First Systematic MALDI/ESI Mass Spectrometry Comparison to Characterize Polystyrene Synthesized by Different Controlled Radical Polymerizations

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Received June 19, 2008; Revised Manuscript Received September 23, 2008

ABSTRACT: Mass spectrometry techniques, specifically matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization time-of-flight (ESI-TOF) are of considerable interest for characterizing very attractive polymers resulting from controlled radical polymerizations (CRP). This work proposes a systematic and experimental comparison of both ionization methods to analyze polystyrene prepared by five different CRP: nitroxide-mediated polymerization (mediated by *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide, known as SG1), atom transfer radical polymerization (Cl- and Br-mediated), reversible addition-fragmentation chain transfer polymerization, and reverse iodine transfer polymerization. All polystyrene chain end-groups obtained in each CRP-polymerization, and detected by both mass spectrometry techniques, are described and discussed. Elemental analyses of all CRP-polymers were also carried out to complete these results. It was found that the number of chain end-groups detected is higher by ESI-TOF than MALDI-TOF mass spectrometry in the polystyrene case. Furthermore, the cationization salt as well as the ionization source play a considerable role on the chain end-group fragmentation process occurring in mass spectrometer for the five CRP-polystyrenes. Concerning molecular weight considerations, the MALDI-TOF mass spectrometry is a better alternative to chromatography techniques than ESI-TOF mass spectrometry which under-estimates the average molecular weights.

Introduction

The main deficiency of conventional radical polymerizations is a lack of control of macromolecular structures including degrees of polymerization, molecular weight distributions, chain end functionalities, chain architectures and compositions. This explains the emergence of controlled radical polymerizations (CRP), which enable the synthesis of well-defined and functional polymers from a wide range of monomers. These CRP were identified by a simultaneous growth process of all chains with very limited side reactions (chain transfer and termination) and by a very fast exchange between active and dormant species in comparison with propagation. The dormant species can be reversibly activated either spontaneously or in the presence of a catalyst. The main CRP techniques[1] are (i) nitroxide-mediated radical polymerization (NMP), (ii) atom transfer radical polymerization (ATRP), (iii) reversible addition-fragmentation chain transfer (RAFT) polymerization, and (iv) reverse iodine transfer polymerization (RITP). Their distinction from each other is based on the mechanism that ensures the controlled character of the polymerization. Briefly, NMP is based on a reversible termination between the propagating polymer radicals and the nitroxide radicals, the ATRP mechanism involves the reversible termination through the redox reactions with an organometallic complex, while in RAFT and RITP, the controlled behavior is achieved by reversible chain transfer.

In this context, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization time-of-flight (ESI-TOF) mass spectrometry have been used to characterize polymers resulting from such CRP. These techniques are indeed very appropriate to the thorough analysis of these polymers for many reasons. The first one is the possible accurate structural identification of their chain end-groups which provides essential information about the polymerization mechanism. Second, the particular narrowness of molecular weight distributions of these polymers is a considerable advantage for these techniques since these latter present a well-known problematic "mass discrimination" effect[2−5] when the polymer polydispersity index (PDI = M_w/M_n) is relatively high (PDI > 1.3). As a result, a correct determination of average molecular weights of these CRP-polymers is feasible, enabling to confirm or not the controlled behavior of the polymerization. Furthermore, this determination from mass spectrometry techniques is achievable by consuming a very low sample amount, as well as a short analysis time with regard to SEC techniques. Often, MALDI is favored as the ionization method in the literature (as illustrated by the references quoted in this work), probably because only singly charged ions are observed producing much clearer mass spectra of polymers. Nevertheless, this choice between MALDI and ESI mass spectrometry to characterize these CRP-polymers is not always obvious. Therefore, a systematic comparison between both techniques to analyze polymers obtained by different CRP is pertinent. To our knowledge, no experimental attempt has been devoted to this comparison between these two "soft" ionization processes for all CRP. Barner-Kowollik et al.[6] previously reported the use of mass spectrometry for probing the CRP mechanism, but this work was not based on an experimental and systematic comparison between both techniques, but rather under the form of a review of different works coming from the literature.

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10.1021/ma8013788

In this paper, a complete and experimental comparison between MALDI and ESI mass spectrometry to analyze chain end-groups and molecular weights of polystyrene synthesized by RAFT polymerization, ATRP, NMP, and RITP is described. All experimental and technical conditions are discussed and optimized to obtain mass spectra with very high quality (i.e., high signal-to-noise ratio, quality resolution, and high accuracy of mass measurements). Similar mass analyzers, time-of-flight (TOF), were selected for ESI and MALDI processes to compare the ionization methods as efficiently as possible. The technical parameters of both TOF (e.g., mass accuracy, sensitivity, upper limit of weight) are indeed analogous. Concerning the CRP, the solvent used for all polymerizations was *tert*-butyl benzene, all polymerizations were stopped at 60−70% monomer conversion, and all polymers were subsequently precipitated in methanol. The polymerizations requiring an initiator were achieved with a similar one (the 2,2′-azo-bis-isobutyronitrile, AIBN).

Note that the analysis of polystyrene by mass spectrometry is relatively tricky due to its nonpolar character and easy loss of functional end-groups. Some CRP-polystyrenes described here have consequently never been studied before by considered mass spectrometry techniques. The main purpose of the present work is to highlight the advantages and the disadvantages of MALDI-TOF and ESI-TOF mass spectrometry to characterize such polymers and to help the reader to choose the most suitable technique for the analysis of polystyrenes synthesized by NMP, ATRP, RITP, or RAFT polymerization.

Experimental Section

Materials. Styrene (Acros, 99%) was purified by vacuum distillation before use. 2,2′-Azo-bis-isobutyronitrile (Fluka, 98%) was recrystallized from methanol. Iodine (I_2, Aldrich, 99,8%), *tert*-butyl benzene (Aldrich, 99%), methyl 2-chloropropionate (Aldrich 98%), methyl 2-bromo-2-methylpropionate (Fluka, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%), *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, Centre de Recherche Rhône-Alpes, ATOFINA, 86%) were used as received. 1-(Ethoxycarbonyl)eth-1-yl dithiobenzoate was synthesized as described previously.[7] CuCl and CuBr (Aldrich, 98%) were purified as reported in the literature.[8]

Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization. AIBN (0.81 mmol, 132.5 mg), 1-(ethoxycarbonyl)eth-1-yl dithiobenzoate (3.27 mmol, 0.8326 g), styrene (98.1 mmol, 10.219 g), and *tert*-butyl benzene (10.028 g) were introduced in a 50 mL Schlenk flask. The reaction medium was degassed by three freeze−pump−thaw cycles. The flask was sealed with a septum under an argon atmosphere and placed in an oil bath at 80 °C under magnetic stirring. At 60% monomer conversion (determined by gas chromatography), the reaction medium was cooled down to room temperature and precipitated in cold methanol. The polymer was finally dried under vacuum at 60 °C and analyzed by SEC ($M_{n,theo} = 2.13 \times 10^3$ g·mol^{-1}, $M_{n,SEC} = 2.07 \times 10^3$ g·mol^{-1}, PDI = 1.10).

Atom Transfer Radical Polymerization (ATRP). Methyl 2-chloropropionate (3.40 mmol, 0.417 g), CuCl (0.906 mmol, 0.089 g), HMTETA (0.96 mmol, 0.220 g), styrene (96.0 mmol, 10.000 g), and *tert*-butyl benzene (10.000 g) were introduced in a 50 mL Schlenk flask. The reaction medium was degassed by freeze−pump−thaw cycles and sealed with a septum under argon. The flask was then placed in an oil bath at 110 °C under magnetic stirring. At 70% monomer conversion (determined by gas chromatography), the reaction medium was cooled, and the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of silica to remove the catalyst. The excess of THF and of unreacted monomer were evaporated under vacuum. The polystyrene was dissolved in THF, precipitated in methanol, filtered, dried under vacuum at 60 °C, and analyzed by SEC ($M_{n,theo} = 2.18 \times 10^3$ g·mol^{-1}, $M_{n,SEC} = 2.50 \times 10^3$ g·mol^{-1}, PDI = 1.32).

The same procedure was used for the polymerization performed with methyl 2-bromo-2-methylpropionate as initiator and CuBr/HMTETA as catalyst ($M_{n,SEC} = 2.51 \times 10^3$ g·mol^{-1}, PDI = 1.14).

Nitroxide-Mediated Polymerization (NMP). SG1 (2.7 mmol, 0.794 g), AIBN (1.35 mmol, 0.221 g), styrene (96.0 mmol, 10.000 g), and *tert*-butyl benzene (10.000 g) were introduced in a 50 mL Schlenk flask. The reaction medium was degassed by freeze−pump−thaw cycles and sealed with a septum under argon. The polymerization was carried out under argon at 123 °C with magnetic stirring. At 60% monomer conversion (determined by gas chromatography), the reaction medium was cooled down to room temperature and precipitated in cold methanol. The polymer was finally dried under vacuum at 60 °C and analyzed by SEC ($M_{n,theo} = 2.58 \times 10^3$ g·mol^{-1}, $M_{n,SEC} = 2.675 \times 10^3$ g·mol^{-1}, PDI = 1.09).

Reverse Iodine Transfer Polymerization (RITP). Iodine I_2 (2.5 mmol, 0.64 g), AIBN (5.0 mmol, 0.82 g), styrene (99.8 mmol, 10.40 g), and *tert*-butyl benzene (10.00 g) were introduced in a 50 mL Schlenk flask. The reaction medium was degassed by freeze−pump−thaw cycles and sealed with a septum under argon. The polymerization was carried out under argon at 70 °C with magnetic stirring. At 60% monomer conversion (determined by gas chromatography), the reaction medium was cooled down to room temperature and precipitated in cold methanol. The polymer was finally dried under vacuum at 60 °C and analyzed by SEC ($M_{n,theo} = 1.44 \times 10^3$ g·mol^{-1}, $M_{n,SEC} = 1.55 \times 10^3$ g·mol^{-1}, PDI = 1.28).

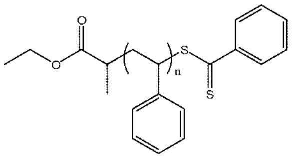
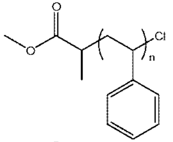
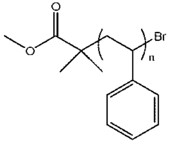
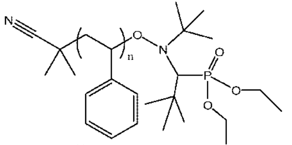
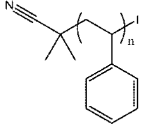
Gas Chromatography (GC). GC was used to determine the monomer conversion vs reaction time by using the solvent as internal standard. Analyses were performed on a Delsi Instruments Serial 330 apparatus coupled with a Shimadzu C-R6A integrator. A 2 m long Carbowax 20 M (poly(ethylene glycol)) column was used with nitrogen as the gas vector at 1 bar. The analyses were achieved in isothermal mode at 130 °C ($T_{injector} = T_{detector} = 200$ °C).

Elemental Analysis. The percentage in weight of C, H, N, O, P, I, Br, and Cl in samples were directly determined from polymer powders obtained by precipitation in methanol, filtration and drying under vacuum. These elemental analyses were realized by the Service Central d'Analyses (SCA) of Solaize (France). The accuracy on the elemental percentages is expected to be ±0.30%.

