Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Mass Spectrometry 238 (2004) 245–255
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Probing chain-end functionalization reactions in living anionic polymerization via matrix-assisted laser desorption ionization time-of-flight mass spectrometry

Mark A. Arnould[a,1], Michael J. Polce[a], Roderic P. Quirk[b], Chrys Wesdemiotis[a,*]

[a] *Department of Chemistry, The University of Akron, Akron, OH 44325, USA*
[b] *Department of Polymer Science, The University of Akron, Akron, OH 44325, USA*

Received 8 July 2003; accepted 7 May 2004

Abstract

Matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) is applied to examine the products arising upon the preparation of chain-end functional polymers via living anionic polymerization techniques. Both post-polymerization functionalizations as well as the use of functionalized initiators are investigated. MALDI-TOF MS is shown to be a sensitive probe for the qualitative analysis of the major and minor oligomers from novel functionalization reactions whose mechanisms are not yet well established. The method is particularly valuable for the identification of the end groups of the minor, and often unexpected, distributions that may be undetectable by other analytical means. Complete characterization of all oligomers generated during functionalization reactions provides an essential tool to the synthetic chemist for understanding the corresponding mechanisms. This insight is necessary for selecting alternative routes or making modifications to the reaction conditions. It is demonstrated that MALDI-TOF MS can convey quantitative information about the yields of the chain-end groups introduced during functionalization. From the cases presented it is evident that post-polymerization reactions allow for better control of chain-end functionality and molecular weight than functionalization with the limited number of currently available protected functionalized initiators.

Keywords: Polymers; Anionic polymerization; MALDI mass spectrometry; End group analysis; Quantitation

1. Introduction

The synthesis of functionalized polymers is important in numerous applications, including colloidal stabilization, dispersion of fillers and the synthesis of new block copolymers [1]. Living anionic polymerization is particularly suited for introducing functional groups at either chain end of a polymer while providing well-defined structures and low degrees of compositional heterogeneity [2]. Due to the stability of the living anion there is neither chain transfer nor termination. The stable carbanionic chain end, resulting after consumption of all monomer, can react with a variety of electrophilic reagents to yield the desired functional group at the terminal (ω) chain end [3]. Introduction of a functional group to the initiating end (α) can be accomplished by the use of functionalized alkyllithium initiators [3]. The combination of these two synthetic methods makes it possible to generate α,ω-difunctional (telechelic) polymers [3]. It is of great importance to characterize all products created by such novel approaches for polymer functionalization in order to understand the underlying mechanisms. For this, sensitive analytical techniques must be utilized, as the detection of minor products is a prerequisite for gaining a greater understanding of the functionalization processes.

* Corresponding author. Tel.: +1 330 972 7699; fax: +1 330 972 7370.
E-mail address: wesdemiotis@uakron.edu (C. Wesdemiotis).
[1] Present address: National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD 20899-8541, USA.

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.05.014

Due to its high sensitivity, mass spectrometry (MS) provides an ideal method for the separation and identification of individual oligomers based on their different architectures and end groups as long as the corresponding structures differ in mass. In order to acquire the mass spectrum of a sample, the polymer must be volatilized and ionized with very little fragmentation (soft ionization) so that the mass-to-charge ratios (m/z) of its constituent oligomers can be measured [4–10]. Matrix-assisted laser desorption ionization (MALDI) [11,12] and electrospray ionization (ESI) [13] have made this possible for a wide variety of polymers that have never been directly analyzed by mass spectrometric methods. MALDI time-of-flight (TOF) mass spectrometry in particular has emerged as the most widely used MS technique in polymer analyses because it is applicable to more types of synthetic polymers than any other MS method and generally leads to simple spectra, displaying only singly charged quasi-molecular ions with little or no fragmentation [10,14]. This study utilizes MALDI-TOF mass spectrometry to identify the microstructure and sample composition of functionalized polymers prepared by living anionic polymerizations [15–22]. The intricate details unveiled help to elucidate how the polymers are formed, thereby yielding a deeper understanding of the polymerization reactions and functionalization mechanisms.

2. Experimental methods

2.1. Polymerizations and functionalizations

The synthesis of ω-functionalized and α-functionalized polymers was performed by living anionic polymerization techniques which have been described in detail elsewhere [2,3,23–27]. The reactions were carried out in all-glass, sealed reactors using break seals and standard high-vacuum techniques [28]. The polymerizations were conducted in hydrocarbon solutions (benzene unless stated otherwise) of the monomer (styrene or butadiene) and were initiated by *sec*-C_4H_9Li or a protected functionalized alkyllithium initiator. Once all monomer was consumed, after the desired reaction time, an aliquot of the living anion solution was removed from the reactor and terminated with degassed methanol. This procedure leads to the base polymer, which was analyzed to gauge the purity, molecular weights (M_n, M_w) and molecular weight distribution (MWD) of the compound before functionalization, so that any unwanted side-products and/or shifts in the polydispersity brought upon the functionalizing step could be identified with confidence. Functionalization was carried out by reaction of the living anions with the electrophilic reagent of choice. Termination followed through the addition of degassed methanol, unless noted otherwise. Occasionally, the polymeric living anions were end-capped before functionalization, either with butadiene or isoprene, to improve solubility, or with diphenylethylene, to decrease aggregation of the chain ends and reduce their reactivity. In certain cases the reaction conditions were systematically varied to optimize the yield of the desired end group, as will be discussed with the presentation of the results below. Solvents and reagents were purchased from Aldrich (Milwaukee, WI) or Fisher Scientific (Pittsburgh, PA). The monomers styrene, butadiene and isoprene were purchased from Aldrich, Matheson Gas Products (Montgomeryville, PA) and Goodyear (Akron, OH), respectively. The alkyllithium initiators were obtained from FMC, Lithium Division (Gastonia, NC). Solvents, reagents and monomers were purified and/or dried as has been described by Quirk et al. in refs. [2,3,23–26].

2.2. Mass spectrometry experiments

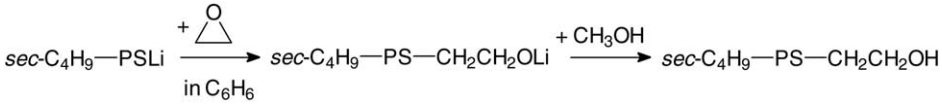
MALDI mass spectra were acquired with a Bruker Reflex III time-of-flight mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument is equipped with a nitrogen laser emitting at 337 nm, a single-stage pulsed ion extraction ion source, a two-stage grid-less reflector and two dual-microchannel plate detectors for detection in the linear and reflectron modes. Mass spectra were measured in the linear and reflectron mode with the ion source and reflector lens potentials kept at 20 and 22.5 kV, respectively. The mass scale was calibrated externally using four peaks of a polystyrene standard at the appropriate molecular weight. Solutions of dithranol at 20 mg/mL (Fluka, Milwaukee, WI), silver trifluoroacetate at 10 mg/mL (Aldrich, Milwaukee, WI) and the polymer (10 mg/mL) were prepared in THF and aliquots of the matrix, salt and polymer were mixed in a 10:1:2 ratio, respectively. A small portion, 0.50 μL, of the final mixture was applied to the MALDI sample target for analysis. The described conditions yielded singly charged adduct ions for each oligomer in the sample under study [15–22]. The m/z values given in the following section are either monoisotopic or average, depending on whether the isotopic clusters were resolved.

