Enhanced Ionization in Electrospray Ionization Mass Spectrometry of Labile End-Group-Containing Polystyrenes Using Silver(I) Tetrafluoroborate as Doping Salt

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ABSTRACT: The use of silver tetrafluoroborate as a doping salt to achieve efficient and soft desorption/ionization of labile end-group-carrying polystyrene during electrospray ionization is demonstrated. Polystyrene carrying a dithioester end group prepared via reversible addition fragmentation chain transfer (RAFT) chemistry (using the RAFT agent cumyl phenyldithioacetate) as well as a commercial polymer standard prepared by anionic polymerization serve as model compounds. By employing silver tetrafluoroborate as ionization agent, an increase in ion count of more than one order of magnitude was achieved compared to ionization with sodium iodide. Little loss of the end group occurred via elimination of the dithioacid to yield vinyl-terminated polymer. A possible mechanism is given for catalysis of the cleavage reaction in the presence of silver salts. Side-product formation due to thermal or collision induced loss of the dithioester was kept at a minimum under optimized source conditions. Thus, we introduce a novel soft ionization protocol for polystyrenes, which are often difficult to ionize.

Introduction

Soft desorption/ionization mass spectrometry (MS) has become a powerful tool in macromolecular research during the past decade. Two ionization techniques are most frequently applied to the characterization of polymers, namely electrospray ionization (ESI)[1] and matrix-assisted laser desorption ionization (MALDI).[2] Although fundamentally different processes are involved in ion formation, both techniques usually allow ionization of the intact synthetic macromolecules with little or no fragmentation. Interfacing these techniques to high-resolution mass analyzers such as quadrupole-time-of-flight (Q-TOF) instruments yields exact molecular masses for the polymer of interest with mass accuracies in the ppm region. This information may be used for extensive characterization of the polymer with regards to functional end groups, molecular weight distribution, and monomer composition. Both MALDI and ESI have found numerous applications in polymer analysis, including functional polymer characterization, polymer degradation studies,[3−6] and mechanistic investigations.[7−10]

In the present study we demonstrate that ESI-MS is able to effectively and softly ionize nonpolar polymers. We are using polystyrene produced by reversible addition fragmentation chain transfer (RAFT) carrying a labile dithioester end group as an example as well as nonfunctional polystyrene. Efficient ionization is achieved by applying silver(I) tetrafluoroborate as a doping salt, while formation of fragmentation products is kept at a minimum under optimized electrospray conditions. The applicability of this technique is thereby extended to yet another interesting and important class of polymers, for which formerly soft desorption/ionization conditions could only be found in limited cases.

The quality of the mass spectrum has a direct impact on the level of certainty with which unknown compounds of low abundance may be assigned to peaks in the spectrum. This is especially important in mechanistic investigations where the majority of components are unknown. Mass resolution and accuracy, as well as sensitivity, are important instrumental parameters determining the spectral quality.[11] Softness and selectivity of the ionization technique are equally important, as degradation products will significantly complicate interpretation of the spectrum.[7]

Although MALDI and ESI each have their individual advantages and drawbacks, today MALDI has found significantly more applications in polymer characterization.[4] A number of matrices exist in MALDI that are tailored to ionize polymers with widely differing repeat unit polarity.[12] Addition of metal salts of Na^+, Cu^+, or Ag^+ is usually necessary for ion formation with nonpolar systems.[13,14]

