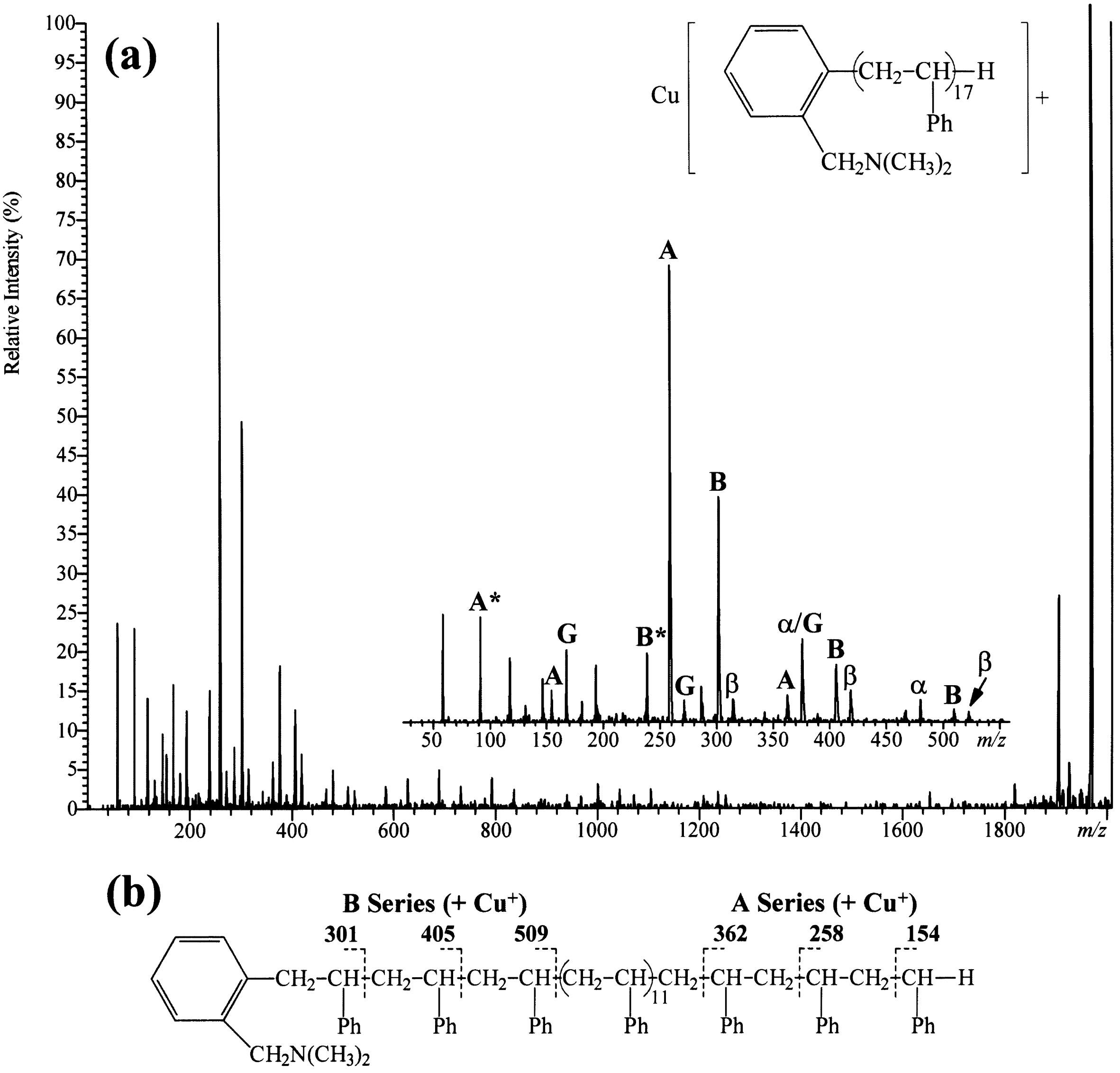


Fig. 4. (a) MALDI-CID spectrum of $[M + {}^{63}Cu]^+$, m/z 1969.1, of the 17-mer of poly(styrene) B (Inset—expansion of m/z 30–550). All fragments ions retain the cation (Cu^+) except where denoted by an asterisk. The A and B series are observed at m/z $154 + 104n$ and $301 + 104n$, where $n = 0$–2. The G series is seen at m/z $167 + 104n$, where $n = 0$–2. The α and β series are seen at m/z $167 + 104n$ and $314 + 104n$, where $n = 0$–10. The C, D, E and F series are observed at m/z $300 + 104n$, $91 + 104n$, $238 + 104n$ and $257 + 104n$, respectively, where $n = 3$–15. (b) Proposed fragmentation pathways of $[M + Cu]^+$, m/z 1969.1, of the 17-mer of poly(styrene) B showing how the A and B series may be used to infer the masses of the end groups of the polymer.

series are seen at lower intensities, relative to those of α and β series, as the m/z of the precursor ion increases. It is apparent, however, that the ion peaks of the C, D, E and F series are relatively intense at higher mass-to-charge ratios compared to those of the α and β series, from the data shown here and that previously described [12].