The molecular weights and molecular weight distributions of the polymers produced were analyzed independently by size exclusion chromatography (SEC) on a Waters 150-C Plus instrument (Milford, MA) equipped with a differential refractometer, a viscosity detector (Viscotek model 150R) and four Phenomenex Phenogel columns (Torrance, CA). SEC spectra were run at 30 °C in THF after calibration with polystyrene standards (Polymer Laboratories, Amherst, MA).

3. Results and discussion

3.1. Polystyrene functionalization with ethylene oxide

Polystyryl anions (PS^-) are inherently nucleophilic and, thus, can react with a multitude of electrophilic reagents to produce a variety of chain-end functionalities. One frequently employed functionalization, which introduces a hydroxy end group, is the reaction of poly(styryl)lithium (PSLi) with ethylene oxide (EO), shown in Scheme 1. An excess of EO is



Scheme 1.

generally used for quantitative functionalization. The functionalized polymer is subsequently quenched in methanol. The mass spectrum of a product, prepared without careful control of the molar excess and dryness of EO and by using acidic (HCl) methanol as the final termination reagent, is depicted in Fig. 1. The product has a narrow molecular weight distribution (MWD), cf. Fig. 1, in agreement with the low polydispersity (PD) of 1.1 determined by SEC. Such a result attests that the rates of initiation and propagation are comparable for this system, as required for living anionic polymerization to yield polymers with a narrow MWD [2]. The expanded trace of the mass spectrum (Fig. 1) reveals that a variety of end groups have been generated during this relatively simple reaction. Based on the measured average *m*/*z* values, all peaks observed are silver cationized (Ag^+) polystyrene (PS) oligomers. The main series A appears at *m*/*z* 104.15*n* + 210 and corresponds to silver ion (average mass of 108 Da) adducts of the desired product with the expected *sec*-C_4H_9 (57 Da) and CH_2CH_2OH (45 Da) end groups (108 + 57 + 45 = 210 Da). Note that masses (in Da) and mass-to-charge ratios (in *m*/*z* units) are identical for singly charged ions, which were exclusively observed in this study. There are three additional unexpected products, giving rise to series B–D. The oligomers of series B appear at *m*/*z* values that are 44 Da greater than those of the A oligomers. Considering that the mass of EO is 44 Da, this series thus provides evidence that dimerization of ethylene oxide has taken place during the functionalization step to yield a $CH_2CH_2OCH_2CH_2OH$ ω-end group, cf. Scheme 2. Series B′, which is observed 18 *m*/*z* units below B, is assigned to the dehydration product of B, carrying the terminal group $CH_2CH_2OCH{=}CH_2$. Finally, series D has a mass that is 44 Da less than that of A, consistent with the incorporation of H instead of CH_2CH_2OH at the ω-end. Based on the abundances of series B′, B and D relative to series A (<3, 1 and 4%, respectively), approximately 4% of the ω-chain ends contain two EO units, while another 4% carry no functional group. At these small proportions, the side products are difficult to detect by NMR.

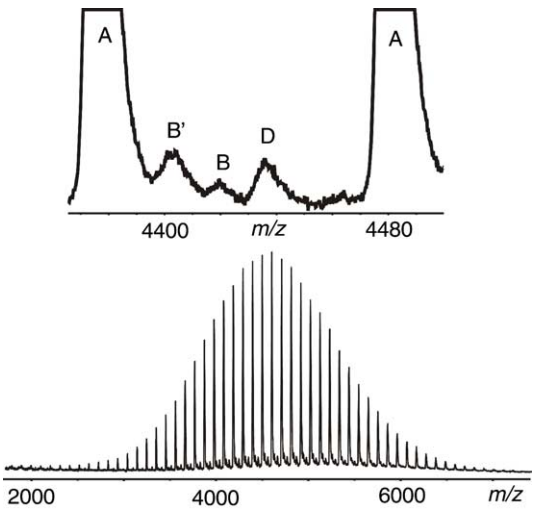
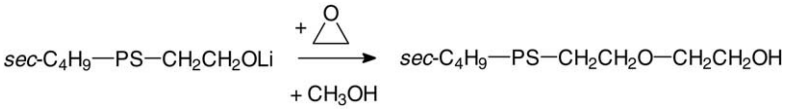


Fig. 1. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation and ethylene oxide for functionalization (Scheme 1). The expanded trace shows the *m*/*z* range between the 40-mer and 41-mer peaks of the desired product, *sec*-C_4H_9Li—PS—CH_2CH_2OH.

The non-functional polymer (series D) forms by the protonation of polystyryl anions with adventitious impurities. On the other hand, series B and B′ prove that oligomerization of EO occurs during the functionalization reaction. This is not surprising, due to the steric strain and high reactivity of EO towards nucleophiles. The very small extent of EO oligomerization points out, however, that lithium alkoxides formed from the addition of one EO are rather unreactive towards other molecules of EO. This could be due to the pronounced aggregation of the chain ends in hydrocarbon solvents.

The discovery of EO oligomerization upon termination provoked intense interest in the reaction conditions under which this process occurs [15,17,27]. A close look at the products generated under various conditions of PSLi hydroxylation was therefore undertaken using MALDI-TOF MS. A series of polystyrenes was synthesized under carefully controlled conditions using purified and dried solvents and ethylene oxide. Polymerization was performed in benzene at 25 °C with either 4 or 10 equivalents of EO (relative to the PSLi concentration), and the reaction times ranged from 12 h to 4 weeks. After the desired reaction time, the samples were quenched with degassed methanol to precipitate the polymer, which was filtered and dried overnight in a vacuum oven prior to analysis by MALDI mass spectrometry.



Scheme 2.

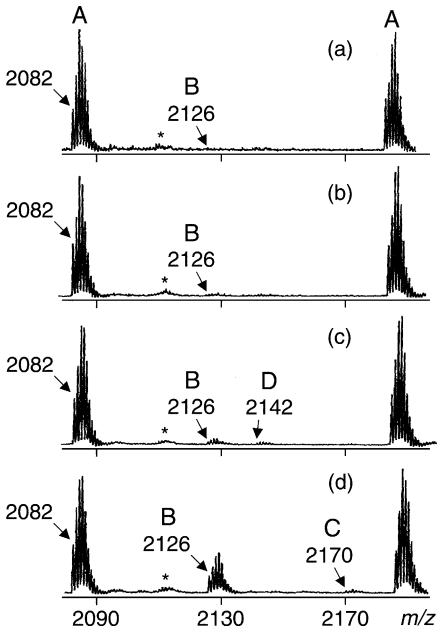


Fig. 2. MALDI mass spectra of polystyrenes prepared under carefully controlled reaction conditions using *sec*-C_4H_9Li for initiation and ethylene oxide for functionalization (see text). Only the *m*/*z* range between the 18-mer and 19-mer peaks of the desired product, *sec*-C_4H_9Li–PS–CH_2CH_2OH, is shown. The entire spectra contain Poisson distributions of oligomers, similar to the distribution of Fig. 1. The number of equivalents of ethylene oxide (EO) and the reaction time used are as follows: (a) four equivalents of EO, 12 h; (b) 10 equivalents of EO, 12 h; (c) 10 equivalents of EO, 1 week; and (d) 10 equivalents of EO, 4 weeks. The asterisks denote fragments from in-source or metastable fragmentation (see text).