Unfortunately for labile end-group-containing polymers and especially for polystyrene, cleavage of the end group may easily occur upon ionization with MALDI. For example, when Nonaka et al. analyzed chlorine-functionalized PS using MALDI with a dithranol/sodium trifluoroacetate (NaTFA) matrix, only spectra of the vinyl-terminated polymer were obtained.[15] Significantly less vinyl-terminated polymer was observed for poly(methyl acrylate) and poly(methyl methacrylate), suggesting that polystyrene is especially prone to cleavage of end groups. Dourges et al., using a dithranol/silver trifluoroacetate (AgTFA) matrix, were not able to detect any polymer carrying the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) end group in nitroxide-mediated polymerization of styrene. Instead, they observed the vinyl and methylene-terminated polystyrene. The methylene-terminated polymer was assigned to fragmentation products in agreement with earlier studies by Zammit et al.[16] By employing mild protonating conditions using 2,5-dihydroxybenzene (DHB) without added salts, the authors were able to observe only the TEMPO-capped polystyrene. More recently Bartsch et al. applied the same conditions to TEMPO-end capped, chlorine-, amine-, and acrylate-functionalized polystyrene.[17] Although they

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were able to obtain spectra of the intact polymers, the authors stated that no ionization of dead chains with DHB would occur due to lack of basic functional groups.

When turning to polymers synthesized by reversible addition fragmentation chain transfer (RAFT), similar problems are encountered: Jiang et al. found that the dithioacid group was lost when they ionized RAFT end-group-containing poly(methyl methacrylate) in MALDI using cyano-4-hydroxycinnamic acid (CHCA) as matrix. This matrix is known to be a so-called "hot" matrix allowing a high amount of in-source and post-source fragmentation.[18] With ESI, however, spectra of the intact polymer could be obtained.[19] In a similar situation to that of Bartsch,[17] Zhou et al. were able to ionize polystyrene produced by phenyl dithioester-mediated RAFT polymerization. As the initiator and the leaving group of the RAFT agent carried terpyridine units, facile protonation was achieved in this special case, allowing the observation of termination products of the intermediate radical.[20] Schilli et al. discussed the occurrence of a high amount of vinyl-terminated polymer in their MALDI spectra of poly(NIPAAM) mediated by dithiocarbamates. They used post-source decay to prove that the RAFT end group is easily lost.[21] However, Venkatesh et al. were able to obtain spectra of unfragmented poly(butyl acrylate) carrying a phenyl dithiobenzoate end group using 2-[2E-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malonitrile (DCTB)/NaTFA as matrix, showing that for polar polymers soft desorption/ionization by MALDI can be possible.[10] It is seen though that soft desorption/ionization of labile end-group-containing polystyrene by MALDI is—except for a few special cases—still not possible to this date.

Since apolar synthetic macromolecules have a rather low affinity toward coordination of metal ions an effective doping salt for polymer ionization by ESI should be selected carefully: (i) The adduct ion should have a high affinity toward complexation of the polymer backbone. (ii) Solubility of the salt in the solvent mixture and especially in the solvent component with the highest boiling point should be very high. (iii) The counterion should be well stabilized and have low coordination affinity toward the co-ion attached to the polymer. (iv) Both the adduct ion and its counterion should be chemically inert, meaning that neither should exhibit excessive Lewis basic or acidic behavior or a high redox potential.

Silver(I) is able to form kinetically labile complexes with arene- and vinyl-containing organic molecules. A number of applications from analytical chromatography[22] to membrane technology[23] have made use of this characteristic. Experimental and computational data on small molecules show that silver binds to alkenes and arenes in an η^2 or η^1 mode,[24] gas-phase bond dissociation energies being in the area of 30−40 kcal mol^{-1}.[25,26] Canty and Colton showed that ESI-MS can be used successfully to investigate species formed by alkene and arene complexation of silver(I).[27]

Despite these findings and the successful application of silver salts in MALDI, only scarce information on ESI-MS of polystyrene is available. Jasieczek et al. employed potassium iodide for the electrospray ionization of polystyrenes and subsequently investigated the influence of cone potential on the observed molecular weight distribution.[28] Deery et al. investigated the use of different alkaline and transition metal salts for ionization of polystyrene using MALDI and ESI.[29] They found that alkaline, copper, and silver salts can be used to obtain polystyrene spectra. Especially silver trifluoroacetate gave excellent spectral quality. Their study was limited to nonfunctionalized polystyrene.