Size Exclusion Chromatography (SEC). SEC was performed with a Spectra Physics Instruments SP8810 pump, three 300 mm columns (mixed-D, 5 μm, 300 × 7.5 mm; 500 Å, 5 μm, 300 × 7.5 mm; 100 Å, 5 μm, 300 × 7.5 mm) from Polymer Laboratories (Varian, Amherst, MA; at $T = 30$ °C) and a Shodex RIse-61 refractometer detector. THF was used as eluent at a flow rate of 0.8 mL·min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories.

MALDI-TOF Mass Spectrometry. All mass spectra were obtained with a Voyager-DE STR (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with a 4 ns pulse duration. The instrument was operated in linear and reflectron modes. The ions were accelerated under a potential of 20 kV. The positive ions were detected in all cases. The spectra were the sum of 300 shots and an external mass calibration of mass analyzer was used (a mixture of peptides, Sequazyme). Samples were prepared by mixing 45 μL of 1,8,9-anthracenetriol or 2,5 dihydroxybenzoic acid (dithranol or DHB, respectively, purchased by Sigma-Aldrich; at 10 g·L^{-1} in THF) with 5 μL of polystyrene solution (at 10 g·L^{-1} in THF) and 5 μL of AgTFA or NaI (both from Sigma-Aldrich; at 10 g·L^{-1} in THF or acetone, respectively). Note that the addition of metal ions such as AgTFA or NaI in the mixtures for characterizing polystyrene by MALDI-TOF mass spectrometry is required to enhance its ionization by cationization. Resulting mixtures (1 μL) were spotted on the MALDI sample plate, and air-dried. Concerning polystyrene obtained by RAFT polymerization, special solvent conditions (45 μL of dithranol solution in distilled chloroform at 10 g·L^{-1} + 5 μL of sample solution at 10 g·L^{-1} in distilled acetone + 5 μL of AgTFA solution at 10

Table 1. Main Characteristics of Controlled Radical Polymerizations (CRP) of Styrene†

CRP	Reagents used for CRP*	Expected dormant chains
RAFT	AIBN[a] $CH_3CH_2OC(=O)CH(CH_3)$-S-C(=S)Ph	
ATRP	$CH_3OC(=O)CH(CH_3)$-Cl CuCl/HMTETA[b]	
ATRP	$CH_3OC(=O)C(CH_3)_2$-Br CuBr/HMTETA[b]	
NMP	AIBN[a] SG1[c]	
RITP	AIBN[a] I_2	

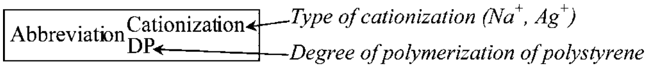
† RAFT = reversible addition-fragmentation chain transfer; ATRP = atom transfer radical polymerization; NMP = nitroxide-mediated polymerization; RITP = reverse iodine transfer polymerization. * The solvent used for all polymerizations was *tert*-butyl benzene, all polymerizations were stopped at 60−70% monomer conversion and all polymers were precipitated in methanol. [a] AIBN = 2, 2′-azobisisobutyronitrile. [b] HMTETA = 1,1,4,7,10,10-Hexamethyltriethylenetetramine. [c] SG1 = *N*-*tert*-Butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide.

Table 2. Formula of End-Groups Expected for the Dormant Chains (X-polystyrene-Y) Synthesized by CRP[a]

CRP	X formula (monoisotopic mass)	Y formula (monoisotopic mass)
RAFT	$C_5H_9O_2$ (101.0602 *m/z*)	$C_7H_5S_2$ (152.9833 m/z)
ATRP (-Cl)	$C_4H_7O_2$ (87.0446 *m/z*)	Cl (34.9688 m/z)
ATRP (-Br)	$C_5H_9O_2$ (101.0602 *m/z*)	Br (78.9183 m/z)
NMP	C_4H_6N (68.0500 *m/z*)	$C_{13}H_{29}NO_4P$ (294.1834 *m/z*)
RITP	C_4H_6N (68.0500 *m/z*)	I (126.9045 m/z)

[a] Monoisotopic mass of monomer C_8H_8 = 104.06260 *m/z*; monoistopic mass of radical initiator C_4H_6N = 68.05002 *m/z*; CRP = controlled radical polymerization.

Scheme 1. Abbreviations of Main Polystyrene Chain Populations Detected in MALDI/ESI-TOF Mass Spectrometry[a]



Abbreviation	Corresponding chain population
D	X-(styrene)$_{DP}$-Y *(«dormant» chain)*
XU	X-(styrene)$_{DP}$-CH=CH(Ph)
$X^•$	X-(styrene)$_{DP}$-CH_2-$HC^•$(Ph)
$D+H_2O$	X-(styrene)$_{DP}$-Y + H_2O
IY	Initiator-(styrene)$_{DP}$-Y
IU	Initiator-(styrene)$_{DP}$-CH=CH(Ph)
C	X-(styrene)$_{DP}$-X
XV	X-(styrene)$_{DP}$-CH_2-C(Ph)=CH_2

[a] With X and Y (see Tables 1 and 2): $CH_3CH_2OC(=O)CH(CH_3)$ and SC(=S)Ph for RAFT polymerization; $CH_3OC(=O)C(CH_3)_2$ and Br for Br-mediated ATRP; $CH_3OC(=O)CH(CH_3)$ and Cl for Cl-mediated ATRP; $NCC(CH_3)_2$ and $ON(C(CH_3)_3)CH(C(CH_3)_3)P(=O)(OC_2H_5)_2$ for NMP; and $NCC(CH_3)_2$ and I for RITP.

g·L^{-1} in distilled acetone) were used for reasons explained in results and discussion part.

ESI-TOF Mass Spectrometry. The mass spectra were acquired with a LCT mass spectrometer (Waters, Milford, MA) in positive mode. Samples of polystyrene were prepared at 1 g·L^{-1} in acetone: acetonitrile (17:83 v/v). A NaI solution (in acetone at 10 g·L^{-1}, 2 μL) was added to mixtures. The latter are directly infused in the source. The cone voltage and desolvation temperature were 200 V and 150 °C, respectively. An internal calibration was performed with NaI salts to improve the accuracy on the mass measurement leading to a precise identification of chemical formula from mass spectra. This mass accuracy study was carried out with MassLynx software (Waters, Milford, MA).

Results and Discussion

Various polystyrenes were prepared by the following CRP: RAFT, ATRP (Cl- and Br-mediated), NMP (SG1-mediated), and RITP. The main characteristics of each one are described in Table 1. The MALDI and ESI mass spectra of resulting CRP-polystyrenes were subsequently and scrupulously examined in terms of (i) chain end-group structures, and (ii) average molecular weights and molecular weight distributions. MALDI-TOF mass spectrometry was carried out in linear and reflectron modes. The former mode allowed us to determine the average molecular weights and molecular weight distributions; and the second mode, the chemical formula of chain end-groups with a very high precision (expected error < 80 ppm at m/z = 1000). This accurate identification of chain end-groups was also performed via ESI-TOF mass spectrometry by using an internal calibration. The end-group chemical formula determined by the MassLynx software from ESI mass spectra were taken into account when their differences with experimental masses were below 20 ppm. For each CRP-polymer, the related Figure displays the global MALDI/ESI mass spectra (insets) as well as enlargements of these mass spectra, all of them performed in the optimal analysis conditions of polystyrene by MALDI-TOF (Figures 1−5A) and ESI-TOF (Figures 1−5B) mass spectrometry.

1. MALDI/ESI Comparison of Chain End-Groups Detected for Each CRP-Polystyrene. The determination of various chain end-groups, notably those corresponding to the so-called dormant species (detailed in Tables 1 and 2), is essential to prove the controlled behavior of the polymerization and to better understand the polymerization mechanism (e.g., about transfer and termination reactions). This determination is successively presented here for the RAFT, ATRP, NMP, and RITP processes. For the sake of clarification of this work, an abbreviation was attributed to each possible chain end-group, taking into account the cationization nature and the number of styrene repeat units of the considered chain (Scheme 1).

1a. RAFT-Polystyrene. Reversible addition-fragmentation chain transfer (RAFT) technique is a well-known strategy for controlling the radical polymerizations.[9] It has been extensively investigated due to the numerous monomers that can be polymerized under various conditions by making a judicious choice of chain transfer agent (CTA), and more precisely, the nature of Z and R substituents of this agent (Z-C(=S)S-R). For efficient transfer and control of the polymerization, R should be a good free-radical leaving group, and Z able to stabilize the intermediate radical.[10,11] In this work, the RAFT agent used to synthesize polystyrene is a dithiobenzoate containing a phenyl moiety as Z substituent, and a $CH(CH_3)COOC_2H_5$ group as R substituent. The MALDI-