Ion peaks, corresponding to $[\mathbf{3} + Cu]^+$, were observed in the MALDI-TOF spectrum of poly(styrene) B when copper (II) nitrate was added as part of the sample preparation (data not shown). The $[\mathbf{3} + Cu]^+$ peaks from the dimer to the 36-mer were seen in the MALDI-TOF spectrum. It should be noted that the corresponding $[\mathbf{3} + H]^+$ ion peaks were also seen in the spectrum. This is a consequence of the fact that one of the end groups of **3** contains a nitrogen atom, which has a relatively high proton affinity. This is the first time, to our knowledge, that protonation of poly(styrene) by means of MALDI has been reported. Further discussion on this phenomenon is beyond the scope of this article and will be presented in a future publication.

The adducts of **3** with copper ions were selected for MALDI-CID experiments, rather than the corresponding silver ion species, because there was overlap in the isotope distributions of the $[\mathbf{3} + Ag]^+$ and $[\mathbf{3} + H]^+$ ion peaks in the MALDI-TOF spectrum. This is a consequence of the fact that these two species differ by only m/z 2, when the value of n is one higher for $[\mathbf{3} + H]^+$ than for $[\mathbf{3} + Ag]^+$. It has previously been shown that abundant ion signals are generated by MALDI for poly(styrene), when copper salts are