The present study investigates the applicability of silver salts in the electrospray ionization of labile end-group-containing polystyrenes, especially with regards to fragmentation reactions and ionization efficiency, with the aim to significantly enhance the mass spectrometric analysis of polystyrenes.

Experimental Section

Materials. Styrene (Aldrich, 99%) was freed from inhibitor by passing through a column of basic alumina prior to use. Sodium iodide (99%, Ajax Chemicals), silver tetrafluoroborate (99%, Aldrich), dichloromethane (HPLC grade, Aldrich), tetrahydrofuran (HPLC grade, Ajax Chemicals), and methanol (HPLC grade, Ajax Chemicals) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, DuPont) was recrystallized twice from ethanol prior to use. Cumylphenyl dithioacetate (CPDA) was synthesized using the CAMD method of Quinn et al.,[30] and its purity was confirmed by NMR spectroscopy. The polystyrene standard prepared by anionic polymerization (peak molecular weight (M_p) = 1570 g mol^{-1}, polydispersity index (PDI) = 1.07) was obtained from Polymer Laboratories (Church Stretton, UK).

CPDA-Mediated Polymerization of Styrene. A bulk solution of CPDA (190 mg, 0.70 mmol) and the initiator AIBN (16.4 mg, 0.10 mmol) in styrene (20 mL, 175 mmol) was prepared and distributed into three Schlenk tubes. The solutions were degassed by three freeze−pump−thaw cycles and then placed into a heated oil bath held at a constant temperature of 60 °C. The samples were removed after 125, 265, and 380 min reaction time and immediately cooled to room temperature. Conversion was determined gravimetrically. Molecular weight distributions were determined by size exclusion chromatography (SEC) to ensure that the polymerization proceeded in a controlled manner. Only the polymer produced after 265 min reaction time was used in the following studies (number-average molecular weight (M_n) = 1080 g mol^{-1}, weight-average molecular weight (M_w) = 1320 g mol^{-1}, PDI = 1.22).

Size Exclusion Chromatography. A Shimadzu liquid chromatography system comprising a solvent degasser (DGU-12A), a pump (LC-10AT), an autoinjector (SIL-10AD), a column oven (CTO-10A), and a refractive index detector (RID-10A) was used. The system was equipped with a Polymer Laboratories (PL) 5 μm bead-size guard column (50 × 7.5 mm), followed by three linear PL columns (10^5, 10^4, and 10^3 Å, 300 × 7.5 mm). The eluent was tetrahydrofuran at 40 °C and a flow rate of 1 mL min^{-1}. Calibration curves were generated using poly(methyl methacrylate) standards (Polymer Laboratories, Church Stretton, UK) with molecular weights between 500 and 10^6 g mol^{-1}. The injection volume was 50 μL (5 mg mL^{-1}). SEC traces were processed using the Cirrus 1.0 software package (PL, Church Stretton, UK).

ESI-MS. Solutions of the polymer (0.5 mg mL^{-1}) were made in a solvent consisting of the doping salt (1 mmol L^{-1}) in a mixture of dichloromethane and methanol (3:1). Spectra were obtained on a Finnigan LCQ Deca mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195−1822 Da using a standard containing caffeine, Met-Arg-Phe-Ala acetate salt (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). Positive ion spectra were obtained by direct infusion at a solvent flow rate of 3 μL min^{-1} and a spray voltage of 5 kV, with nitrogen as sheath gas. Capillary voltage, capillary temperature, tube lens offset, and the number of scans acquired are denoted in the caption of each spectrum in the results section. Xcalibur ver. 1.2 (Finnigan Co.) was used for spectral processing.