The results of the mass spectrometric analysis can be seen in Fig. 2. Polystyrenes (PS) of lower molecular weight (M_w) were prepared for the investigation of reaction conditions (M_n = 2300 based on SEC); for this reason, the isotopic clusters of the peaks observed are adequately resolved to measure monoisotopic masses (cf. Figs. 1 and 2). Again, all oligomers are detected as Ag-cationized ions. The mass spectrum of the product from the reaction of poly(styryl)lithium with four equivalents of EO after 12 h is shown in Fig. 2a. The spectrum contains a major distribution, A, whose *m*/*z* values correspond to the Ag^+ adducts of PS oligomers with C_4H_9 and CH_2CH_2OH end groups. For example, the 18-mer of this distribution is expected to produce a signal at *m*/*z* (monoisotopic) 18×104.06 ($18 \times C_8H_8$) + 57.06 (C_4H_9) + 45.03 (CH_2CH_2OH) + 106.9 ($^{107}Ag^+$) = 2082, as indeed observed. Dimeric oligomerization of EO would have led to an increase in mass by 44 Da from series A (vide supra), which is not observed, i.e., no peak at *m*/*z* 2126 above noise level.

The asterisks (*) in Fig. 2 denote unresolved peaks that originate by in-source or metastable fragmentation [29–31]. They are distinguished from peaks for molecular or quasi-molecular ions by their broad unresolved shape, an intensity dependence on laser power and disappearance and/or significantly reduced intensity in the linear mode [29–31]. The broadness results from kinetic energy release upon fragmentation; the laser power dependence is caused by the higher energy requirements of fragment ions; and the disappearance of metastable fragment peaks in the linear mode reflects the fact that fragment ions formed metastably (i.e., in a field-free region located between the ionization area and the detector) have the same velocities as the corresponding precursor ions and, hence, reach the linear mode detector (reflectron turned off) simultaneously. On the other hand, in the reflectron mode, the metastable fragments are dispersed from their precursor ions inside the reflector lens (because of different kinetic energies) and, thus, appear at distinct *m*/*z* values.

It is found that the degree of oligomerization increases with the reaction time or the amount of EO added to PSLi. The spectrum of the product after functionalization using 10 equivalents of EO and a reaction time of 12 h (Fig. 2b) reveals two additional products at very low abundance but discernable from noise. Series B is now observed at 44 *m*/*z* units above A. As previously discussed, such a product arises from the incorporation of one more unit of EO at the ω-chain end via an ether linkage, viz. $CH_2CH_2OCH_2CH_2OH$. The intensity of B increases significantly, relative to that of A, in the spectrum of the product obtained from the reaction time of 1 week, Fig. 2c. A further dramatic increase in the intensity of series B is observed after a reaction time of 4 weeks (Fig. 2d). In fact, EO oligomerization is so efficient at this longer reaction time that a third series (C) is detected at 44 *m*/*z* units above B and 88 *m*/*z* units above A. Series C represents polystyrene chains with three units of EO at the ω-chain end. All spectra also show traces of unfunctionalized polymer (series D), which is most abundant in the spectrum for the reaction time of 1 week (Fig. 2c). This product is attributed to adventitious impurities introduced during functionalization, which apparently were highest in the synthesis with a functionalization reaction time of 1 week. It is noteworthy that the dehydration product of B (series B′) is not observed. Evidently, this side reaction is avoided when the functionalized product is treated with degassed methanol for final termination instead of with acidic (HCl) methanol.

A PS with an authentic $CH_2CH_2OCH_2CH_2OH$ group at the ω-chain end can be prepared by reacting PSLi with the di-*p*-toluenesulfonate (ditosylate) of ethylene glycol [17]. This functionalization leads to a mixture of monomeric PS–$CH_2CH_2OCH_2CH_2OTs$ and dimeric PS–$CH_2CH_2OCH_2CH_2$–PS which can be separated quantitatively by silica gel column chromatography [17]. Subsequent removal of the tosyl protecting group in the monomeric polymer by sodium naphthalide gives rise to $CH_2CH_2OCH_2CH_2OH$-terminated polystyrene. The mass spectrum of the polymer produced this way, using *sec*-C_4H_9Li as initiator, is shown in Fig. 3. Only distribution B is observed, confirming that the purification and deprotection steps proceeded quantitatively. The 18-mer of this product would appear at *m*/*z* (monoisotopic) 18×104.06 ($18 \times C_8H_8$) + 57.06 (C_4H_9) + 89.06 ($C_2H_4OC_2H_4OH$) + 106.9 ($^{107}Ag^+$) = 2126, which matches the observed *m*/*z* value (Fig. 3) as well as the *m*/*z* value of the

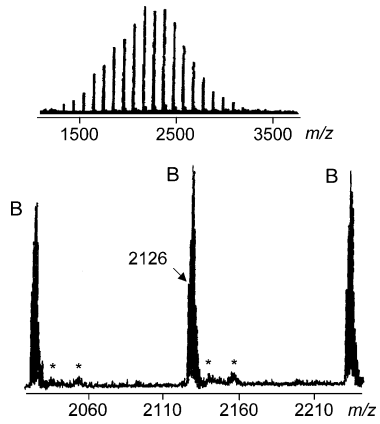


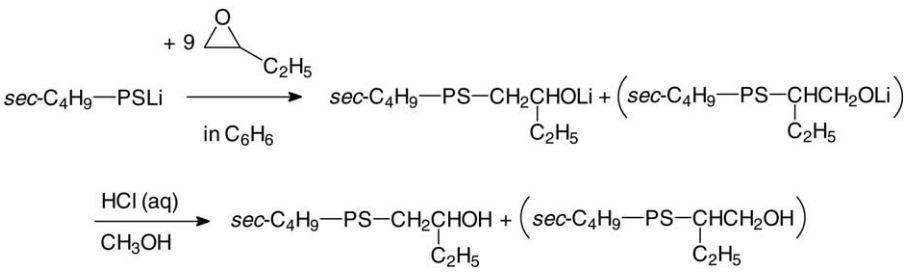
Fig. 3. MALDI mass spectrum of the model polystyrene *sec*-C_4H_9—PS—$CH_2CH_2OCH_2CH_2OH$ prepared using *sec*-C_4H_9Li for initiation and the ditosylate of ethylene glycol for functionalization. The expanded trace shows the *m*/*z* range between the 17-mer and 19-mer peaks of the desired product. The asterisks denote fragments from in-source or metastable fragmentation (see text).

product that was increasing in intensity in Fig. 2 as reaction time and EO concentration increased.