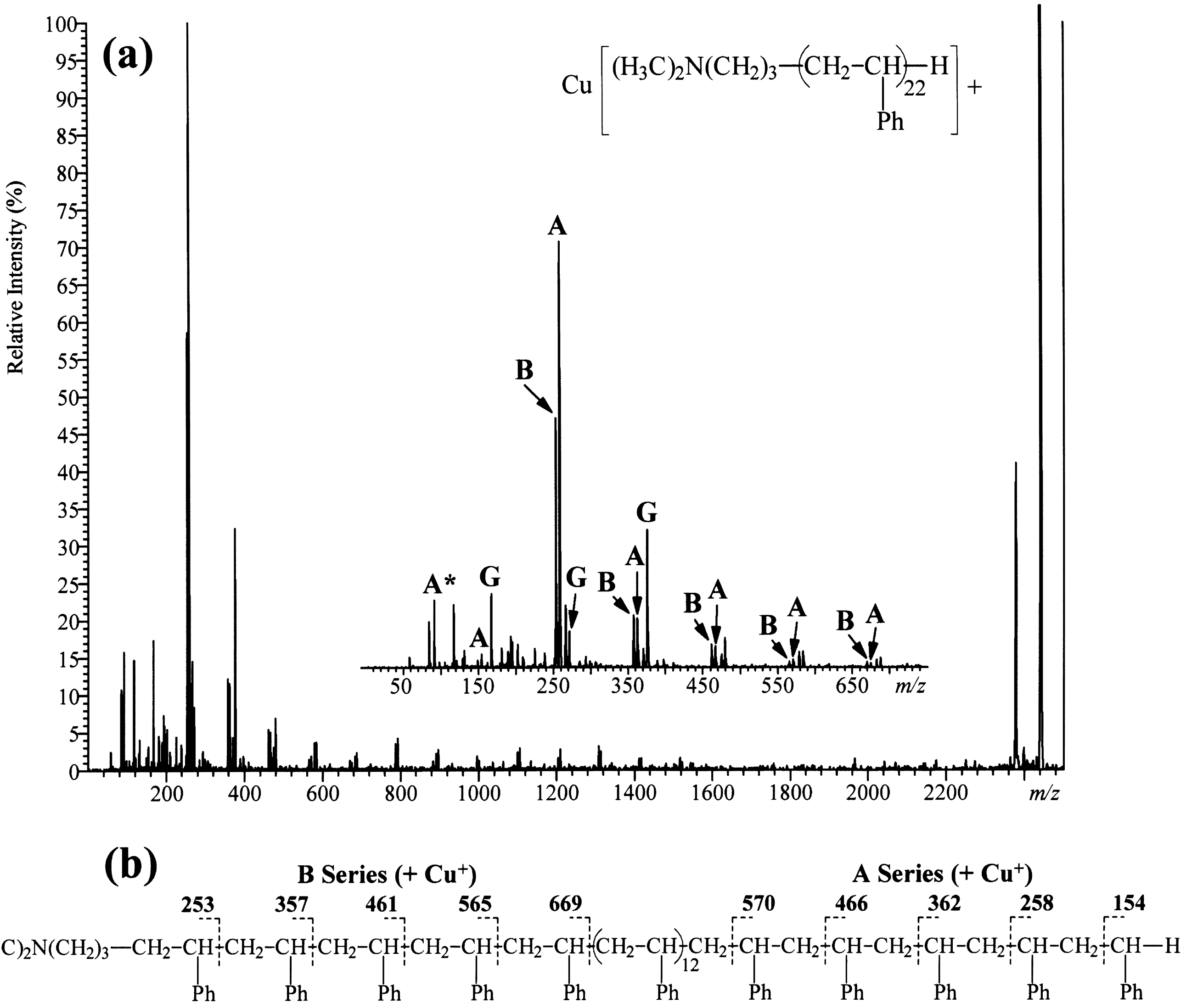


Fig. 5. (a) MALDI-CID spectrum of [M + ^{63}Cu]$^+$, *m/z* 2439.4, of the 22-mer of poly(styrene) C (inset—expansion of *m/z* 30–750). All fragments ions retain the cation (Cu$^+$) except where denoted by an asterisk. The A and B series are observed at *m/z* 154 + 104*n* and 253 + 104*n*, where *n* = 0–4. The G series is seen at *m/z* 167 + 104*n*, where *n* = 0–2. The α and β series are seen at *m/z* 167 + 104*n* and 266 + 104*n*, where *n* = 0–20. The C, D, E and F series are observed at *m/z* 252 + 104*n*, 91 + 104*n*, 190 + 104*n* and 257 + 104*n*, respectively, where *n* = 4–20. (b) Proposed fragmentation pathways of [M + Cu]$^+$, *m/z* 2439.4, of the 22-mer of poly(styrene) C showing how the A and B series may be used to infer the masses of the end groups of the polymer.

used to promote cationisation rather than silver salts [23]. The MALDI-CID spectrum of the [**3** + ^{63}Cu]$^+$ ion from the 17-mer of poly(styrene) B is shown in Fig. 4(a). The [M + Cu]$^+$ molecule ion from the 17-mer of **3** was chosen for further study as the peak from this species was the most intense in the MALDI-TOF spectrum. Sequences of intense ion peaks are again seen at low mass-to-charge ratios from which the masses of both of the end groups of 3 may be calculated. These peaks are labelled A and B in the expansion of the spectrum shown in Fig. 4(a). Fig. 4(b) shows the proposed cleavage points in the polymer backbone for formation of the A and B series of ions from the [**3** + ^{63}Cu]$^+$ species of the 17-mer of poly(styrene) B. The mass-to-charge ratios of these ion peaks are consistent with those expected from Eq. (1) and Scheme 1 (A series), and Eq. (2) and Scheme 2 (B series).

It is again interesting to compare these data to that from the poly(styrene) standards [12], as the initiating group of **3** is different but both species have the same terminating end group (hydrogen). The expected shift in mass-to-charge ratio for the B series (*m/z* 77) of ion peaks is observed, whereas the ion peaks of A series are seen at the same values in both sets of data.