Results and Discussion

A 3:1 mixture of dichloromethane/methanol doped with 1 mM silver tetrafluoroborate ($AgBF_4$) gave excellent spectral quality. Silver trifluoroacetate (AgTFA) used in an earlier study on anionic PS by Deery et al. showed similar ionization efficiencies, but adducts of the general formula [M + Ag-

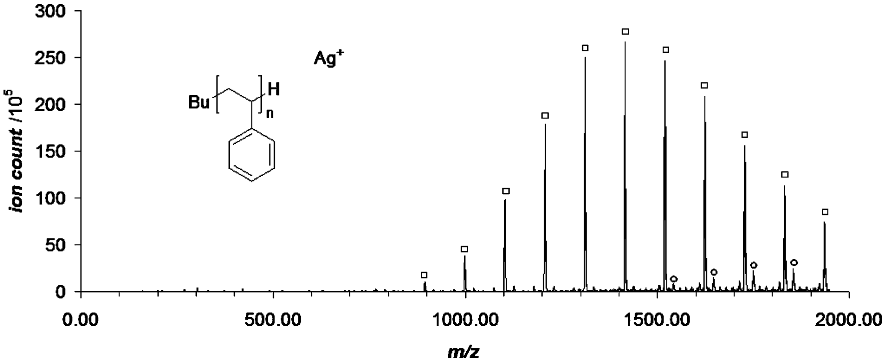


Figure 1. Electrospray ionization mass spectrum of a polystyrene standard prepared by anionic polymerization (□) using $AgBF_4$ as dopant (capillary temperature: 275 °C; capillary voltage: 40 V; tube lens offset: 20 V). A minor codistribution due to adduct formation with methanol (○) can be seen. Signal-to-noise ratio of the base peak is 3041. The spectrum was obtained by averaging 100 single scans.

(AgTFA)]$^+$ were identified by the authors.[29] In our study, we did not notice adduct formation with $AgBF_4$ for the investigated spray voltages between 3 and 5 kV and capillary voltages between −50 and +50 V. Additionally, the background obtained by infusing only the $AgBF_4$-doped solvent showed far fewer salt cluster ions than infusion of AgTFA-doped solvent at the same concentration. This was attributed to the fact that BF_4^- is a resonance stabilized, weakly coordinating counterion, which significantly reduces the possibility of cluster formation.

Analysis of Polystyrene Standard Prepared by Anionic Polymerization. Initial experiments using a commercial narrow MWD polystyrene standard were performed on a Finnigan LCQ Deca ion trap mass spectrometer equipped with a nebulizer-assisted electrospray source. Spectra of excellent quality were obtained. Figure 1 shows a typical spectrum of the standard. The main distribution is that of the polystyrene end-capped with a butyl group and a proton as expected. No peaks are visible in the lower mass region of the spectrum, which is indicative of the good selectivity of the method toward ionization of the polystyrene. The molecular weight distribution as apparent in the mass spectrum has its apex at $m/z = 1413.80$ (theoretical monoisotopic mass = 1413.74). This value agrees well with the molecular weight obtained from SEC as indicated by the manufacturer ($M_p = 1570$ g mol^{-1}). Mass distributions obtained by ESI-MS are biased to some extent, since ionization efficiency is a function of molecular weight. Usually ESI-MS underestimates the molecular weights, as ionization efficiency decreases with increasing repeat unit number,[31,32] which is consistent with our results. Jasieczek et al., however, found their ESI-MS distributions of low molecular weight polystyrene to be shifted to slightly higher mass values compared to SEC.[28]

In their MALDI analysis of polystyrene using a 9-nitroanthracene/AgTFA matrix, Zammit et al. observed peaks that they assigned to fragmentation products of the polymer backbone.[16] This creates, among others, polystyrenes carrying a vinyl or methenyl group as one end group and a butyl or a proton as the other. However, no such fragmentation products were identified in our studies (refer to Supporting Information, Figure S1).

Signal-to-noise ratio (S/N) of the base peak was calculated by estimating the noise level from the standard deviation of the baseline in the acquired spectrum. An excellent S/N of 3041 was achieved after summing 100 single scans, corresponding to a limit of detection (S/N: 3) of ~0.5 μg mL^{-1} total polymer concentration.