The extent of EO oligomerization upon functionalization with 10 equivalents of EO can be assessed from the relative intensities of the B and A series. The monoisotopic peaks from the corresponding 18-mers are observed at *m*/*z* 2126 and 2082, respectively (Fig. 2). Based on the abundance ratio [*m*/*z* 2126]/[*m*/*z* 2082], the proportion of PS with two EO terminal units increases from 3.4% to 4.9% to 35% if the reaction time is increased from 12 h (Fig. 2b) to 1 week (Fig. 2c) to 4 weeks (Fig. 2d); a replicate experiment on a PS functionalized with 10 equivalents of EO for 12 h led to 3.6% dimeric ω-end group, attesting excellent reproducibility. Similarly, the ratio [*m*/*z* 2170]/[*m*/*z* 2082] reveals that the amount of polymer with three EO terminal groups is 1.0% after 1 and 5.0% after 4 weeks. The quality of such quantitation was evaluated by comparison to H NMR data. Using NMR resonances specific to the CH_2CH_2OH and $CH_2CH_2OCH_2CH_2OH$ terminal groups, the percentage of the sample containing two EO units was calculated at 3.7% (3.4% in the replicate experiment), 5.5 and 33% for reaction periods of 12 h, 1 week and 4 weeks, respectively. The excellent agreement between NMR and MALDI mass spectrometry results clearly shows that MALDI-TOF MS can be used as an absolute, independent method for both the qualitative as well as quantitative analysis of side products, provided their structures and sizes do not vary substantially from those of the main product [17]. The high sensitivity and dispersive nature of MS allow for the detection of minor products at the parts-per-thousand (or lower) concentration level; in contrast, the integrative NMR method requires unique signal(s) that stand(s) out from those created by the polymer backbone as well as significantly larger concentrations (>3% for the hydroxylated PS studied).

3.2. Polystyrene functionalization with ethylene oxide homologs

Oligomerization of the functionalizing reagent should be prohibited by using a bulkier epoxide, such as propylene oxide or 1-butene oxide (1,2-epoxybutane) [17,25]. The latter reagent was selected for investigation of its termination chemistry by MS. In this case, the living poly(styryl)lithium anion was functionalized at 25 °C with a nine-fold excess of 1-butene oxide (Scheme 3) [16]. The reaction mixture was stirred for 2 days and then quenched with acidic methanol to recover the polymer. The MALDI mass spectrum (Fig. 4) reveals the presence of one dominant and one side product. The main distribution A originates from the desired polymer shown in Scheme 3. The measured *m*/*z* values of this series agree well with the composition $[C_4H_9—PS—C_4H_8OH + Ag]^+$; for example, the peak centered at *m*/*z* 2942.2 (monoisotopic value) represents the Ag^+ adduct of a 1-butene oxide end-capped polystyrene 26-mer, while the adjacent peak at *m*/*z* 3046.2 is the corresponding 27-mer. Potentially, the PSLi anion can attack either ring C-atom of 1-butene oxide, leading to isomeric end groups (Scheme 3). The primary alcohol, which is formed from the less favorable attack on the more hindered methine C-atom, is not detected by ^{13}C NMR [16]; hence, the reaction of PSLi with 1-butene oxide is highly regioselective and preferentially produces a secondary alcohol at the ω-chain end. Note that such regiochemistry information cannot be obtained by mass spectrometry; obviously, the best possible structural characterization of a polymer often necessitates the combination of complementary analytical techniques.



Scheme 3.

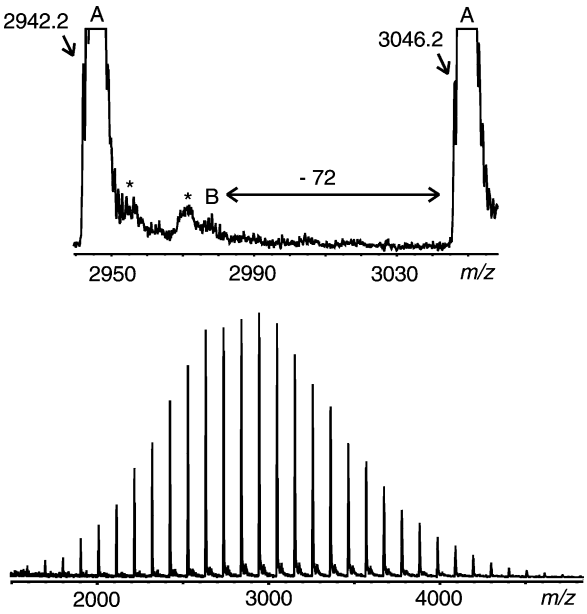


Fig. 4. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation and 1-butene oxide for functionalization (Scheme 3). The expanded trace shows the *m*/*z* range between the 26-mer and 27-mer peaks of the desired product, *sec*-C_4H_9─PS─C_4H_8OH. The asterisks denote fragments from in-source or metastable fragmentation.

The minor series B, which has a mass that is 72 Da (mass of butane oxide) lower than series A, represents unfunctionalized oligomers (H as the ω-end group). The low peak intensity of series B (∼3% of series A) reveals a high degree of functionalization via Scheme 3. It is important to note that there are no peaks at 72 *m*/*z* units higher than series A; this result provides strong evidence that a second unit of 1-butene oxide is not added to the ω-chain end, in concert with the above stated expectation that bulkier epoxides do not undergo oligomerization during the functionalization step.

An alternative means to suppress oligomerization of the functionalizing reagent is by using a less strained and, hence, less reactive electrophile. This is exemplified in Fig. 5 by the mass spectrum of a PS prepared by reacting poly(styryl)lithium with oxetane, a cyclic ether with a 4-membered ring. The only distribution detected (A) are Ag^+ adducts of the desired polymer, $[C_4H_9–PS–CH_2CH_2CH_2OH + Ag]^+$.

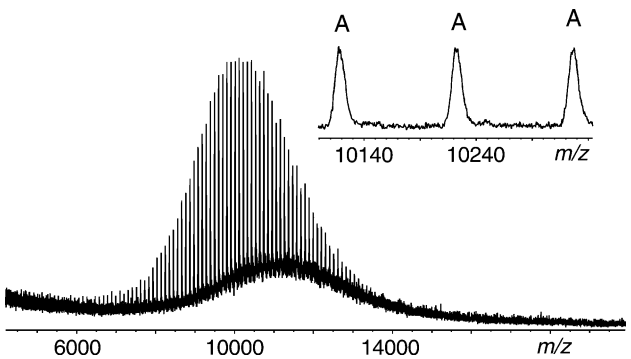


Fig. 5. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation and oxetane for functionalization. The expanded trace shows the *m*/*z* range between the 95-mer and 97-mer peaks of the desired polymer, *sec*-C_4H_9─PS─$CH_2CH_2CH_2OH$.

A positive aspect of oligomerization is that it may be useful for the preparation of tailored end groups via the sequential addition of different epoxides to the living anion. In a pilot experiment without careful control of reaction conditions, EO and propylene oxide (PO) were added sequentially to poly(styryl)lithium. After isolation, the resulting polystyrene gives rise to the MALDI mass spectrum of Fig. 6. The main distribution observed (A) corresponds to polymer chains that incorporated one EO unit at their ω-end, viz. $[C_4H_9–PS–C_2H_4OH + Ag]^+$. There is a second significant distribution (B) that appears 58 Da above A and arises from the incorporation of EO and PO units, viz. $[C_4H_9–PS–C_2H_4OC_3H_6OH + Ag]^+$. A third distribution (C) appearing just above baseline is attributed to Ag^+ adducts of $C_4H_9–PS–CH_2CH_2OCH{=}CH_2$, generated via water loss from $C_4H_9–PS–CH_2CH_2OCH_2CH_2OH$ oligomers which themselves are barely detectable. Oligomerization of mixed epoxides could develop into a promising method for creating customized end groups if optimum reaction conditions can be found that make polymer B the main product.