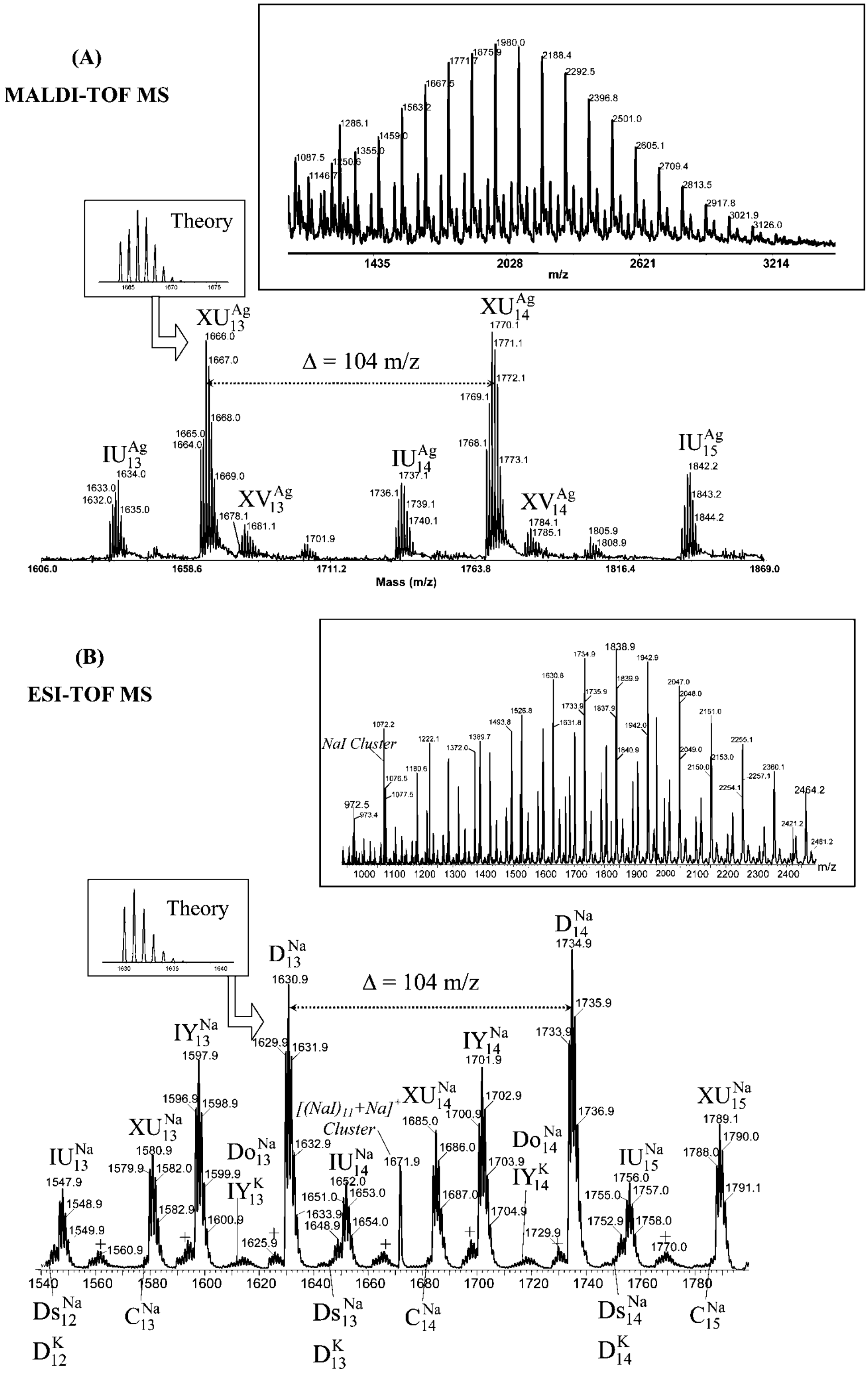


Figure 1. Enlarged region of mass spectra of polystyrene obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization acquired by (A) MALDI-TOF (reflectron mode) with AgTFA salt/dithranol matrix, and (B) ESI-TOF mass spectrometry (MS) with NaI salt, both in positive mode. Insets: global mass spectra of MALDI-TOF (linear mode) and ESI-TOF mass spectrometry in the same analysis conditions. The theoretical isotopic patterns are given for $[C_{117}H_{120}O_2+Ag]^+$ (MALDI mass spectrum) or $[C_{116}H_{118}O_2S_2+Na]^+$ (ESI mass spectrum). NaI cluster in inset = $[(NaI)_7+Na]^+$, (+) = may be terminated intermediate radicals, see the assignments in the Results and Discussion part. See abbreviations of chain populations in Scheme 1.

TOF and ESI-TOF mass spectra of resulting polystyrene are presented in Figure 1.

MALDI-TOF Analyses. Before all, it is important to pay attention to the special experimental conditions that must be used for the chain end-group analysis of polymers synthesized by RAFT polymerization. The first one concerns the nature of solvent employed to dissolve polymers. For example, tetrahydrofuran (THF), commonly used, has to be used with many cautions. Indeed, the presence of peroxides easily formed in THF may favor the oxidation of S-containing polymers, as demonstrated by Zagorevskii et al.[12] and observed by Favier et al.[13] in MALDI-TOF mass spectrom-

Table 3. Elemental Analyses of CRP-Polystyrenes

CRP		C%	H%	N%	O%	S%	P%	I%	Br%	Cl%
RAFT	*theo*	87.71	7.51		1.59	3.19				
	exp	87.78	7.70		1.47	3.07				
ATRP (-Cl)	*theo*	88.40	7.60		1.90					2.10
	exp	88.60	7.57		1.90					1.62
ATRP (-Br)	*theo*	88.56	7.57		1.11				2.77	
	exp	89.30	7.72		1.34				2.31	
NMP	*theo*	88.29	7.96	0.85	1.95		0.94			
	exp	86.76	7.34	1.01	2.21		1.00			
RITP	*theo*	84.75	7.23	0.80				7.22		
	exp	84.91	7.36	0.76				6.36		

[a] *theo* = theoretical values calculated from M_{peak}, determined by MALDI-TOF mass spectrometry. *exp* = experimental values. Experimental error = 0.30% for all elements. CRP = controlled radical polymerization.

etry. Indeed, the latter work evidenced the presence of species at +16 m/z (oxidation of dithioester moiety in sulfine) and −16 m/z (oxidation of sulfine moiety in thioester)[13] with regard to SC(=S)-containing polymer chains. This is the reason why we employed in this study another solvent that does not form peroxide (i.e., acetone, see details in experimental part). The second difficulty encountered in the characterization of polymers synthesized by RAFT polymerization is the observation of their labile dithioester end-group, particularly for polystyrene. In this case, the dithioester end-group elimination, due to the weakness of the C−S bond[14] between polymer and chain transfer agent, leads to a stable conjugated double bond. This explains why Destarac et al.[15] have only observed the population of polystyrene chains terminated by an unsaturated moiety (i.e., with loss of dithioester group) by MALDI-TOF mass spectrometry, and not at all the population corresponding to the expected dormant chains (i.e., initiated by the R substituent and terminated by the S-C(=S)-Z group). Our results confirmed these observations: (i) no peak corresponding to polymer with transfer agent end-groups (monoisotopic mass of $[\text{X-polystyrene-Y+Ag}]^+$ expected at 1713.8 m/z in the enlargement of MALDI mass spectrum in Figure 1A), and (ii) detection of a main population (with a monoisotopic peak at 1768.1 m/z) matching the structure terminated by an unsaturated moiety (i.e., the dormant chain with loss of H−S−C(=S)-Ph group, population abbreviated XU in Figure 1A). This unsaturated species could result from chain termination reactions by the disproportionation mode, but only chain olefinic end-groups were found and no chain corresponding to hydrogen-terminated chains as one would expect for the disproportionation reaction. Moreover, the mode of termination in the polymerization process is highly dependent on monomer structure, and for styrene, it is well-known that the termination reactions essentially occur by combination of two chains rather than disproportionation. Finally, the elemental analyses of different atoms composing the polymer, notably the sulfur atom (S%; Table 3), are in good agreement with theory, which proves that there is no loss of the S atom in the sample. In the literature, the origin of these vinyl-terminated polymer chains is now clearly ascribed to a fragmentation of the labile end-group in the mass spectrometer and not to the polymerization process, because (i) these unsaturated species are not observed in the NMR spectra of corresponding polymers, and (ii) the molecular weight considerations of polymers display the controlled behavior of the polymerization, which would be inconsistent with the formation of such unsaturated species. With the aim of decreasing this fragmentation phenomenon and detecting the dormant chains, we made various attempts with other analysis conditions such as the laser power decrease, the modification of matrix (DHB instead of dithranol), and cationization salt (NaI instead of AgTFA). Following all trials, the cationization agent was proven to play a considerable role. Indeed, the MALDI mass spectrum acquired by using NaI and the same matrix (dithranol) evidenced the dormant chains (Supporting Information, S1) contrary to Figure 1A (with AgTFA salt). This fact confirms the very recent results of Gruendling et al.,[16] which point out the catalyst role of silver salt to cleave the dithioester of RAFT-polystyrene in ESI mass spectrometer. The authors even postulated a mechanism for the elimination of dithioester involving the Ag^+ cation. According to our results, this phenomenon is ionization method-independent since it also arises here with a MALDI ionization. However, despite this presence of dormant chains in mass spectrum with NaI salt, numerous fragmented species also existed (Supporting Information, S1). The fragmentation process of polymers occurring in the mass spectrometer is indeed very complex since it depends not only on analysis conditions (as above-shown) but also on the nature of repeat unit and chain end-groups of polymer. Interestingly, about the repeat unit nature, it can be noticed that this fragmentation yields hydrogen-terminated chains for poly(*N*-acryloymorpholine),[13] poly(*N*-isopropylacrylamide),[17] poly(vinyl acetate),[18] as well as poly(methyl methacrylate),[19] and not exclusively to unsaturated-terminated chains as in the case of polystyrene. Regarding the chain end-group nature, Zhou et al.[20] showed that by using complex CTA (dithiobenzoate functionalized with a bipyridine or terpyridine group as R substituent), the cationization agent was not necessary to study the resulting polystyrene by MALDI-TOF mass spectrometry. In these conditions, the authors detected the fragmented chains but also the dormant chains. Vosloo et al.[21] also reported the observation of the dormant chain population of polystyrene by using the same analysis conditions as here (dithranol/AgTFA as matrix/cationization salt) without indicating if this population corresponded to the main one.

We showed above that it was possible to limit the polymer end-group fragmentation by using NaI instead of AgTFA salt, but the latter salt allowed us to obtain the most intense, reproducible, and with the highest resolution MALDI mass spectra of polystyrene, as this was already demonstrated by Deery et al.[22] and Belu et al.[23] This suggests that the affinity of Ag^+ cations for unsaturated hydrocarbon polymers such as the polystyrene promotes more efficiently the adduct formation than the Na^+ cations. The interaction of silver cations with polystyrene is even thought to occur at the electron-rich phenyl rings along the repeat unit of the polymer chain, and may interact with two phenyl rings.[24] Because the choice of this paper is to show mass spectra with the highest quality in terms of signal-to-noise ratio, resolution, and accuracy of mass measurements, Figure 1A corresponds to MALDI-TOF mass spectrum acquired with AgTFA salt.

Beside the XU population, this Figure also displays three other populations (which exist in the mass spectrum with NaI salt too, Supporting Information, S1). The one at 1735.1 m/z (monoisotopic peak) is assigned to chains initiated by an AIBN radical and terminated by an unsaturated function (called IU population). These initiator-derived chains are not always observed in mass spectrometry. Note that their presence is favored in the samples for which a low [CTA]-to-[initiator] ratio is used in the polymerization process (in this study: [CTA]-to-[AIBN] = 4). For example, Schilli et al.,[17] Destarac et al.,[18] Zhou et al.,[20] and Xu et al.[25] observed these AIBN-initiated chains in MALDI-TOF mass spectra of poly(*N*-isopropylacrylamide), poly(vinyl acetate), polystyrene, and poly(methyl methacrylate) synthesized by RAFT polymerization with a [CTA]-to-[AIBN] ratio equal to 2.8, 5, 5, and 2.5, respectively. Conversely, MALDI-TOF mass spectra of poly(*N*-acryloylmorpholine),[13] poly(*N*-isopropylacrylamide),[26] poly(*N*-acryloyl-L-

Table 4. Monoisotopic Masses of Different Chain Populations[a] of CRP-Polystyrenes Detected by MALDI-TOF Mass Spectrometry (Ag^+ Cationization)[b]

	DP	calcd mass	expt mass	formula
RAFT				
XU	14	1767.9	1768.1	$C_{125}H_{128}O_2Ag$
XV	14	1781.9	1782.1	$C_{126}H_{130}O_2Ag$
IU	14	1734.9	1735.1	$C_{124}H_{125}NAg$
ATRP(-Cl)				
XU	11	1441.7	1441.7	$C_{100}H_{102}O_2Ag$
C	11	1425.7	1425.6	$C_{96}H_{102}O_4Ag$
ATRP(-Br)				
D	18	2160.0	2160.8	$C_{149}H_{153}O_2BrAg$
XU	17	2080.1	2079.8	$C_{149}H_{152}O_2Ag$
XV	17	2094.1	2093.8	$C_{150}H_{154}O_2Ag$
NMP				
XU	21	2463.3	2463.3	$C_{180}H_{181}N_1Ag$
XV	21	2477.3	2477.3	$C_{181}H_{183}N_1Ag$
C	22	2532.4	2532.4	$C_{184}H_{188}N_2Ag$
RITP				
XU	13	1630.8	1630.7	$C_{116}H_{117}NAg$

[a] See abbreviations of chain populations in Scheme 1. [b] Calculated and experimental masses are monoisotopic. CRP = controlled radical polymerization.