Ion peaks from the G, α and β series are also annotated in Fig. 4(a). Furthermore, peaks from α and β series are also observed at higher mass-to-charge ratios (less than *m/z* 1300) in the spectrum. Peaks from the E and F series are

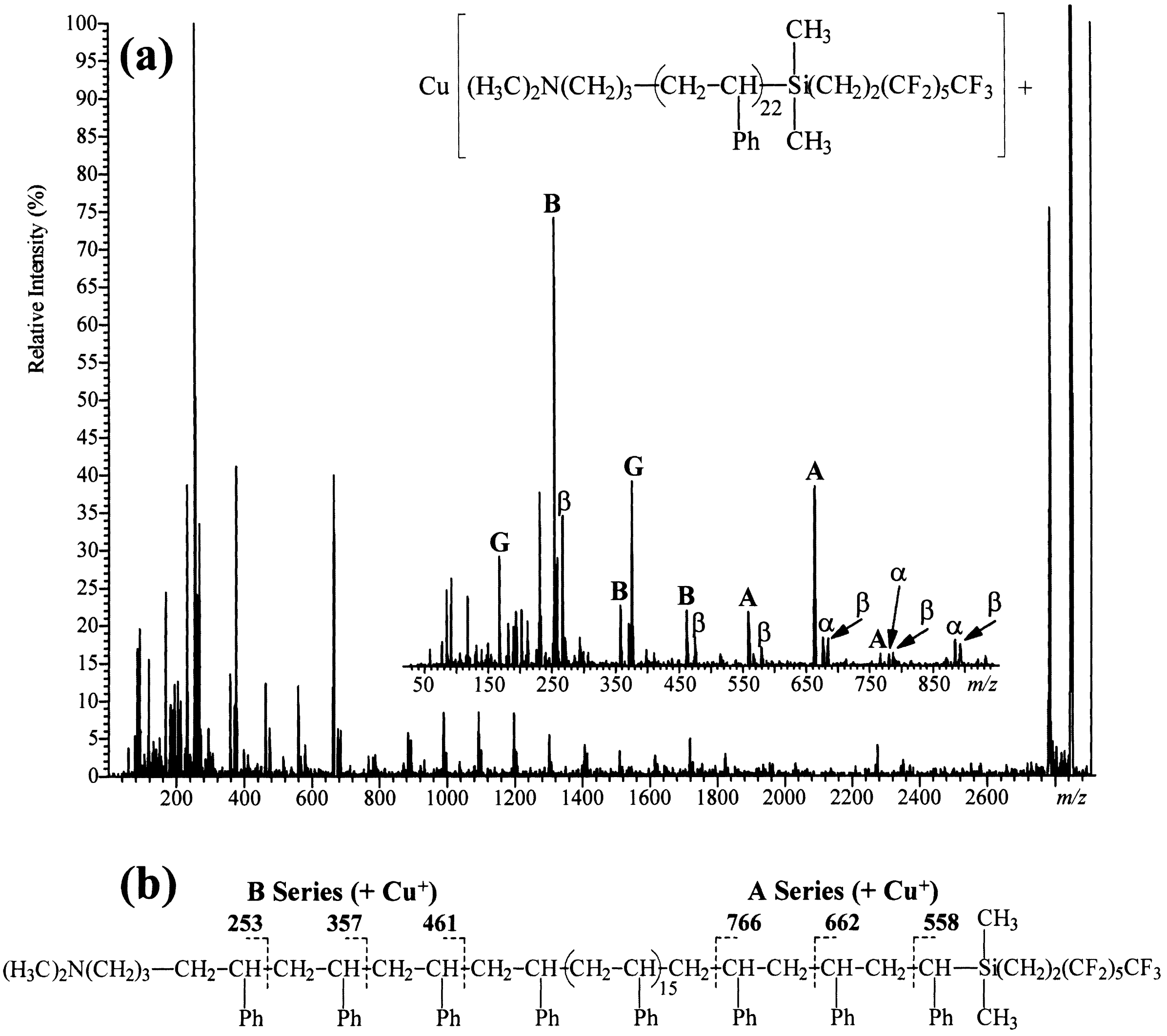
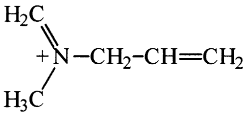