Polystyrene Sample Prepared by CPDA-Mediated Free Radical Polymerization. Figure 2 shows the mass spectra of polystyrene synthesized via the cumylphenyl dithioacetate (CPDA)-mediated RAFT polymerization of styrene using AIBN as initiator at 60 °C. When using silver(I) tetrafluoroborate as doping salt, a high ion count of 4.5×10^6 and an excellent signal-to-noise ratio (S/N) of 2803 were achieved.

Mass spectra were also acquired using sodium iodide as a doping agent (Figure 3) in order to demonstrate the magnitude of signal enhancement with $AgBF_4$. It can be seen that under optimized conditions the signal intensity as well as the S/N are lower by more than one order of magnitude for NaI, making it difficult to distinguish polymer peaks from background noise (Figure 3 (bottom)). Furthermore, baseline noise in the lower mass regions is significantly increased owing to the lower affinity of sodium ions toward coordination with the polystyrene. Salt clusters of [Na(NaI)]$^+$ are visible, which is not the case when using $AgBF_4$. Acceptable spectra can however be obtained by acquiring data over an extended period of time.

Peak Assignments. We were mainly concerned with enhancement of spectral quality in our study, and styrene/CPDA is a well-behaved RAFT system, in that it shows no rate retardation or inhibition effects.[30,33] Therefore, only a brief section on peak assignment is given here (Table 1). A zoomed spectrum of the region around $m/z = 1390$ (Figure 2 (bottom)) reveals the most prominent peaks. The base peak corresponds to the silver adduct of the intact RAFT polystyrene (A_R). After careful optimization of the source parameters (see Supporting Information, Figures S2 and S3) only little side product due to cleavage of the dithioester (V) is formed. Some initiator-derived RAFT polystyrene (A_I) is also present in the spectrum.

With AIBN as initiator and CPDB as reversible chain transfer agent, peaks of the dead polymer formed by combination (C_{RR}), if present, are partially obscured by peaks of the RAFT polystyrene. The molecular weight distribution of dead polymer should have its apex at about double the mass of the RAFT polystyrene, and therefore only a few dead chains may be present at low molecular weights. However, inspection of the spectrum at higher masses did not show evidence of termination products. It is therefore possible that presence of RAFT polystyrene suppresses ionization of nonpolar end-group-containing polymers. Gidden et al. investigated the mode of complexation of alkaline metals to poly(methyl methacrylate) using molecular modeling studies and drift tube experiments.[34] The lowest energy structures had a U-shape with the metal coordinated to both ends of the polymer, implying that the end group may have a significant effect on ionization efficiency. However, in our investigation similar ionization efficiencies were achieved for the RAFT polystyrene and for the anionic polystyrene carrying no end groups, which supports the assumption that ionization of polystyrene containing RAFT end groups is not favored. The problem of “missing” or suppressed species is inherent to mass spectrometric investigations of functional polymers and has to be kept in mind when performing