Table 5. Mass Measurement Accuracies of Different Chain Populations[a] of CRP-Polystyrenes Detected by ESI-TOF Mass spectrometry (Na^+ Cationization)[b]

	DP	calcd mass	expt mass	difference	formula
RAFT					
D	13	1629.8470	1629.8549	4.8 ppm	$C_{116}H_{118}O_2S_2Na$
XU	14	1683.9812	1683.9841	1.7 ppm	$C_{125}H_{128}O_2Na$
IY	14	1700.8994	1700.8917	−4.6 ppm	$C_{123}H_{123}NS_2Na$
IU	14	1650.9709	1650.9572	−8.4 ppm	$C_{124}H_{125}NNa$
ATRP(-Cl)					
D	12	1393.7544	1393.7549	0.3 ppm	$C_{100}H_{103}O_2ClNa$
XU	11	1357.7778	1357.7710	−5.0 ppm	$C_{100}H_{102}O_2Na$
C	12	1445.8302	1445.8367	4.5 ppm	$C_{104}H_{110}O_4Na$
ATRP(-Br)					
D	15	1763.9074	1763.8894	−10.2 ppm	$C_{125}H_{129}O_2BrNa$
XU	15	1788.0438	1788.0172	−14.9 ppm	$C_{133}H_{136}O_2Na$
C	15	1786.0493	1786.0239	−14.2 ppm	$C_{130}H_{138}O_4Na$
NMP					
D	6	1009.5988	1009.5780	−20.6 ppm	$C_{65}H_{83}N_2O_4PNa$
$X^{\bullet}$	10	1131.6658	1131.6769	9.8 pmm	$C_{84}H_{86}NNa$
D + H_2O	7	1131.6720	1131.6769	4.3 pmm	$C_{73}H_{93}N_2O_5PNa$
XV	10	1144.6736	1144.6846	9.6 ppm	$C_{85}H_{87}NNa$
C	8	991.5906	991.5801	−10.6 ppm	$C_{72}H_{76}N_2Na$
RITP					
D	9	1154.5077	1154.4983	−8.1 ppm	$C_{76}H_{78}NINa$
XU	9	1130.6580	1130.6473	−9.4 ppm	$C_{84}H_{85}NNa$
C	10	1199.7158	1199.7000	−13.2 ppm	$C_{88}H_{92}N_2Na$

[a] See abbreviations of chain populations in Scheme 1. [b] Calculated and experimental masses are monoisotopic. CRP = controlled radical polymerization.

proline methyl ester),[27] and poly(ethyl acrylate)[28] synthesized with a higher [CTA]-to-[AIBN] ratio (10, 7.5, 10, and 33.8, respectively) did not display these chains.

The other population at 1782.1 *m*/*z*, that is to say at +14 *m*/*z* with regard to XU population, can be ascribed to an internal scission of polystyrene chains, again induced by MALDI mass spectrometry, and leading to a methylene end-group[29] (i.e., $[\text{X-(styrene)}_{13}\text{-CH}_2\text{-C(Ph)=CH}_2\text{+Ag}]^+$, abbreviated XV^{Ag}_{13}). This scission via an intramolecular back-bitting process for polystyrene has recently been much more examined by MALDI-TOF/TOF and -Q/TOF CID experiments.[14,30,31] The experimental and calculated masses of this population and all the main above-described species are shown in Table 4.

Finally, the last population at 1699.9 *m*/*z* is still unknown, but it probably comes from technical and experimental conditions of MALDI because it does not exist in corresponding ESI mass spectrum (Figure 1B). Note that it was checked that it did not match with terminated intermediate radicals,[32] with combination products ($[\text{X-(styrene)}_{14}\text{-X+Ag}]^+$ expected at 1766 *m*/*z*), or with thermal initiation via a Diels−Alder reaction in free radical polymerization.[29,32,33]

ESI-TOF Analyses. Figure 1B exhibits the analysis of the same polymer by ESI-TOF mass spectrometry. The number of peaks detected is significantly higher than one obtained by MALDI-TOF mass spectrometry (Figure 1A). Furthermore, the expected chains with transfer agent end-groups are observed in the ESI-TOF mass spectrum, they represent the main population (abbreviated D) even if the corresponding population with unsaturated termination (XU) is also present to a lesser extent. The differences between Figure 1A and B, explaining why the dormant chains are only visible in the latter case, are not only the ionization source (MALDI and ESI, respectively), but also the cationization salt (AgTFA and NaI, respectively), which has a considerable effect in the fragmentation process, as above-mentioned. This effect was again confirmed by an ESI-TOF analysis of the same polymer with a silver cationization instead of the sodium one: dormant chains were not longer observed; only the fragmented counterparts were observed (see Supporting Information, S2). Besides this confirmation of the salt role, this experiment also evidenced once more that the fragmentation process in mass spectrometer is even more complex than the only effect of salt nature since the fragmentation of the RAFT-polystyrene studied in the present work is total (Supporting Information, S2), while it is partial in the work of Guendling et al.[16] (by using exactly the same experimental conditions and a slightly different Z substituent, -Ph group instead of $\text{-CH}_2\text{-Ph}$). In addition to these fragmentation remarks and about ESI mass spectrum sensitivity and resolution considerations, it is also worth noting that, contrary to these authors, we obtained ESI mass spectra of RAFT-polystyrene with high-quality by employing NaI as cationization salt, without requiring inevitably Ag salt.

Beside the main populations, as in the MALDI-TOF mass spectrum, the chains initiated by AIBN radical (IY and related IU populations) are detected. The mass measurement accuracies (difference < 10 ppm, Table 5) absolutely strengthen the assignment of these different main populations. Other very minor populations are present and could be ascribed to a very slight oxidation of dithioester moiety: Ds (oxidation of dithioester moiety in sulfine, at +16 *m*/*z* vs D population) and Do (oxidation of sulfine moiety in thioester, at −16 *m*/*z* vs D population).[13] But these *m*/*z* values could also correspond to K^+ species of dormant and IY chains (located to +16 *m*/*z* vs these species cationized by sodium). The distinction between oxidized and K^+ species is thus very tricky. Note that Gruendling et al.[16] suggested the presence of the oxidized species of dithioester-polystyrene (with cumyl phenyl dithioacetate as dithioester) in their ESI-TOF mass spectrum, but the signal-to-noise ratio of mass spectra is not high enough to be certainly proven.

Another minor population is visible in Figure 1B in the beginning of XU population (at −2 *m*/*z*) and could coincide with dead polymer chains formed by termination by combination (monoisotopic mass of C^{Na}_{14} population is expected at 1682.0 *m*/*z*). This is not surprising to detect them because, as previously indicated, the combination of growing radicals is expected for polystyrene rather than the disproportionation mode in termination reactions. Finally, the unambiguous assignment of minor populations, marked by (+) in ESI mass spectrum, is difficult due to their low signal-to-noise ratio and resolution (making a mass accuracy study impossible), but they may be terminated intermediate radicals (three-arm stars) described in very few works,[34] with the following chemical formula $[\text{A-(styrene)}_m\text{−S-C((styrene)}_n\text{-A)(Ph)-S-(styrene)}_p\text{-A + Na}]^+$, where A = X or I

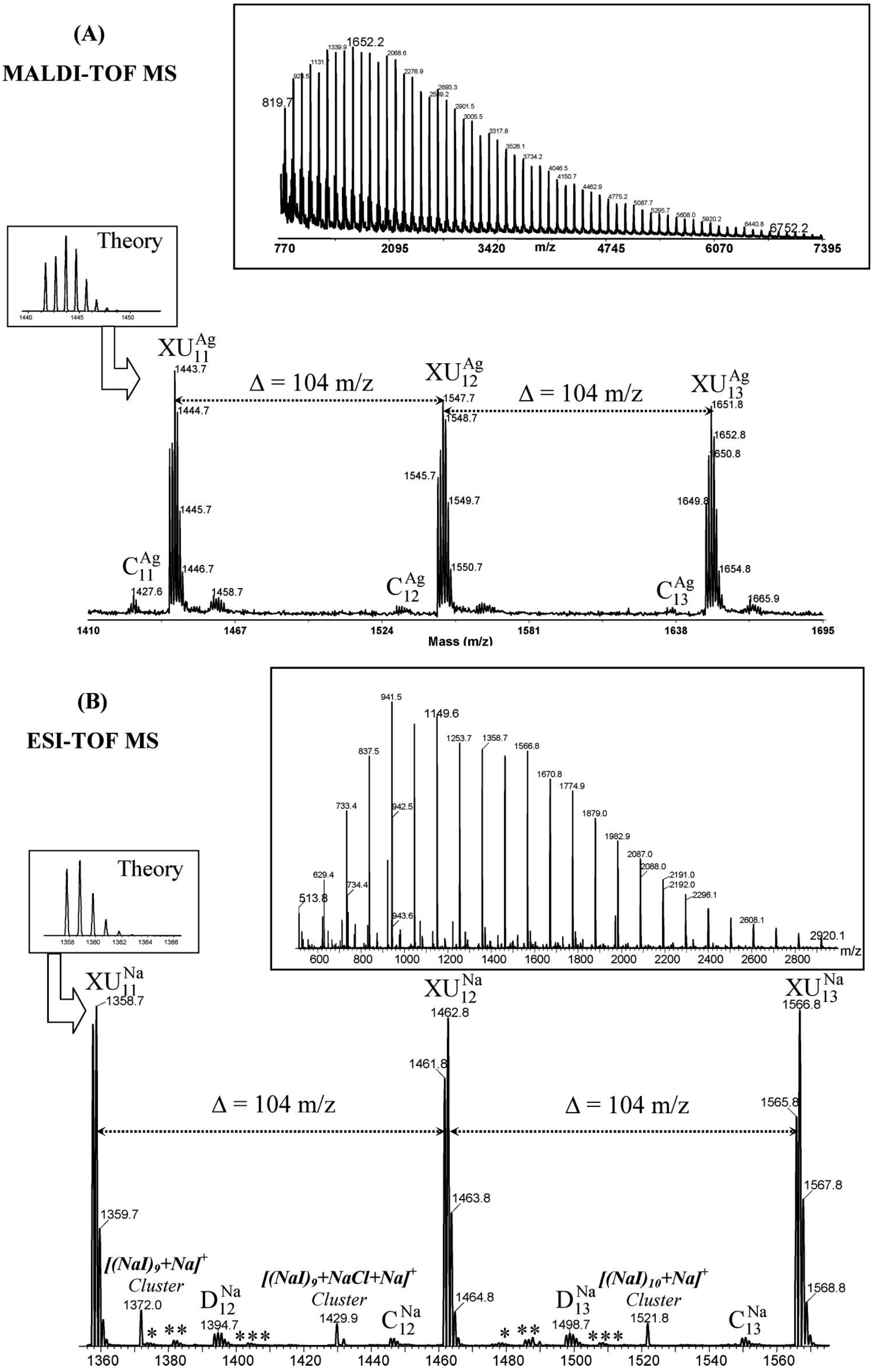


Figure 2. Enlarged region of mass spectra of polystyrene obtained by Cl-mediated atom transfer radical polymerization (ATRP) acquired by (A) MALDI-TOF (reflectron mode) with AgTFA salt/dithranol matrix, and (B) ESI-TOF mass spectromery (MS) with NaI salt, both in positive mode. Insets: global mass spectra of MALDI-TOF (linear mode) and ESI-TOF mass spectrometry in the same analysis conditions. The theoretical isotopic patterns are given for $[C_{100}H_{102}O_2+Ag]^+$ (MALDI mass spectrum) or $[C_{100}H_{102}O_2+Na]^+$(ESI mass spectrum). (*) = $[XU+K]^+$, (**) $[XU+Na(HI)]^+$ cluster, (***) $[XU+Na(NaI)]^+$ cluster. See abbreviations of chain populations in Scheme 1.