3.3. Polystyrene macromonomers

Macromonomers or macromers® are macromolecules with a polymerizable end group [32] that can copolymerize with a backbone forming monomer to yield comb-type graft copolymers [33,34]. Hard segments in the grafts (for example, polystyrene chains) and a soft-segment backbone (for example, polydiene-based) often give rise to thermoplastic elastomers [35]. A convenient and efficient route to diene-functionalized macromonomers involves reaction of living

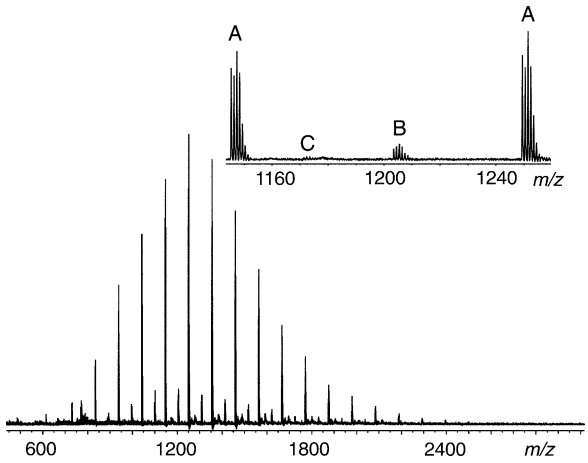
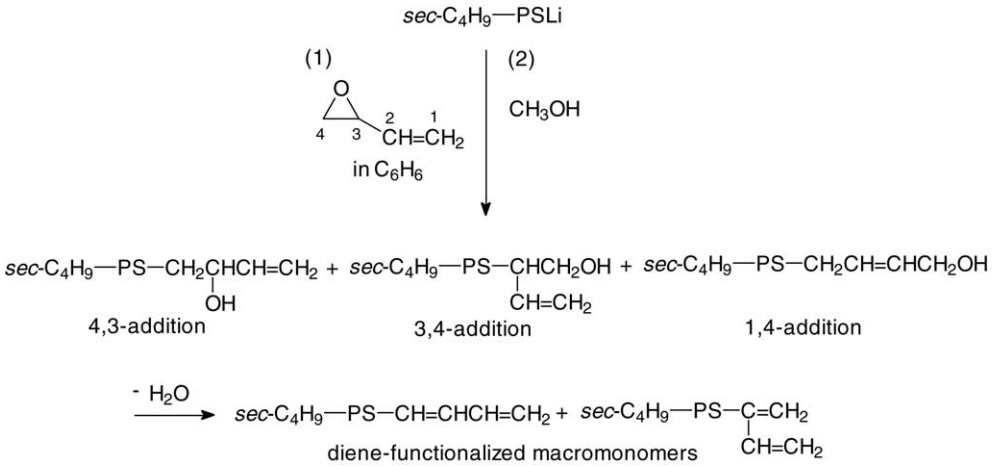


Fig. 6. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation. The polymer was functionalized by sequential addition of ethylene oxide (EO) and propylene oxide (PO). The expanded trace shows the *m*/*z* range between the 9-mer and 10-mer peaks of the main product, *sec*-C_4H_9─PS─CH_2CH_2OH.



Scheme 4.

poly(styryl)lithium with 3,4-epoxy-1-butene (EPB) to produce butene-ol end groups (Scheme 4) that are later dehydrated [18,20]. This reaction is typically carried out for 5 h at 25 °C with 1.2 equivalents of EPB [20]. Poly(styryl)lithium can undergo 4,3-, 3,4- or 1,4-addition to EPB, ultimately generating three isomeric butene-ols (Scheme 4) which cannot be distinguished by mass spectrometry. NMR experiments indicated that all three isomers are formed under the conditions stated in approximately equal proportions [20].

The MALDI mass spectrum of the compound of the crude sample before dehydration is depicted in Fig. 7. It essentially contains one distribution (A), whose *m*/*z* values are assigned the composition $[C_4H_9{-}PS{-}C_4H_6OH + Ag]^+$, as the calculated monoisotopic mass-to-charge ratios of this series (for example, 2420.3 for the 21-mer) match the observed *m*/*z* values (2420.1 for the peak of the 21-mer). The expanded view shows traces of a second series, distribution B, corresponding to unfunctionalized polymer, $[C_4H_9{-}PS{-}H + Ag]^+$ (ca. 2%); calculated and observed *m*/*z* values of the 21-mer of this minor series are 2350.3 and 2350.2, respectively. The mass difference between the same *n*-mer of distributions A and B is 70 Da, i.e., the mass of the EPB reagent. The minor product can be removed completely by column chromatography using basic alumina as the stationary phase and toluene as the eluent [20].

Dehydration of the purified butene-ol-terminated polystyrene was effected with *p*-toluenesulfonic acid or Amberlyst® 15 ion-exchange resin [18,20]. The mass spectrum of the dehydrated product obtained with the sulfonic acid is shown in Fig. 8. Its major distribution corresponds to Ag^+-cationized dehydrated oligomers, having the structure $[C_4H_9{-}PS{-}C_4H_5 + Ag]^+$, with the 21-mer expected at (monoisotopic) *m*/*z* 2402.3 and actually measured at *m*/*z* 2402.0. The mass difference observed between EPB-functionalized and diene-functionalized oligomers with the same number of repeat units is 18.1 Da, which corresponds to water loss, confirming the formation of a diene-functionalized macromonomer. It should be mentioned that the spectrum of Fig. 8 displays several other minor distributions whose composition is difficult to discern; they most likely result from side reactions occurring during the dehydration process. Further investigation into the dehydration conditions is needed to understand the formation of these byproducts and determine reaction conditions that eliminate them.

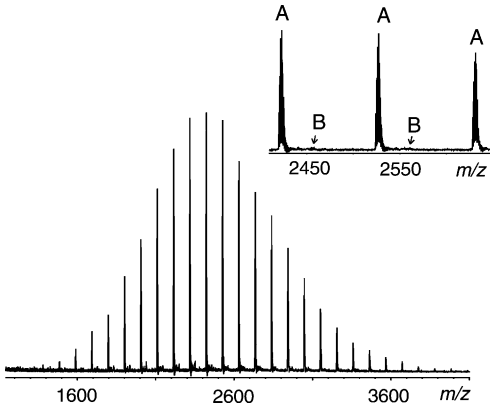


Fig. 7. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation and 3,4-epoxy-1-butene (EPB) for functionalization (Scheme 4). The expanded trance shows the *m*/*z* range between the 21-mer and 23-mer peaks of the desired product, *sec*-$C_4H_9{-}PS{-}C_4H_6OH$.