Fig. 6. (a) MALDI-CID spectrum of $[M + {}^{63}Cu]^+$, *m*/*z* 2843.4, of the 22-mer of poly(styrene) D (Inset—expansion of *m*/*z* 30–950). All fragments ions retain the cation (Cu^+) except where denoted by an asterisk. The A and B series are observed at *m*/*z* 558 + 104*n* and 253 + 104*n*, where *n* = 0–2. The G series is seen at *m*/*z* 167 + 104*n*, where *n* = 0–2. The α and β series are seen at *m*/*z* 571 + 104*n* and 266 + 104*n*, where *n* = 1–20. The C, D, E and F series are observed at *m*/*z* 252 + 104*n*, 495 + 104*n*, 190 + 104*n* and 661 + 104*n*, respectively, where *n* = 2–20. (b) Proposed fragmentation pathways of $[M + Cu]^+$, *m*/*z* 2843.4, of the 22-mer of poly(styrene) D showing how the A and B series may be used to infer the masses of the end groups of the polymer.

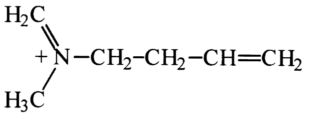
also seen at low signal-to-noise ratios. The ion peaks of the C and D series are not resolved in the spectrum as they are observed at higher mass-to-charge ratios (greater than *m*/*z* 1000) and only are differentiated by *m*/*z* 1. These ion peaks are also proposed to retain the cation (Cu^+). Relatively intense ion peaks are seen at lower mass-to-charge ratios (less than *m*/*z* 200) that are propounded as being formed without charge retention. Two of these peaks are labelled A* and B* in Fig. 4(a) as the mass-to-charge ratios are consistent with these ions having similar structures to those shown for the A and B series, where *y*–*n* (Scheme 1) or *x*–*n* (Scheme 2) are zero, except that they are formed without retention of the cation (Cu^+). The abundant ion at *m*/*z* 58 [unlabelled in Fig. 4(a)] is proposed to be generated by cleavage adjacent to the phenyl portion of the nitrogen containing end group [possibly $(H_3C)_2NCH_2^+$]. Other, less prominent peaks, are seen at mass-to-charge ratios that are consistent with the fragment ions having been formed by pathways that are similar to those generated by collision induced dissociation of molecular ions ($M^{+\cdot}$) of poly(styrene) standards in field desorption-tandem mass spectrometry (FD-MS/MS) experiments [21,22]. Ion peaks, of low relative intensities, were observed at the same mass-to-charge ratios in the MALDI-CID spectra from $[\mathbf{2} + Ag]^+$ and in previous experiments [12].

Protonated and copper ion adduct peaks are observed in the MALDI-TOF spectra, when copper salts are added to promote formation of the latter species, from poly(styrene) C and poly(styrene) D (data not shown). The $[\mathbf{4} + Cu]^+$ and $[\mathbf{5} + Cu]^+$ ion peaks, from the dodecamer to the 40-mer, are seen in both of the spectra. The MALDI-CID spectra from the [**4** + ^{63}Cu]$^+$ and [**5** + ^{63}Cu]$^+$ ion peaks of the 22-mer are shown in Figs. 5(a) and 6(a), respectively. Intense ion peaks, from the A and B series, are observed in both spectra at the mass-to-charge ratios that are expected from Eq. (1) and Scheme 1 (A series), and Eq. (2) and Scheme 2 (B series). The peaks of the B series are observed at the same mass-to-charge ratios in both Figs. 5(a) and 6(a), but the difference in *m*/*z* for the ions of the A series may be accounted for by the change in terminating end group for **4** and **5** [see Figs. 5(b) and 6(b)]. The ion peaks of the A series are observed at higher average mass-to-charge ratios in Fig. 6(a) than from the other poly(styrene) polymers that were studied in these and previous experiments [12]. This is because of the higher mass (405 u) of the terminating end group of **5**.