(see details of calculations in ref 32). In any case, they can not be assigned to a thermal initiation via a Diels–Alder reaction[29,33] ($[C_{16}H_{15}$-(styrene)$_{12}$-Y+Na]$^+$ expected at 1632 *m/z*).

1b. ATRP-Polystyrene. Atom transfer radical polymerization (ATRP) was developed in 1995 as a new controlled radical method.[35,36] This process is able to polymerize a wide range of monomers, and is tolerant of trace impurities (water, oxygen, inhibitor). The control is the result of a formation of radicals that can grow but which are reversibly deactivated to form dormant species, suppressing side reactions thanks to a process known as the persistent radical effect.[37] ATRP commonly uses simple alkyl halides as initiators and transition metals (iron, copper) as catalysts. These catalysts provide an equilibrium between the active (or propagating) polymer and the inactive

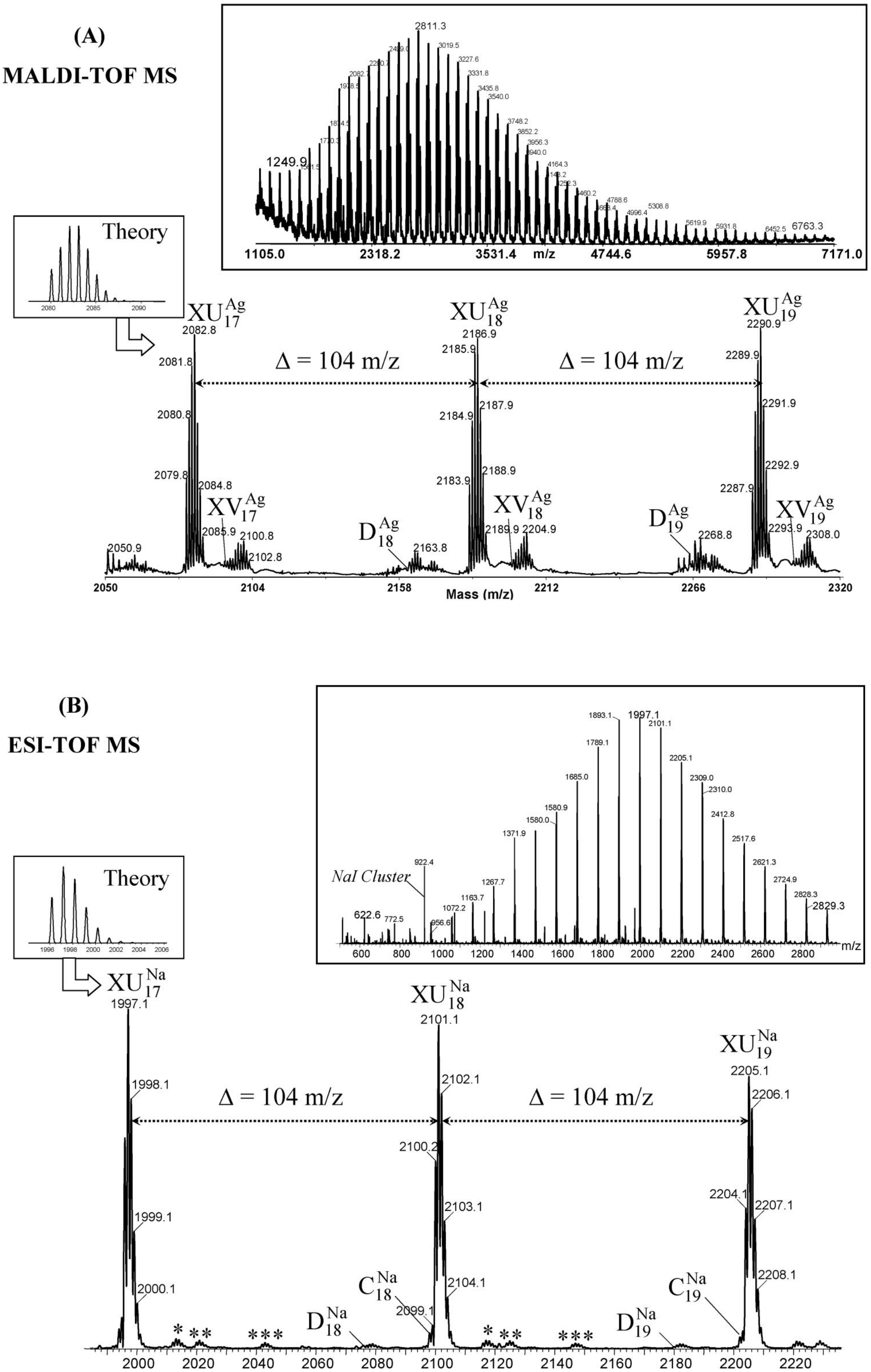


Figure 3. Enlarged region of mass spectra of polystyrene obtained by Br-mediated atom transfer radical polymerization (ATRP) acquired by (A) MALDI-TOF (reflectron mode) with AgTFA salt/dithranol matrix, and (B) ESI-TOF mass spectrometry (MS) with NaI salt, both in positive mode. Insets: global mass spectra of MALDI-TOF (linear mode) and ESI-TOF mass spectrometry in the same analysis conditions. The theoretical isotopic patterns are given for $[C_{149}H_{152}O_2+Ag]^+$ (MALDI mass spectrum) or $[C_{149}H_{152}O_2+Na]^+$ (ESI mass spectrum). NaI cluster in inset = $[(NaI)_6+Na]^+$, (*) = $[XU+K]^+$, (**) $[XU+Na(HI)]^+$ cluster, (***) $[XU+Na(NaI)]^+$ cluster. See abbreviations of chain populations in Scheme 1.

state of the polymer (the dormant form). In this work the catalysts used were CuCl or CuBr (with 1,1,4,7,10,10-hexamethyltriethylenetetramine, HMTETA as ligand) and the initiators $CH_3OC(=O)CH(CH_3)$-Cl or $CH_3OC(=O)C(CH_3)_2$-Br, respectively.

MALDI-TOF Analyses. Figures 2 and 3 present the MALDI-TOF mass spectra of polystyrene synthesized with CuCl/$CH_3OC(=O)CH(CH_3)$-Cl and CuBr/$CH_3OC(=O)C(CH_3)_2$-Br system, respectively. Figures 2A and 3A display more precisely the mass spectra obtained in linear mode (insets) and reflectron mode with AgTFA (because the signal-to-noise ratio and the resolution of mass spectra were not sufficient with NaI salt, see Supporting Information, S3). The main population observed in the reflectron mass spectra correspond to the double bond-

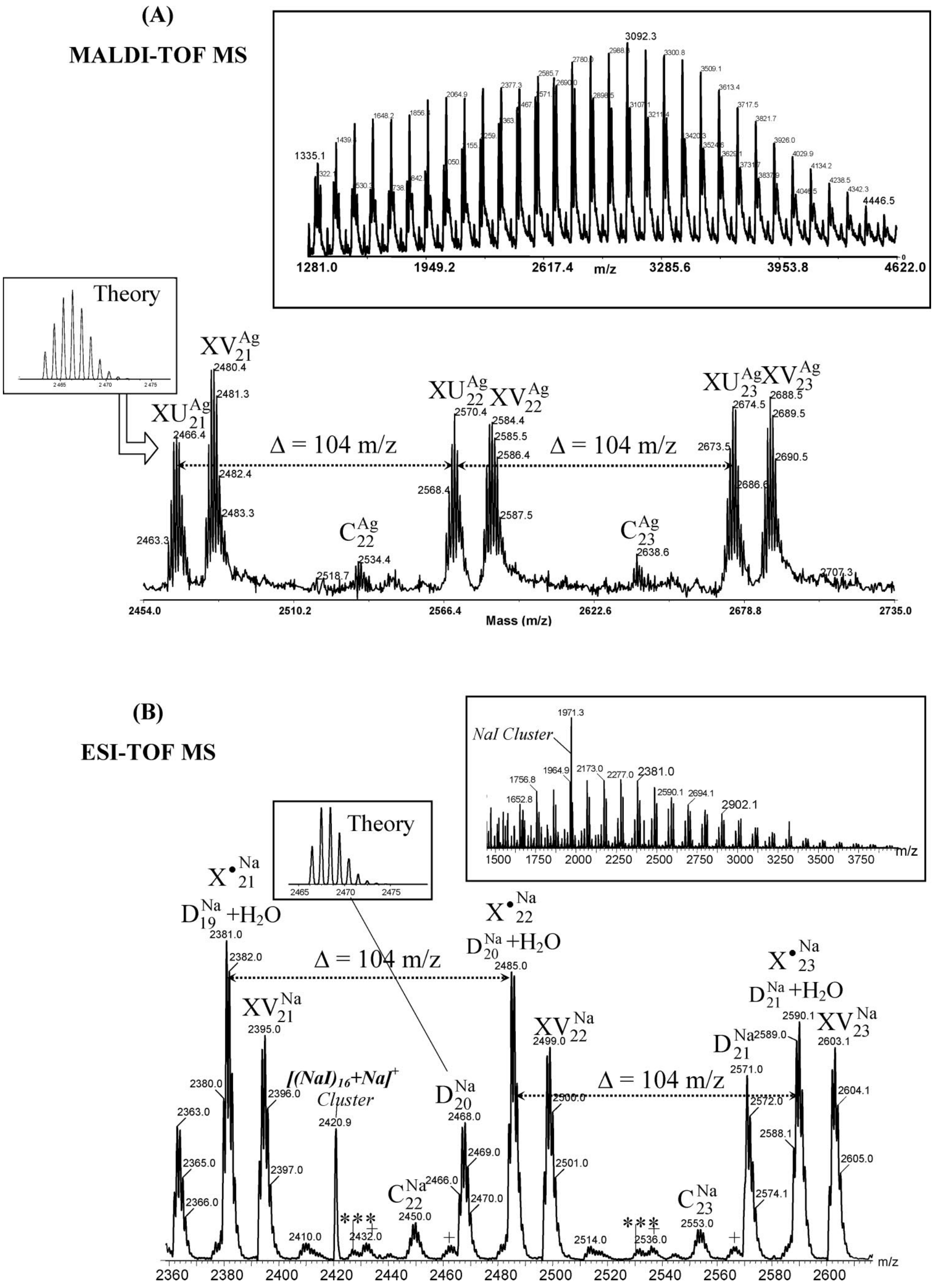


Figure 4. Enlarged region of mass spectra of polystyrene obtained by nitroxide-mediated polymerization (NMP) acquired by (A) MALDI-TOF (reflectron mode) with AgTFA salt/dithranol matrix, and (B) ESI-TOF mass spectrometry (MS) with NaI salt, both in positive mode. Insets: global mass spectra of MALDI-TOF (linear mode) and ESI-TOF mass spectrometry in the same analysis conditions. The theoretical isotopic patterns are given for $[C_{180}H_{181}N_1+Ag]^+$ (MALDI mass spectrum) or $[C_{177}H_{195}O_4N_2P_1+Na]^+$ (ESI mass spectrum). NaI cluster in inset = $[(NaI)_{13}+Na]^+$, (***) $[X^{\bullet}$ and/or D+H$_2$O +Na(NaI)$]^+$ cluster. (+) = unknown clusters probably coming from analysis conditions. See abbreviations of chain populations in Scheme 1.

terminated chains (XU population), that is to say the dormant chains with the loss of HCl and HBr, respectively. These species result from dehalogenation of the halogen-capped polymer chains during the mass spectrometry analysis. The corresponding dormant populations are not detected in Figure 2A (D_{12}^{Ag} = 1477.7 *m/z*) and could be in the peak pattern at 2160 *m/z* with very low intensity in Figure 3A (D_{18}^{Ag} = 2160.0 *m/z* but the accurate identification is difficult). The elemental analyses of the Cl atom (Cl%) and Br atom (Br%) of the polymers evidence that there are not significant losses of HCl and HBr, respectively (Table 3). In the Cl% case, a difference (slightly above the experimental error) exists between the theoretical and experimental value of Cl% but the analysis of other elements is in perfect agreement.