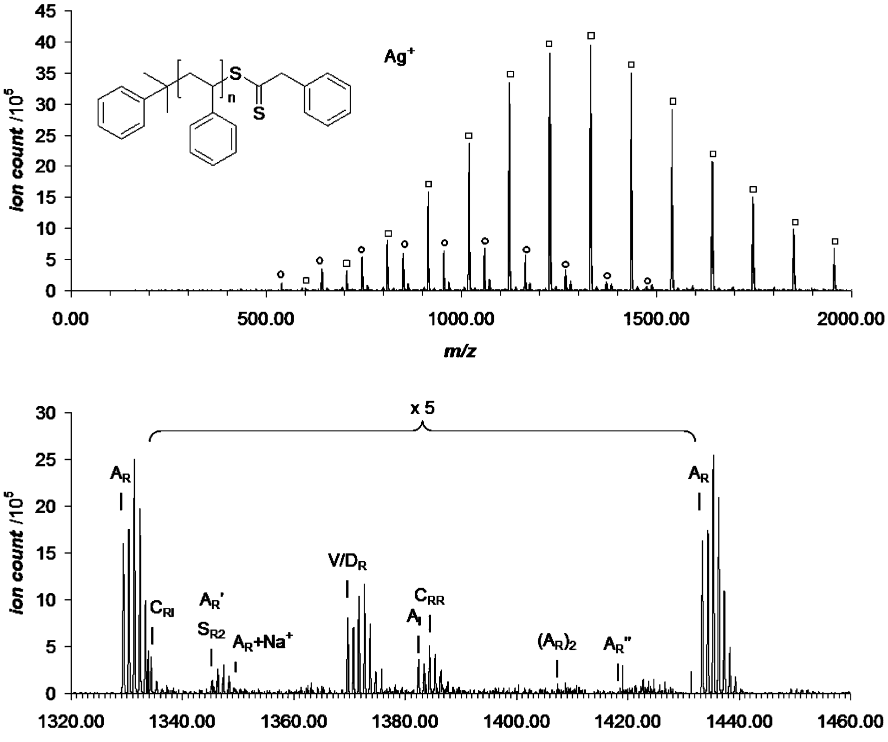


Figure 2. **(top)** Electrospray ionization mass spectrum of polystyrene synthesized via CPDA-mediated RAFT polymerization (□) using $AgBF_4$ as dopant (capillary temperature: 220 °C; capillary voltage: 0 V; tube lens offset: −50 V). Little vinyl-terminated polymer is formed (○). Signal-to-noise ratio (S/N) of the base peak is 2803. **(bottom)** Mass spectrum recorded in zoom scan mode. Ion counts in the region indicated by a curly brace are amplified by a factor of 5. Refer to Table 1 for peak assignments. S/N of the base peak is 2778. Both spectra were obtained by averaging 100 single scans.

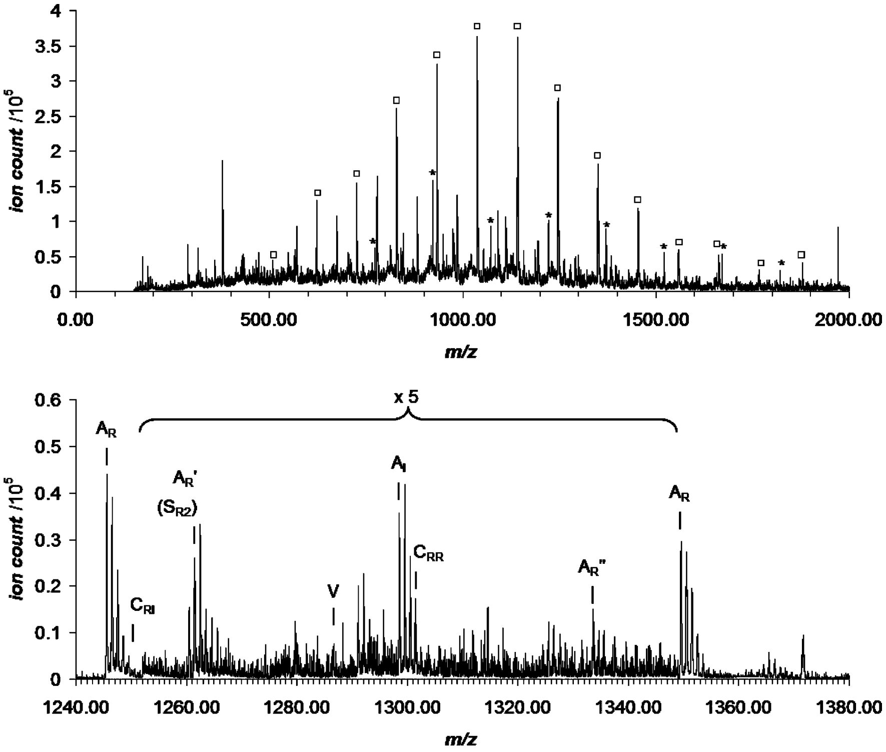
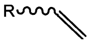