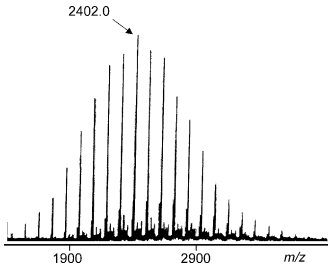
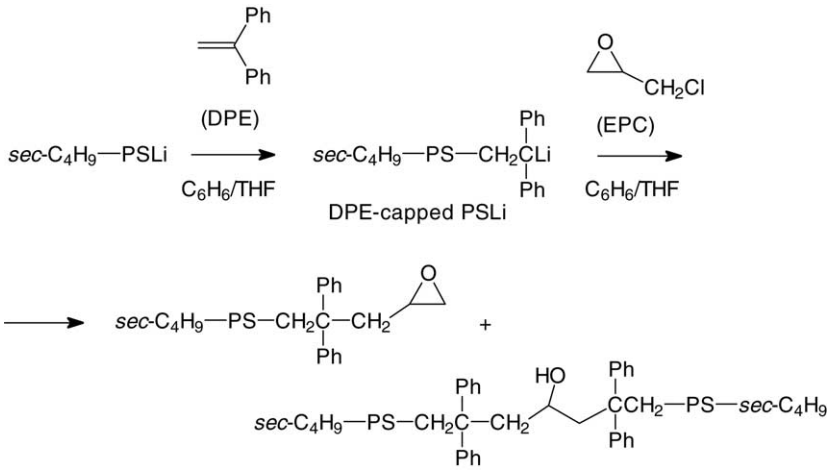


Fig. 8. MALDI mass spectrum of the dehydration product of *sec*-$C_4H_9{-}PS{-}C_4H_6OH$ (Scheme 4). The peak at *m*/*z* 2402.0 (monoisotopic value) corresponds to the ionized 21-mer of *sec*-$C_4H_9{-}PS{-}C_4H_5$.



Scheme 5.

Epoxide substituents constitute an alternative polymerizable end group. Epoxide-functionalized styrene-based macromonomers can be prepared using epichlorohydrin (EPC) as the functionalizing reagent (Scheme 5) [36]. EPC carries two electrophilic CH_2 groups with which PSLi can react. The favored pathway is substitution of Cl^- by PS^-, but addition of PS^- to the epoxide ring also is possible. To eliminate the latter pathway, the polystyryl anion was end-capped with diphenylethylene (DPE), which slows down the attack at the epoxide carbon due to steric effects, and the mixing of living anion and functionalization reagent was performed in reverse addition mode (anion solution added to EPC solution) [36]. Based on MALDI mass spectrometry (Fig. 9), reaction of the DPE-extended polystyryl anions with EPC indeed mainly produces oligomers that are ω-end-capped with 2,3-epoxypropyl groups (Scheme 5). Such an end group can be hydrolyzed to form the corresponding 1,2-diol which is a condensation macromonomer. A minor distribution of oligomers at ca. twice the mass is also observed, however, and corresponds to a dimeric product in which an additional DPE-extended anion has been added to the epoxide ring (Scheme 5). Overall, quantitative functionalization is obtained (no trace of any product other than the mentioned ones), indicating that DPE-extension (combined with the use of THF [2]) reduces aggregation of the lithiated living anions; aggregation is a major cause for the production of unfunctionalized polymer [2]. End-capping by DPE also reduces significantly the yield of the dimeric product, although it does not eliminate it completely [36].

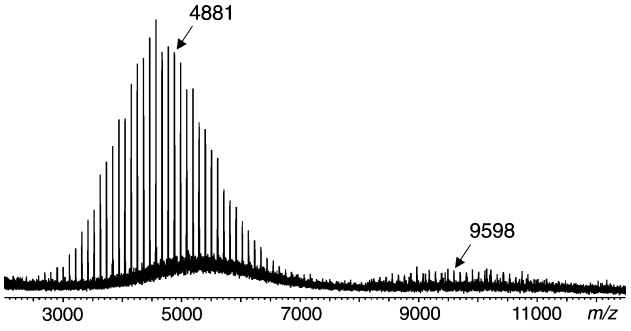


Fig. 9. MALDI mass spectrum of a polystyrene prepared using *sec*-C_4H_9Li for initiation and EPC for functionalization; before the latter reaction, the living polystyryl anion was end-capped with 1,1-diphenylethylene (DPE). Only one product is observed in both the low- and high-mass distributions (see text). The peaks at *m*/*z* 4881 and 9598 (average values) correspond to the ionized 43-mers of the desired polystyrene and the dimeric byproduct, respectively (cf. Scheme 5).

3.4. Functionalization with amine groups

When termination is effected by a reagent that can only undergo nucleophilic substitution with the living polymeric anion, oligomerization of the terminating electrophile and often other side reactions are avoided [37]. One example of such a reagent is $Cl–CH_2CH_2CH_2N(CH_3)_2$, which is suitable for quantitative ω-amination. A polybutadiene (PBD) was prepared by mixing *sec*-C_4H_9Li with butadiene and LiCl in cyclohexane and reacting the resulting poly(butadienyl)lithium first with the mentioned reagent and subsequently with CH_3Cl in methylene chloride. The lithium salt cross-associates with the chain ends of PBDLi to form mixed aggregates; this affects the reactivity of the living organolithium compound (i.e., the living anion), which in turn may lead to a more quantitative functionalization [2]. CH_3Cl converts the $N(CH_3)_2$ end group into a quaternary ammonium chloride, $N^+(CH_3)_3Cl^-$. The MALDI mass spectrum of the product (Fig. 10) displays only one distribution (A), whose monoisotopic *m*/*z* values reveal the composition $C_4H_9–PBD–CH_2CH_2CH_2N^+(CH_3)_3$. Analogous nucleophilic substitutions can be employed to introduce other heteroatoms at the ω-chain end with high yield [37].

The ions observed in the spectrum of Fig. 10 do not contain Ag^+. Further, the same mass spectrum is obtained with or without addition of silver trifluoroacetate upon sample preparation. Any not permanently charged PBD byproducts would be ionized by Ag^+ addition. The covalently pre-charged poly-

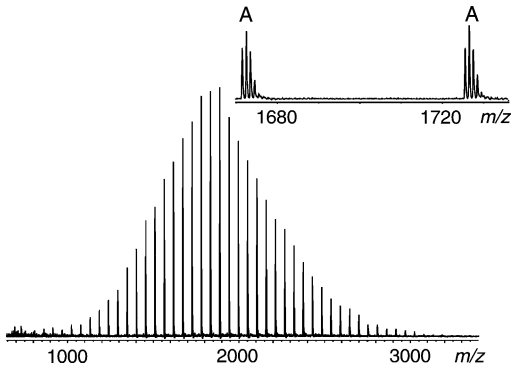


Fig. 10. MALDI mass spectrum of a polybutadiene prepared using *sec*-C_4H_9Li for initiation and $Cl{-}CH_2CH_2CH_2N(CH_3)$ for functionalization followed by precipitation of the product as a quaternary ammonium chloride with CH_3Cl. The expanded trace shows the *m*/*z* range between the 28-mer and 29-mer peaks of the product, *sec*-$C_4H_9{-}PBD{-}CH_2CH_2CH_2N^+(CH_3)_3$. Note that this is the only spectrum in which the observed ions do not contain Ag^+.

mer could, however, produce a larger ion flux upon MALDI than any non-charged admixtures, thereby compromising the detection sensitivity for the latter products. In such a case, the MS characterization of the minor functionalization products requires prior chromatographic separation.