The dechlorination in mass spectrometer of polystyrene synthesized by ATRP was also observed by Nonaka et al.[38] In their MALDI-TOF mass spectrum acquired with Na salt, the resulting species (XU) are only detected, contrary to Figure 2A in which two other minor peaks are identified. The first peak pattern, visible at ca. 1426 *m/z* (Figure 2A), could correspond to product issued from termination by combination ([X-(styrene)$_{12}$-X+Ag]$^+$ expected at 1425.7 *m/z*, Table 4) but the signal-to-noise ratio is too low for a totally certain identification. Finally, the assignment of last minor population (at ca. +16 *m/z* vs XU population) is unknown for this moment but its origin is probably in the experimental and/or technical conditions since it is not detected in the equivalent ESI mass spectrum (Figure 2B). It was checked that this population at +16 *m/z* did not

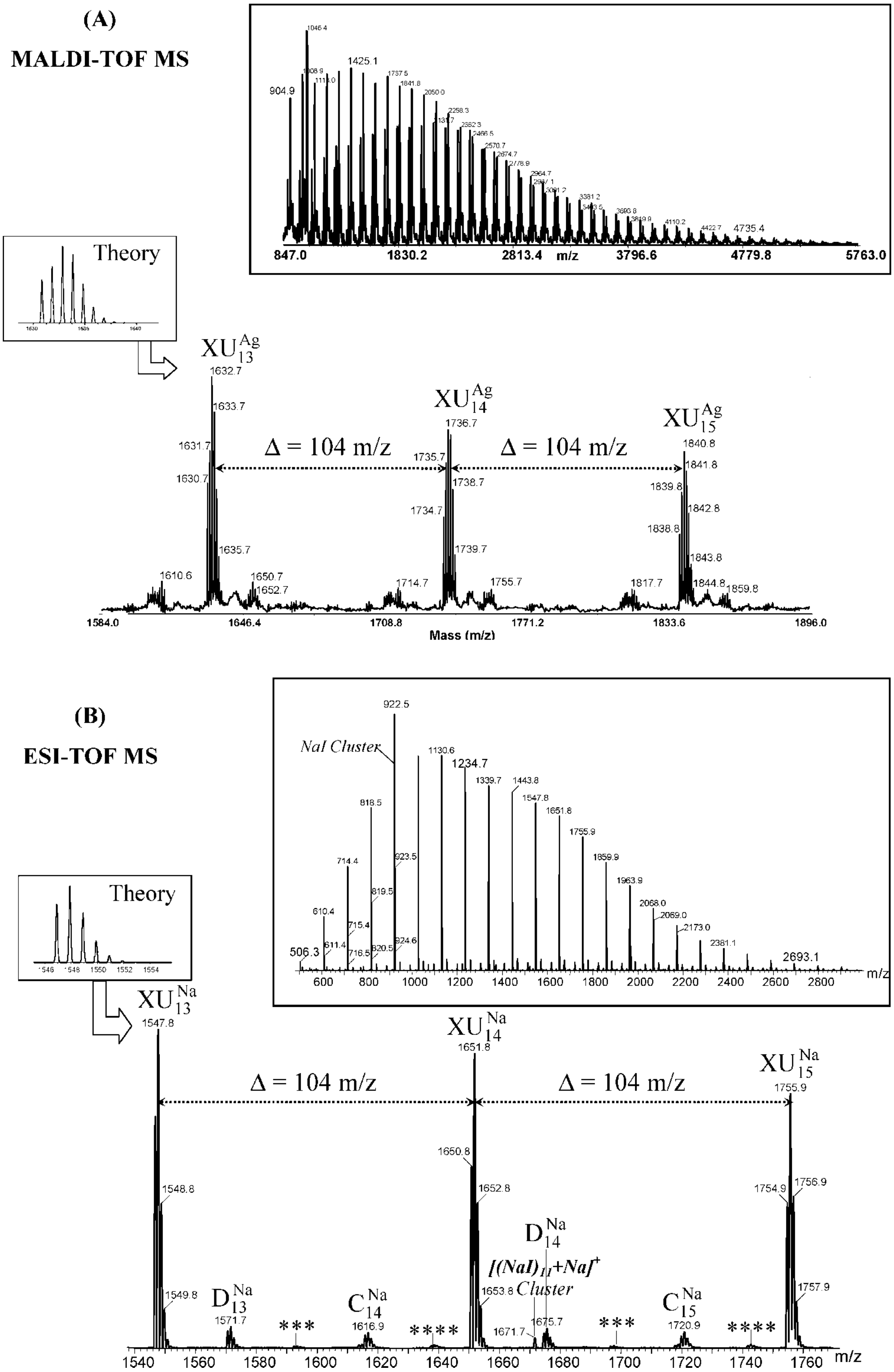


Figure 5. Enlarged region of mass spectra of polystyrene obtained by reverse iodine transfer polymerization (RITP) acquired by (A) MALDI-TOF (reflectron mode) with AgTFA salt/dithranol matrix, and (B) ESI-TOF mass spectrometry (MS) with NaI salt, both in positive mode. Insets: global mass spectra of MALDI-TOF (linear mode) and ESI-TOF mass spectrometry in the same analysis conditions. The theoretical isotopic patterns are given for $[C_{116}H_{117}N_1+Ag]^+$ (MALDI mass spectrum) or $[C_{116}H_{117}N_1+Na]^+$ (ESI mass spectrum). NaI cluster in inset = $[(NaI)_6+Na]^+$, (***) $[XU+Na(NaI)]^+$ cluster, (****) $[XU+Na(2NaI)]^+$ cluster. See abbreviations of chain populations in Scheme 1.

correspond to species cationized by Na^+ (e.g., due to the glassware use) as reported by other works.[15] Indeed, this alternative Na-cationization may provide a peak pattern at about +20 *m/z* (= 104.06 (styrene) − 106.90 (Ag) + 22.99 (Na) *m/z*) vs Ag^+ species.

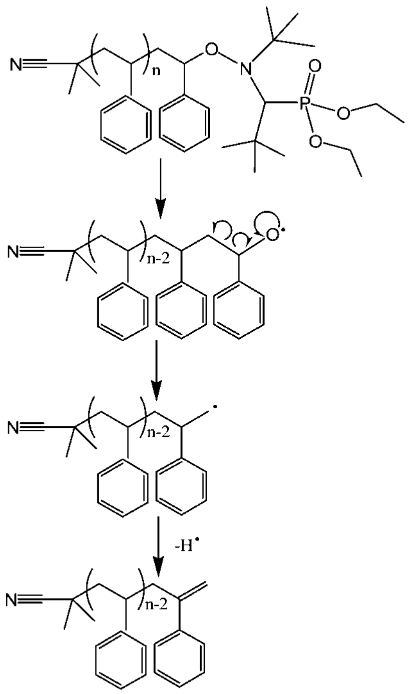
Concerning Figure 3A, the unresolved bumps following the XU populations can be ascribed to ions fragmented in the flight tube (i.e., not focalized in the reflectron) and not fragmented in the source ion (as this is the case of XU species which are fragmented in the source ion prior to their extraction and are thus focalized in the reflectron). As in Figure 1A, species at about +14 *m/z* with regard to XU population are present and could be assigned to a MALDI-induced scission of polystyrene chains (XV population, with a tricky assignment due to its low sensitivity and unresolved bumps) as above-described (i.e., with methylene as chain end-group). Other species with mass increments of +18 *m/z* (overlapping with the precedent population) and −22 *m/z* relative to the XU population are present, their assignments have not been fully elucidated yet, but they are probably related to experimental and technical conditions (as in Figure 1A for the population at +16 *m*/*z*), because these species do not exist in the corresponding ESI-TOF mass spectrum (Figure 3B). The experiment with another salt (NaI instead of AgTFA, Supporting Information, S3) also shows mainly the XU population and no peak matching the dormant population.

The majority of works reported in the literature about the analysis of polystyrene by MALDI-TOF mass spectrometry deals with Br-mediated ATRP. For example, Shen et al.[39] also used this technique with analysis conditions similar to those used in our work (dithranol/AgTFA/THF as matrix/cationization salt/polymer solvent). As in Figure 3A, no polystyrene chain with bromo chain end-group was detected in their mass spectrum, but two ion series of populations were observed: (i) one with a double bond as a chain end-group (i.e., with HBr loss, the XU population) and (ii) another due to scission of polystyrene chain, as previously discussed ([X-polystyrene-CH_2-C(Ph)=CH_2+Ag]$^+$ with X-=(CH_3)CH(Ph)-). Bernaerts et al.[40] also analyzed by MALDI-TOF mass spectrometry (with same analysis conditions: dithranol/AgTFA/THF) *ω*-bromo-terminated polystyrene synthesized by ATRP. They observed two series of peaks too. The most abundant one corresponds to the loss of HBr ([X-polystyrene-CH=CH(Ph)+Ag]$^+$ with X-=HO-$(CH_2)_4$−O-C(=O)-$C(CH_3)_2$-). The second series was not identified by the authors but interestingly this population is located to +18 *m*/*z* with regard to their XU population as in Figure 3A. The dithranol/NaI/THF combination was employed by Francis et al.[41] to analyze the same polymer, and in their case, only one population was obtained with the following chemical structure: [X-polystyrene-CH=CH(Ph)+Na]$^+$ with X-=CH_3-CH_2-O-C(=O)-$C(CH_3)_2$-. Cheng et al.[42] employed DHB matrix and AgTFA as cationization agent, and observed only one population corresponding to the double bond-terminated chain end-group (HOOC-$C(CH_3)_2$-polystyrene-CH=CH(Ph), the XU population). As a result, whatever the cationization salt and matrix used, the dormant chains are not observed. Only one work[43] by using same analysis conditions as those reported in our work (dithranol/AgTFA/THF) reported bromo-terminated dormant chains, but a main family of peaks which corresponded to fragmented chains (PhCH(CH_3)-polystyrene-CH=CH(Ph)) was also detected. The comparison of all these works evidence once more the complexity of the origin of the polymer end-group fragmentation in mass spectrometer, it depends on many parameters.