Figure 3. **(top)** Electrospray ionization mass spectrum of polystyrene synthesized via CPDA-mediated RAFT polymerization (□) with NaI as dopant (capillary temperature: 275 °C; capillary voltage: 0 V; tube lens offset: −50 V). Some $[Na(NaI)]^+$ salt clusters are present (∗). Signal-to-noise ratio (S/N) of the base peak is 208. **(bottom)** Mass spectrum recorded in zoom scan mode. Ion counts in the region indicated by a curly brace are amplified by a factor of 5. Refer to Table 1 for peak assignments. S/N of the base peak is 176. Both spectra were obtained by averaging 100 single scans.

Table 1. Assignment of Peaks Observed in the Spectra of Polystyrene Obtained via the Cumyl Phenyl Dithioacetate (CPDA)-Mediated Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization Using 2,2′-Azobis(isobutyronitrile) (AIBN) as Initiator at 60 °C[a]

		$[M + {}^{107}Ag]^+$		$[M + Na]^+$	
Short	**Species**	**Calculated**	**Exper. (error)**	**Calculated**	**Exper. (error)**
A_R	R∿∿Z	1329.55	1329.32 (-0.22)	1245.64	1245.59 (-0.05)
A_R’	R∿∿Z(+O)	1345.55	1345.25 (-0.30)	1261.63	1261.48 (-0.15)
A_R’’	R∿∿Z(+O,-S)	1417.64	-	1333.72	1333.63 (-0.09)
A_I	I∿∿Z	1382.58	1382.33 (-0.25)	1298.66	1298.52 (-0.14)
V/D_R		1369.67	1369.65 (-0.02)	1285.75	-
C_{RR}	R∿∿R	1385.70	obsc. by A_I	1301.79	obsc. by A_I
C_{RI}		1334.67	obsc. by A_R	1250.75	obsc. by A_R
S_{R2}	I/R∿∿Z∿∿R/I H	1345.58	1345.25 (A_R’)	1261.67	1261.48 (A_R’)
S_{RI}		1398.61	-	1314.70	-
S_{R3}	I/R∿∿Z∿∿R/I ∿ R/I	1359.60	-	1275.69	-
S_{R2I}		1412.63	-	1328.71	-
$(A_R)_2$	(R∿∿Z)$_2$	1407.51	(1407.35) (-0.16)	1323.60	-

[a] R = cumyl, I = cyanoisopropyl, Z = benzyl dithioacetyl, ∿ = oligostyrene. Values in parentheses are peaks exhibiting a signal-to-noise ratio <2. A dash denotes where a species could not be detected in the spectrum. For detailed chemical structures of the concerned species refer to the Supporting Information, Figure S5. Calculated masses are monoisotopic.

this kind of analysis. It should, however, not prevent the suggested method from gaining popularity.

A smaller peak is seen at *m/z* = 1345.25, which corresponds to either the sulfine formed by oxidation of the RAFT group (A_R') or possibly to a two-armed “star” formed by hydrogen abstraction (S_{R2}) by the intermediate RAFT radical. CPDA-mediated styrene polymerization proceeds in a well-controlled manner. Furthermore, no induction period or retardation was observed during polymerization. Intermediate radical termination products—if they occur at all in detectable quantities—are therefore not expected. MS^2 was employed to gain absolute certainty about the identity of the peak. A neutral loss of *m/z* = 183.10 corresponding to the dithioacid oxide yielding the vinyl-terminated polymer confirmed that the peak belonged to the sulfine (A_R') (see Supporting Information, Figure S4).

When using sodium iodide as a dopant, increased acquisition times have to be used to allow spectral assignment. The product spectrum observed using NaI is similar to that using $AgBF_4$. RAFT polystyrene (A_R) forms the main distribution. No combination products (C_{RR}) were visible. Interestingly, no elimination products (V) were found in the spectrum with NaI as dopant.