3.5. Initiation with protected functionalized alkyllithiums

A protected functionalized initiator introduces a substituent at the initiating or α-chain end of every macromolecule synthesized; consequently, functionalization should be more quantitative than with post-polymerization reactions, where aggregation of the chain ends may prevent complete functionalization (vide supra). Furthermore, combining the use of protected functionalized initiators with post-polymerization functionalization offers a promising route to telechelic or star-branched polymers. The initiator $(CH_3)_3Si{-}OCH_2C(CH_3)_2CH_2Li$, which contains a protected hydroxy group, was used for the preparation of a PBD in cyclohexane. The MALDI mass spectrum of the product obtained by termination with methanol (H at ω-chain end) displays a major and a minor distribution of oligomers with the expected repeat unit of 54 Da (Fig. 11). All peaks are Ag^+ attachment ions. The main series, A, arises form the expected polybutadiene oligomers, viz. $(CH_3)_3Si{-}OCH_2C(CH_3)_2CH_2{-}PBD{-}H$. The minor distribution, series B (ca. 14%), arises from oligomers that are missing the protecting group, i.e., $HOCH_2C(CH_3)_2CH_2{-}PBD{-}H$, presumably formed during isolation of the product. It can be concluded that complete functionalization was achieved, substantiating the promise of this non-traditional type of initiator. A drawback is the generation of a low molecular weight tail, which is also observed upon SEC. A plausible cause of this tail is a significant difference in initiation and propagation rates; these rates must be comparable for the formation of well-defined, narrow molecular weight polymers [2].

Chain extension of the initiator with isoprene (C_5H_8) would make the initiator and growing polybutadienyl anions structurally analogous, which in turn should lead to more similar initiation and propagation rates. To test this expectation the commercially available initiator shown in Scheme 6 was used; it contains a protected hydroxy group and is chain-extended with one equivalent of isoprene. The PBD prepared in cyclohexane with this initiator and with methanol for termination furnishes the MALDI mass spectrum shown in Fig. 12. Four distributions with the butadiene repeat unit (54 Da) are readily detected (A–D). Based on the corresponding monoisotopic *m*/*z* values, the A–D series contain Ag^+-cationized polybutadiene oligomers with the general structure $(CH_3)_3C{-}OCH_2C(CH_3)_2CH_2{-}(isoprene)_x{-}PBD{-}H$, where $x = 0$ (series A), 1

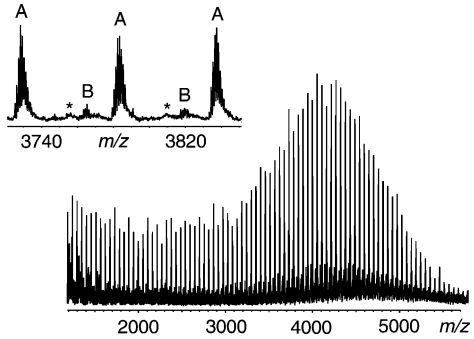
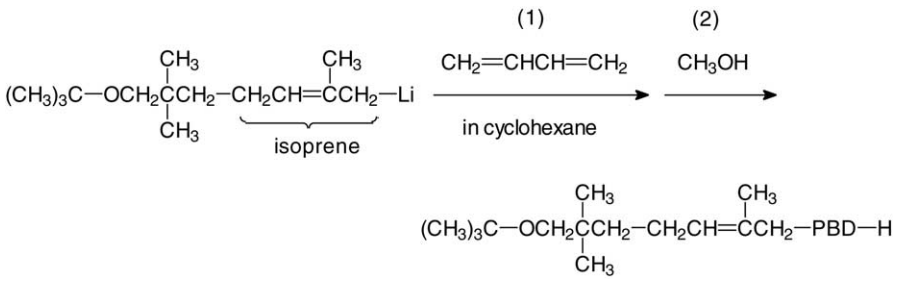


Fig. 11. MALDI mass spectrum of a polybutadiene prepared using the protected functionalized initiator $(CH_3)_3Si{-}OCH_2C(CH_3)_2CH_2Li$ and no ω-functionalization reagent. The expanded trace shows the *m*/*z* range between the 64-mer and 66-mer peaks of the desired product, $(CH_3)_3Si{-}OCH_2C(CH_3)_2CH_2{-}PBD{-}H$. The asterisks denote fragments from in-source or metastable fragmentation.



Scheme 6.

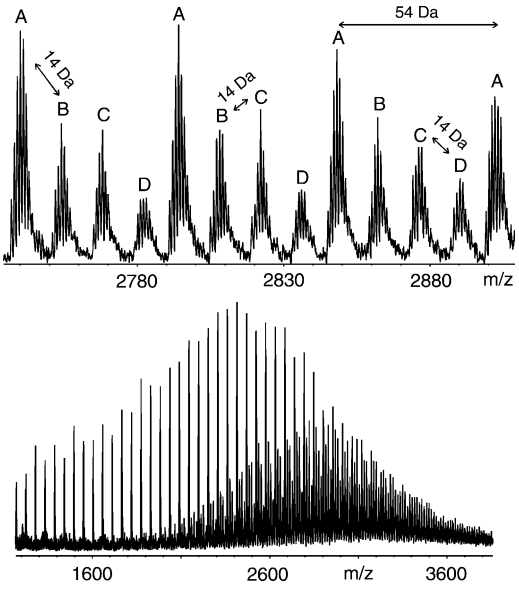


Fig. 12. MALDI mass spectrum of a polybutadiene prepared using the protected functionalized initiator $(CH_3)_3C{-}OCH_2C(CH_3)_2CH_2{-}CH_2CH{=}C(CH_3)CH_2Li$ and no ω-functionalization reagent (Scheme 6). The expanded trace shows the *m*/*z* range between the 46-mer and 49-mer peaks of the main product, $(CH_3)_3C{-}OCH_2C(CH_3)_2CH_2{-}PBD{-}H$.

(series B), 2 (series C) or 3 (series D). Presumably, small amounts of polymer containing more than three units of isoprene are also present. Even though the initiator was reacted with one equivalent of isoprene (vide supra), the PBD product shows a substantial amount of chains without any isoprene (series A) as well as substantial amounts of oligomers with two and three isoprene units (series C and D). This distribution points out that the rate for adding one isoprene unit to the unextended initiator is lower than that for adding a second or third isoprene molecule to an already extended initiator. Further studies are necessary to overcome this problem and develop well-characterized protected functionalized initiators.

A closer look at Fig. 12 also reveals that only distribution A extends into the low M_w tail; series A contains PBD that was formed from the unextended initiator. In sharp contrast, the polymer derived from the chain-extended initiator, viz. series B–D, exhibits the narrow MWD characteristic of well-controlled anionic polymerizations. Gratifyingly, the initiator molecules that were chain-extended lead to competitive initiation versus propagation rates and, hence, a narrow molecular weight distribution with low polydispersity.