ESI-TOF Analyses. The ESI-TOF mass spectra of the identical polymers are shown in Figures 2B and 3B. The main populations are the same as ones obtained by MALDI-TOF mass spectrometry (i.e., the XU populations). Beside these main XU populations, dead chains by termination by the combination mode are also detected as in the ESI mass spectrum of RAFT-polystyrene. Dormant chains can be observed in Figure 2B (and are only supposed in Figure 3B). The other minor peaks are related to salt clusters (e.g., [$(NaI)_9$+Na]$^+$ in Figure 2B), as well as salt clusters with polymer. Indeed, Deery et al.[22] have evidenced the formation of adduct complexes with polystyrene represented by [polystyrene+$M(MX)_n$]$^+$, where MX stands for the metal salt, M the metal cation, and with $n = 1$ or 2 in ESI mass spectra. These species are marked by asterisks in the different Figures of this paper. To our knowledge, no work is reported in the literature about the ESI-TOF analysis of polystyrene synthesized by Br- and Cl-mediated ATRP.

1c. NMP-Polystyrene. Nitroxide-mediated polymerization (NMP) involves the reversible dissociation of a nitroxyl end-capped of polymer dormant chains into carbon-centered radical and persistent nitroxyl radical.[44] The nitroxide and initiator used in this work are *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (so-called SG1) and AIBN, respectively. Due to the fast initiation and the reversible trapping reaction, the growth of the polymer chains proceeds in a controlled manner, leading to controlled molecular weights and narrow molecular weight distributions of resulting polymers. To our knowledge, no work on the SG1-polystyrene has been reported by MALDI-TOF or by ESI-TOF mass spectrometry.

Scheme 2. Suggested Mechanism for the NMP-Chain End Degradation during Mass Spectrometry Analysis



MALDI-TOF Analyses. The MALDI-TOF mass spectrum of SG1-polymer shows two main peak families (the third minor one being probably the combination product at 2532.4 *m*/*z*) in Figure 4A: (i) at 2463.3 *m*/*z* matching the fragmented population, the XU one (with loss of H-SG1, Table 4), and (ii) at 2477.4 *m*/*z*, that is to say, with a mass increment of +14 *m*/*z* vs XU population, corresponding to a scission of polystyrene chains induced by MALDI as aforementioned, and to a chain end-group degradation mechanism (Scheme 2), analogous to that postulated by Schulte et al.[45] for 2,2,6,6-tetramethylpiperidine-*N*-oxyl-poly(*N*-isopropyacrylamide) (TEMPO-PNIPAM). This latter reaction could explain why the proportion of the peak at +14 *m*/*z* is much higher in this case than for the other CRP-polystyrenes.

Table 3 shows a very satisfactory agreement between the experimental values of elemental analyses and the theoretical ones (notably N% and P% values which are involved in the SG1 group), confirming the presence of expected end-groups in polymer and its fragmentation in mass spectrometer. Different works[46−48] have reported the use of DHB (without cationization salt) to analyze TEMPO-polystyrene. Dourges et al.[47] have even shown that the use of theses conditions instead of dithranol with AgTFA salt allowed them to observe the dormant chains and not the fragmented chains. As a result, we tested similar analysis conditions for the SG1-polystyrene, but there was no signal when conditions without salt were employed. Moreover, mass spectra with poor quality, as well as similar species to silver conditions, were obtained when NaI and dithranol were employed (Supporting Information, S3). Dempwolf et al.[49] analyzed the fragmentation in the MALDI-TOF mass spectrometer of one alkoxyamine analogous to SG1. They postulated a fragmentation mechanism inside the nitroxide group resulting in the loss of the *t*-butyl group located on the N atom with a subsequent addition of a hydrogen atom (leading to a difference of −56 *m*/*z* vs dormant chains) while the TEMPO compound is stable under same conditions. It was consequently checked that the corresponding peak (involving the *t*-butyl group loss) was not present in the mass spectrum (Figure 4A). Only one paper[50] in the literature detailed the study of SG1-polymer by MALDI-TOF mass spectrometry to our knowledge, where an initiator fragment and a SG1 group were detected as end-groups, but it concerned poly(*n*-butyl acrylate) (analysis conditions: dithranol/NaI/THF).

ESI-TOF Analyses. The ESI-TOF mass spectrum of SG1-polystyrene is presented in Figure 4B. Three main peak families are detected (Table 5): (i) at 2393.0 *m*/*z* corresponding to XV population due to the chain end-group degradation according to mechanism depicted in Scheme 2, (ii) at 2466.0 *m*/*z* matching the dormant chains ($[\mathrm{X\text{-}(styrene)_{20}\text{-}SG1+Na}]^+$), and finally, (iii) at 2380.0 *m*/*z*. This latter population is much more difficult to assign with certitude, nevertheless, it does not correspond to XU population since it is located to +1 mass unit vs the *m*/*z* value expected for this fragmented population. The chemical formula matching this mass with 9.8 ppm (Table 5) may be $[\mathrm{X\text{-}polystyrene\text{-}CH_2\text{-}HC^{\bullet}(Ph)+Na}]^+$ but such species (radical cationized) are very unusual in ESI-TOF mass spectrometry.[14] Another assumption could be the attachment of a water molecule at the phosphate end-group of dormant chains ($\mathrm{D+H_2O}$) because this population significantly decreases with a ESI desolvation temperature of 400 °C.

Another minor peak at about 2408 *m*/*z* is still unknown and can not be assigned to a loss of groups located on the N atom. The others very minor peaks (i) at 2428 and 2460 *m*/*z* (marked by +) may correspond to clusters formed in ESI source with unknown assignments, and (ii) at 2425 *m*/*z*, to salt clusters attached to polystyrene (marked by asterisks).

1d. RITP-Polystyrene. Reverse iodine transfer polymerization (RITP) is a controlled radical polymerization based on the use of molecular iodine I_2 as control agent.[51] Radicals formed by the initiator dissociation (AIBN in this study) react with iodine to give the iodinated transfer agents in situ. Once iodine is consumed, the equilibrium of degenerative chain transfer between active and dormant chains takes place. Since one iodine molecule control two polymer chains, the targeted number-average molecular weight (M_n targeted) of the polymer is controlled by the ratio between the mass of monomer and twice the initial number of moles of iodine.

MALDI-TOF Analyses. Figure 5A displays the MALDI-TOF mass spectra of polystyrene synthesized by this type of CRP. The main population is consistent with the fragmented species, that is to say the XU population. The iodine percent (I%) measured in sample (Table 3) is below the theoretical one although there is a very good correlation for the other elements (C, H, N%). The corresponding dormant chains and combination products are not detected (monoisotopic masses of D_{13}^{Ag} and C_{14}^{Ag} populations expected at 1654.6 *m*/*z* and 1699.8 *m*/*z*, respectively). As in the precedent MALDI-TOF mass spectra, other minor peaks exist, at +18 *m*/*z*, −22 *m*/*z*, and −26 *m*/*z*. It was checked that their origin did not come from (i) matrix by testing DHB or *trans*,*trans*-1,4-diphenyl-1,3-butadiene and (ii) cationization salt by employing NaI (Supporting Information, S3).

Very few studies of ITP- and RITP-polystyrene analyzed by MALDI-TOF mass spectrometry were reported in the literature. Lansalot et al.[52] and Valade et al.[53] synthesized ITP-polystyrene by using $C_6F_{13}I$ and $C_6F_{13}\text{-}CH_2CF_2\text{-}I$ as transfer agents, respectively. The MALDI mass spectra of obtained polystyrene showed two series of peaks. According to these authors, these series corresponded to the XU population (with $X = C_6F_{13}$) cationized by silver (or sodium), and polystyrene resulting from the direct initiation and combination (I-polystyrene-I where I represents the fragment arising from the decomposition of AIBN, $(CH_3)_2(CN)C$-). Similarly, the XU population was the main population detected in the case of polystyrene synthesized by RITP (X being the group $(CH_3)_2(CN)C$ in the case of RITP).[54] Note that with another polymer (RITP-poly(methyl acrylate)), Lacroix-Desmazes et al.[55] observed the dormant chains by MALDI-TOF mass spectrometry, and, to a lesser extent, the corresponding XU population.

Table 6. Summary of Different End-Groups of CRP-Polystyrenes Detected by MALDI-TOF and ESI-TOF Mass Spectrometry in Optimal Analysis Conditions[a]

CRP population[a]	MALDI-TOF analysis (Ag^+ cationization)	ESI-TOF analysis (Na^+ cationization)
RAFT		
D	no	yes - major population
Do, Ds	no	yes (and/or K^+ species)
XU	yes - major population	yes
IU	yes	yes
IY	no	yes
C	no	yes
XV	yes	no
ATRP-Cl		
D	no	yes
XU	yes - major population	yes - major population
C	yes	yes
XV	no	no
other population	+16 *m*/*z* vs XU	no
ATRP-Br		
D	yes	yes
XU	yes - major population	yes - major population
C	no	yes
XV	yes	no
other populations	+18, - 22 *m*/*z* vs XU	no
NMP		
D	no	yes
XU	yes - major population	no
$X^{\bullet}$ and/or $D+H_2O$	no	yes - major population
C	yes	yes
XV	yes - major population	yes - major population
other populations	no	+14 *m*/*z* vs XV
RITP		
D	no	yes
XU	yes - major population	yes - major population
C	no	yes
XV	no	no
other populations	+18, −22, −26 *m*/*z* vs XU	no

[a] See abbreviations of chain populations in Scheme 1. CRP = controlled radical polymerization.

ESI-TOF Analyses. The ESI-TOF mass spectrum in Figure 5B evidence the XU population as being the main one. The dormant chains (e.g., D 13 Na) and combination products (e.g., C 14 Na) are also visible to a lesser extent (assignments in Table 5). Finally, the salt clusters and salt clusters attached to polystyrene are observed too (marked by asterisks).

1e. Different Chain End-Groups of CRP-Polystyrenes Detected by MALDI/ESI-TOF Mass Spectrometry: Summary and Discussion. Table 6 summarizes the various chain end-groups of polystyrene (synthesized by the different CRP) detected by MALDI-TOF and ESI-TOF mass spectrometry. For both ion sources, the fragmentation of dormant chains is observed (i.e., the XU population) whatever the CRP, confirming the easiness for losing the HY group and forming a very stabilized double bond as chain end-group for polystyrene. Note that this behavior is indeed particularly enhanced for this polymer with regard to other polymers. For instance, Nonaka et al.[38] reported a systematic comparison between MALDI-TOF mass spectra of ATRP-polystyrene and ATRP-poly(methyl acrylate) acquired in exactly the same analysis conditions (dithranol/NaTFA/THF). All mass spectra showed only one series of peaks corresponding to dormant chains for poly(methyl acrylate) and fragmented ones for polystyrene.

Table 6also evidences that the number of end-groups of polystyrene chains detected by ESI-TOF mass spectrometry is higher than one by MALDI-TOF mass spectrometry whatever the CRP. For example, the expected dormant chains (D population) are observed for all CRP (this population is even the main one in the RAFT-polystyrene system) by ESI-TOF mass spectrometry, while they are only detected with a very low extent by MALDI-TOF mass spectrometry in the Br-mediated ATRP-polystyrene system. Additionally, the products of combination (the well-known mode of termination of this polymer) are discerned by ESI-TOF mass spectrometry for all CRP despite their low amounts in the samples. Conversely, they are just observed by MALDI-TOF mass spectrometry in one CRP (Cl-mediated ATRP). This detection difference between the MALDI and ESI analyses can not be explained in terms of dissimilarity to sensitivity between both techniques but rather in terms of discrimination of ionization and desorption of species in the case of MALDI-TOF mass spectrometry. Many reasons can actually cause this discrimination such as the nature of polymer end-groups,[56] or the value of the laser intensity. Indeed, in the RITP-polystyrene mass spectrum, the detection of combination products was possible by decreasing the MALDI laser intensity (from 2492 to 2272 arbitrary units, Supporting Information, S4) and, consequently, the proportion of fragmented chains. Unfortunately, this solution is not always feasible because the decrease of this technical parameter can also lead to a significant signal-to-noise ratio reduction.