As discussed earlier, especially in the presence of metal salts, labile end-group-containing polymers may undergo fragmentation upon ionization. Styrenes are prone to elimination as a stable conjugated double bond is formed upon reaction. With dithioesters and xanthates, the prominent decomposition reaction is the thermal Chugaev elimination, yielding vinyl-terminated polystyrene[35−37] and the dithioacid. In xanthate elimination, a C=S double bond is converted to a more stable C=O double bond, and the reaction proceeds at low temperatures. For dithioesters there is no such thermodynamic drive. Furthermore, photoinduced cleavage of the RAFT group due to UV laser pulses, a possible pathway in MALDI, cannot occur in electrospray. Therefore, it comes with some surprise that when using ESI, some elimination products can still be seen when silver(I) salts are used as dopants.

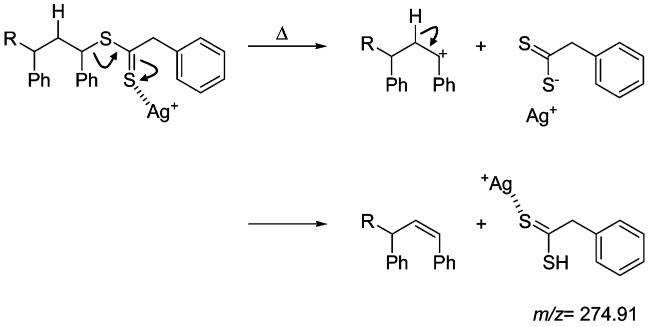


Figure 4. Possible E1 elimination pathway leading to the loss of the dithioester end group upon ionization during MALDI/ESI in presence of Ag^+ salts. The ion with *m/z* = 275.00 (theoretical monoisotopic mass: 274.91) was identified as the major species in ESI-MS spectra of cumylphenyl dithioacetate.

The most probable explanation for this behavior is that the rate of elimination is enhanced in the presence of silver(I). A mechanism is suggested in Figure 4, with silver(I) acting as a soft Lewis acid to catalyze cleavage of the dithioester. The reaction scheme is supported by ESI-MS spectra of the RAFT agent CPDA, where the silver adduct of the dithioacid (found: *m/z* = 275.00; theoretical monoisotopic mass: 274.91) forms the most prominent ion. However, in the case of the macro-RAFT agent, no dithioacid is observed in the spectrum, despite the presence of adduct ions of the vinyl-terminated polymer. This is possibly due to preferential coordination of the silver cation by the polymer backbone instead of the dithioester group.

On balance, this side reaction is only a slight disadvantage for the significant enhancement of ionization efficiency gained using silver salts as ionizing agents. Preliminary investigations show the possibility of employing nanospray to ionize RAFT polystyrene using silver salts without the occurrence of any fragmentation. This is due to significantly decreased source temperatures in nanospray.

Conclusions

The present study demonstrates that silver tetrafluoroborate can be used as a doping salt to achieve efficient ionization of polystyrene synthesized via RAFT polymerization. To our knowledge, this is the first time that high-quality spectra of a labile end-group-containing polystyrene have been obtained without the need for basic functionalities within the polymer backbone or on end groups. Side products due to thermal or collision induced loss of the dithioacetic acid can be minimized using optimized source conditions. Although ionization is possible with soluble sodium salts, efficiency is significantly decreased when compared to silver ionization. With sodium salts, however, no loss of the RAFT end group was observed. A possible mechanism is given for catalysis of the cleavage reaction in presence of silver salts. Spectral assignment showed that the expected main peaks corresponding to polystyrene carrying the initiator or a leaving group on one side and the phenyldithioacetate group on the other were present, but no combination products could be observed.

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Supporting Information Available: Additional spectra, MS^2 data, and results of ESI optimization. This material is available free of charge via the Internet at http://pubs.acs.org.

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