4. Conclusions

The cases presented demonstrate that MALDI-TOF MS is a sensitive probe for the analysis of the major and minor oligomers produced during novel functionalization reactions whose mechanisms are not yet well established. The technique is particularly valuable for the identification of the end groups of the minor distributions that may be undetectable by other analytical means. Complete characterization of all the oligomers generated during functionalization reactions provides an essential tool to the synthetic chemist for understanding the reactions occurring, which facilitates the selection of alternative synthetic routes or the optimization of existing methods.

An important finding reported in this study is that MALDI-TOF MS can be used for the quantitative determination of the end groups of oligomers with similar size. Mass spectrometry allows for the detection of unexpected reaction pathways that proceed with low yield. In the same vein, MS is a particularly sensitive method for monitoring any unfunctionalized product.

Analysis of the products from novel functionalization reactions by MALDI-TOF MS provides fast, accurate and detailed insight into the corresponding end group microstructures. The method is especially suitable for polymers prepared by living anionic polymerization techniques, for which molecular weights are spread over a relatively narrow range; this precludes dramatic differences in ionization and/or detection efficiencies, so that (at least qualitatively) all components of the polymer mixture can be observed above noise level. This sensitivity, combined with the speed of mass spectral acquisition, is resulting in a steadily increasing use of MS-based characterizations in the development of polymerization and polymer functionalization conditions.

Acknowledgements

We thank The Ohio Board of Regents, the National Science Foundation and The University of Akron for generous financial support of the Mass Spectrometry Center. We are grateful to Dr. Youngjoon Lee, Dr. Robert T. Mathers, Dr. Qing Ge, Dr. Deanna L. Gomochak and Dr. Joseph Pickel for the synthesis of the polymers as well as to Mrs. Kathleen M. Wollyung for experimental assistance and helpful discussions in the mass spectrometry analyses.

References

[1] J. Jagur-Grodzinski, React. Funct. Polym. 49 (2001) 1.
[2] H.L. Hsieh, R.P. Quirk, Anionic Polymerization: Principles and Applications, Marcel Dekker, New York, 1996.
[3] R.P. Quirk, S.H. Jang, H. Yang, Y. Lee, Macromol. Symp. 132 (1998) 281.
[4] M.W.F. Nielen, Mass Spectrom. Rev. 18 (1999) 309.
[5] S.D. Hanton, Chem. Rev. 101 (2001) 527.
[6] J.H. Scrivens, A.T. Jackson, Int. J. Mass Spectrom. 200 (2000) 261.
[7] C.N. McEwen, P.M. Peacock, Anal. Chem. 74 (2002) 2743.
[8] G. Montaudo, R.P. Lattimer (Eds.), Mass Spectrometry of Polymers, CRC Press, Baca Raton, 2002.
[9] R. Murgasova, D.M. Hercules, Int. J. Mass Spectrom. 226 (2003) 151.
[10] H. Pasch, W. Schrepp, MALDI-TOF Mass Spectrometry of Polymers, Springer, Berlin, 2003.

[11] K. Tanaka, H. Waki, Y. Ido, S. Akita, Y. Yoshida, T. Yoshida, Rapid Commun. Mass Spectrom. 2 (1988) 151.
[12] M. Karas, F. Hillenkamp, Anal. Chem. 60 (1988) 2299.
[13] M. Yamashita, J.B. Fenn, J. Phys. Chem. 88 (1984) 4451.
[14] G. Montaudo, M.S. Montaudo, F. Samperi, in: G. Montaudo, R.P. Lattimer (Eds.), Mass Spectrometry of Polymers, CRC Press, Boca Raton, 2002, p. 419.
[15] C. Wesdemiotis, M.A. Arnould, Y. Lee, R.P. Quirk, Polym. Prepr. 41/1 (2000) 629.
[16] R.P. Quirk, Q. Ge, M.A. Arnould, C. Wesdemiotis, Macromol. Chem. Phys. 202 (2001) 1761.
[17] R.P. Quirk, R.T. Mathers, C. Wesdemiotis, M.A. Arnould, Macromolecules 35 (2002) 2912.
[18] R.P. Quirk, D.L. Gomochak, C. Wesdemiotis, M.A. Arnould, Polym. Mater. Sci. Eng. 87 (2002) 160.
[19] R.P. Quirk, R.T. Mathers, J.-J. Ma, C. Wesdemiotis, M.A. Arnould, Macromol. Symp. 183 (2002) 17.
[20] R.P. Quirk, D.L. Gomochak, C. Wesdemiotis, M.A. Arnould, J. Polym. Sci. A Polym. Chem. 41 (2003) 947.
[21] C. Wesdemiotis, M.A. Arnould, D.L. Gomochak, J.M. Pickel, R.P. Quirk, Polym. Mater. Sci. Eng. 88 (2003) 130.
[22] R.P. Quirk, Y. Guo, C. Wesdemiotis, M.A. Arnould, J. Polym. Sci. A Polym. Chem. 41 (2003) 2435.
[23] R.P. Quirk, Q. Zhuo, S.H. Jang, Y. Lee, G.M. Lizarraga, in: R.P. Quirk (Ed.), Applications of Anionic Polymerization Research, ACS Symp. Ser. 696, American Chemical Society, Washington, DC, 1998, p. 2.
[24] R.P. Quirk, Polym. Prepr. 40/1 (1999) 590.
[25] R.P. Quirk, G.M. Lizarraga, Macromolecules 31 (1998) 3424.
[26] R.P. Quirk, S.H. Jang, K. Han, H. Yang, B. Rix, Y. Lee, in: A.O. Patil, D.N. Schulz, B.M. Novak (Eds.), Functional Polymers: Modern Synthetic Methods and Novel Structures, ACS Symp. Ser. 704, American Chemical Society, Washington, DC, 1998, p. 71.
[27] H. Ji, N. Sato, W.K. Nonidez, J.W. Mays, Polymer 43 (2002) 7119.
[28] M. Morton, L.J. Fetters, Rubber Chem. Technol. 48 (1975) 359.
[29] E. DeHoffmann, V. Stroobant, Mass Spectrometry: Principles and Applications, second ed., John Wiley & Sons, Chichester, 2001.
[30] R.J. Cotter, Time-of-Flight Mass Spectrometry: Instrumentation and Applications in Biological Research, American Chemical Society, Washington, DC, 1997.
[31] D.J. Harvey, A.P. Hunter, R.H. Bateman, J. Brown, G. Critchley, Int. J. Mass Spectrom. 188 (1999) 131.
[32] V. Perzec, C. Pugh, O. Nuyken, S.D. Pask, in: G.C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Eds.), Comprehensive Polymer Science, vol. 6 (Polymer Reactions), Pergamon Press, Elmsford, 1989, p. 551.
[33] K. Ito, Prog. Polym. Sci. 23 (1998) 581.
[34] F. Peruch, J.-F. Lahitte, F. Isel, P.J. Lutz, Macromol. Symp. 183 (2002) 159.
[35] G. Holden, N.R. Legge, R.P. Quirk, H. Schroeder (Eds.), Thermoplastic Elastomers, second ed., Hanser Publishers, New York, 1996.
[36] R.P. Quirk, Q. Zhuo, Macromolecules 30 (1997) 1531.
[37] R.P. Quirk, Y. Lee, Macromol. Symp. 157 (1999) 161.