The α, β, C, D, E, F and G series of ion peaks are also seen in the MALDI-CID spectra from both polymers. The ion peaks of the α, D and F series are shifted by *m*/*z* 404 in the spectrum from [**5** + ^{63}Cu]$^+$ over [**4** + ^{63}Cu]$^+$ as a consequence of the difference in mass of the terminating end group of **4** and **5**. Relatively intense ion peaks are again observed in the spectra, which may be assigned as fragments that do not retain the copper ion. Many of these ions are again at the same mass-to-charge ratios as those peaks seen previously in FD-MS/MS data [21,22]. Furthermore, ions may also be assigned as fragments of the nitrogen containing initiating end group of **4** and **5**. These ions include those with *m*/*z* 58, 84 and 98. The ion at *m*/*z* 58 may have the same structure as that shown above, arising from dissociation of [**3** + ^{63}Cu]$^+$. The ions at *m*/*z* 84 and 98 are proposed to have the structures below and are generated from the precursor ion by at least two hydrogen rearrangement reactions.

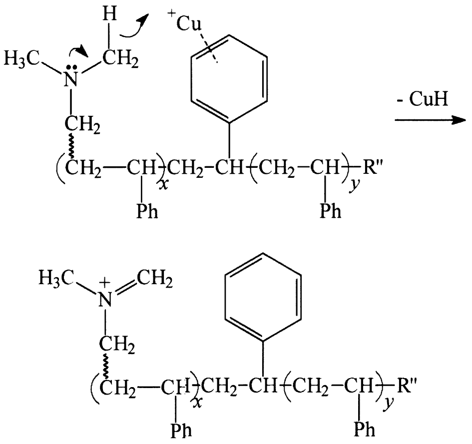


***m*/*z* 84**



***m*/*z* 98**

An intense fragment ion peak is observed in the spectra from [**3** + ^{63}Cu]$^+$, [**4** + ^{63}Cu]$^+$ and [**5** + ^{63}Cu]$^+$ that is *m*/*z* 64 less than that of the intact precursor ion. Peaks corresponding to this loss are not prominent, however, in the MALDI-CID spectra from oligomers of poly(styrene) that do not contain nitrogen. This ion is proposed to be generated by loss of copper (I) hydride from the precursor, by means of a mechanism that is similar to that shown below, and is possibly stabilised by the ability of the nitrogen to hold a positive charge. This ion may be an intermediate in the formation of ions at low mass-to-charge ratios that do not retain the copper ion, from which peaks are seen in the MALDI-TOF spectra shown in Figs. 4(a), 5(a) and 6(a).



4. Conclusions

MALDI-CID has been shown in these, and other [12], experiments to be a powerful technique for determining the masses of the end groups from poly(styrene) polymers. The synergy of MALDI-CID, MALDI-TOF and NMR spectroscopy should be a very considerable combination, as a tool for end group analysis, for both poly(styrene)s and poly(alkyl methacrylate)s [10]. Furthermore, the MALDI-CID technique could have a role to play in the determination of chain length distributions from block copolymers.

Equations, that were proposed previously [12], have been shown to adequately predict the mass-to-charge ratios of the two series (A and B series) of ion peaks from which the masses of the end groups may be determined. It should be noted that complementary information on end group masses may be obtained from the mass-to-charge ratios of the peaks from the α and β series that are observed in the MALDI-CID spectra of poly(styrene)s.

A major advantage of MALDI-TOF and MALDI-CID mass spectrometry, over NMR spectroscopy, is the former technique's ability to resolve peaks from oligomers with different end group structures. Information may be inferred about the whole sample by means of NMR spectroscopy, but generally not about individual species. The combination of NMR, MALDI-TOF and MALDI-CID should therefore be especially useful when analysing polymers with unknown end group structures. End group information may generally be obtained, by means of MALDI-TOF, from oligomers with molecular weights below approximately 10–20 kDa. The limit is approximately 5 kDa for MALDI-CID experiments, at present. Information may still be generated from polymers with higher average molecular weights, using these techniques, if there are oligomers of low molecular weight in the sample. Pre-concentration of these low oligomers may be required before analysis, either by means of solvent extraction or GPC fractionation.

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