In addition to this technical parameter, we also proved that the cationization salt played a considerable role in (i) the quality of mass spectrum (much better with a silver cationization of polystyrene in MALDI-TOF mass spectrometry) which governs the exactness of the chain end-group identification and (ii) the species fragmentation in mass spectrometer (the Ag^+ cations being involved in the chain end-group fragmentation mechanism). Nevertheless, note that the use of Na salt limits the fragmentation but without suppressing it totally. These both criteria (quality vs fragmentation) were taken into account to make a MALDI/ESI comparison as efficiently as possible. Therefore, the results obtained by MALDI-TOF analyses from an Ag^+ cationization of polystyrene are given in Table 6, whereas those by ESI-TOF analyses from a Na^+ cationization are provided.

However, a MALDI/ESI comparison with same cationization salt and same polymer (RAFT-polymer) (Supporting Information, S5) seems to prove a stronger fragmentation in the former ionization method by the presence of fragmented XV populations and unresolved peak patterns. This finding was also achieved by Jiang et al.[19] for a RAFT-poly(methyl methacrylate). With the aim of explaining this difference, the comparison of both sources is very tricky since the ionization processes are completely distinct. Briefly, in the MALDI process, the ionization of sample is triggered by a UV laser beam, and is promoted by a matrix which is mixed with the sample. The various requirements of this matrix are to be able to embed and isolate samples, to be soluble in solvents compatible with sample, be vacuum stable, absorb the laser wavelength, cause codesorption of the sample upon laser irradiation, and finally promote sample ionization. The UV light adsorption by the matrix changes it to a compressed gas, in which charge transfer reactions with samples can take place. As the gas expands, it transports entrapped ions and macromolecules from the surface into the gas phase, where multiple collisions and further charge transfer reactions from matrix to neutral sample macromolecules are possible.[57] In ESI process, a strong electric field is applied to the capillary carrying the macromolecule solution, the spray is produced at atmospheric pressure. Desolvation of the droplets is then provided by a warm nitrogen gas.[57] The technical characteristics given by the supplier of MALDI-TOF mass spectrometer indicate an energy produced by laser of 300 μJ per pulse but it is very difficult to compare this value to an equivalent one for the ESI-TOF mass spectrometer. The numerous collisions between species in the compressed gas in MALDI, as well as the energy supplied by the laser beam, contrary to ESI process, may favor the fragmentation in the former ionization method.[58] In the particular polystyrene case, the UV laser ($\lambda = 337$ nm) could have a special strong influence on the fragmentation, and for example, on the formation of the XV population. Indeed, Nurmukhametov et al.[59] highlighted the susceptibility of this polymer to photodegradation, but the UV spectra of different polymer-CRP show that their UV absorbance in solution is negligible at 337 nm (Supporting Information, S6; except RAFT-polystyrene but no special behavior during MALDI process is specially remarked for it).

Finally, other minor populations detected in the MALDI-TOF mass spectra, and absent in the ESI-TOF mass spectra, are still not identified to date. Their presence in literature is unsystematic. These facts seem to reveal that the origin of these populations may be rather due to experimental and/or technical MALDI conditions than polymerization process.

2. MALDI/ESI Comparison of Average Molecular Weights and Polydispersity Indexes of Each CRP-Polystyrene

The molecular weight and molecular weight distribution considerations are of the greatest importance in CRP since the controlled behavior of a polymerization can be evidenced by predictable degrees of polymerization (i.e., the number-average molecular weight, M_n) and by narrow molecular weight distributions (i.e., with low polydispersity indexes, PDI $= M_w/M_n$). Consequently, the opportunity of obtaining these parameters simultaneously with the chain end-group structure by mass spectrometry reveals to be very interesting. Additionally to this advantage, these data can be determined by consuming a very low sample amount, a well as a short analysis time. The well-established and commonly used method for determining molecular weights and molecular weight distributions is size exclusion chromatography (SEC). As a result, number-average molecular weights (M_n) and polydispersity indexes (PDI) obtained by SEC were compared with their counterparts measured by MALDI-TOF and ESI-TOF mass spectrometry (Table 7). The values measured by MALDI-TOF mass spectrometry for all CRP are in very good agreement with SEC ones (differences $\leq$ 10%), a part for RITP-polymer. For the latter, the difference can be explained by the relatively high PDI determined in SEC, and a general low signal-to-noise ratio hindering the analysis of peaks at low molecular weight (presence of the matrix peaks at low m/z values).

The HY loss in mass spectrometer has not important consequence on the number-average molecular weights and molecular weight distributions in this molecular masse range since similar values were obtained from a mass spectrum of RAFT-polystyrene achieved with NaI ($M_n = 2120$ g·mol^{-1}, PDI = 1.06). The general satisfactory correlation between SEC and MALDI-TOF mass

Table 7. Number-Average Molecular Weights and Polydispersity Indexes Measured by SEC, MALDI-TOF, and ESI-TOF Mass Spectrometry

	SEC M_n (g·mol^{-1}) – PDI	MALDI-TOF M_n (g·mol^{-1}) – PDI	ESI-TOF M_n (g·mol^{-1}) – PDI
RAFT	2070 − 1.10	1900 − 1.14	1650 − 1.08
ATRP (-Cl)	2050 − 1.32	2060 − 1.38	1525 − 1.11
ATRP (-Br)	2510 − 1.14	2760 − 1.16	1910 − 1.08
NMP	2675 − 1.09	2940 − 1.20	1820 − 1.14
RITP	1550 − 1.28	2090 − 1.20	1560 − 1.13

spectrometry was also demonstrated for polystyrene or other polymers synthesized by RAFT,[13,20,26] ATRP,[38,60−63] and NMP.[45]

Conversely, there is a significant difference with ESI-TOF mass spectrometry results. Indeed, the number average molecular weights obtained by ESI-TOF are always below the SEC ones (despite the use of a same analyzer, TOF, with similar technical characteristics in ESI and MALDI mass spectrometry). The origin of this distinction can sometimes be justified by the presence of multiply charged ion peaks in the ESI mass spectra of synthetic polymers, especially for polar ones such as poly(ethylene glycol) and poly(methyl methacrylate), but here, this is not the case. This would come rather from the ESI source difficulty in ionizing high molecular weights, leading to an under-estimation of resulting average molecular weights.[64] Note that Jasieczek et al.[65] evidenced an effect of the cone voltage value on the mass distribution of polystyrene in ESI mass spectrometry. They found that relatively high cone voltages (120 V) were required to obtain a good agreement with SEC values (generally within 10%). However, despite the use of a maximal cone voltage (200 V) in our case, the difference between SEC and ESI data stays high. Therefore, the polymer end-group nature (Bu-polystyrene-H in the quoted work[65]) should have an influence not only on the mass spectrum quality, but also on the accuracy of the average molecular weight determination. Concerning the PDI values, a total loss of signification of these data is inevitable if the average molecular weights measured by the ESI process are under-estimated.

Conclusions

MALDI and ESI mass spectrometry are nowadays commonly used to characterize polymers synthesized from different CRP (RAFT polymerization, ATRP, NMP, and RITP). However, to our knowledge no systematic experimental comparison between both techniques for the analysis of these CRP-polymers has been reported. In the present work, this comparison is achieved for CRP-polystyrenes by analyzing their various chain end-groups, as well as average molecular weights. Indeed, both characteristics are of great interest in CRP to get information about the polymerization mechanism, and to check the controlled behavior of polymerization. This systematic comparison allowed us to evidence the advantages and disadvantages of each mass spectrometry technique to answer to these issues. Concerning the number of chain end-groups detected, this work displayed that it was higher by ESI-TOF than MALDI-TOF in the polystyrene case and whatever the CRP. The main reason of this difference may be the more pronounced fragmentation of polystyrene chains in MALDI mass spectrometer due to the inevitable use of silver salt to obtain mass spectra with high-quality. Various populations resulting from this fragmentation were examined. However, it is worth noting that this fragmentation feature is difficult to generalize for all CRP-polymers because the fragmentation process arising in mass spectrometer is dependent on analysis conditions, polymer chain end-groups and repeat units, as discussed in this work. About the determination of average molecular weights and molecular weight distributions of CRP-polystyrenes by means of MALDI and ESI mass spectrometry, it was demonstrated that the MALDI data were in a better agreement with SEC values than the ESI results despite the use of similar TOF analyzers. The number-average molecular weights were indeed under-estimated in the ESI case, contrary to the MALDI-TOF technique which revealed to be a good alternative to well-established SEC technique. Both mass spectrometry techniques are consequently very complementary to get a lot of information about CRP-polymerizations.

Acknowledgment. The authors thank Natali Henriquès, Aurélie Fildier, and Barbara Giroud (SCA/CNRS, Solaize, France), as well as Cyrille Boyer and Belkacem Otazaghine, for their help in the ESI-TOF mass spectrometry analyses and the polymer syntheses, respectively.

Supporting Information Available: (S1) MALDI-TOF mass spectrometry of RAFT-polystyrene with sodium salt as cationization agent in reflectron and linear modes. (S2) ESI-TOF mass spectrometry of RAFT-polystyrene with silver salt as cationization agent. (S3) MALDI-TOF mass spectrometry of Cl-mediated ATRP-polystyrene, Br-mediated ATRP-polystyrene, NMP-polystyrene, and RITP-polystyrene with sodium salt as cationization agent. (S4) Influence of laser intensity on the population detection (for RITP-polystyrene). (S5) MALDI/ESI comparison with the same polymer (RAFT-polymer) and the same cationization salt (sodium or silver cationization). (S6) UV spectra of different CRP-polystyrenes in dichloromethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) See papers in ref 32. Calculations of monoisotopic mass values of different possible terminated intermediate radicals: (1) 3-arm stars (present in ESI mass spectrum): [X-(styrene)$_m$-S-C((styrene)$_n$-X)(Ph)-S-(styrene)$_p$-X+Na]$^+$ at 1727.9 *m/z* for $m + n + p = 12$, [X-(styrene)$_m$-S-C((styrene)$_n$-X)(Ph)-S-(styrene)$_p$-I+Na]$^+$ at 1694.9 *m/z* for $m + n + p = 12$, [I-(styrene)$_m$-S-C((styrene)$_n$-X)(Ph)-S-(styrene)$_p$-I+Na]$^+$ at 1661.9 *m/z* for $m + n + p = 12$, and the last possibility is [I-(styrene)$_m$-S-C((styrene)$_n$-I)(Ph)-S-(styrene)$_p$-I+Na]$^+$ at 1732.9 *m/z* for $m + n + p = 13$ and is not observed on the ESI spectrum; (2) 4-arm stars (absent in ESI mass spectrum): [A-(styrene)$_{m+n}$-S]2-C(Ph)-C(Ph)-[S-(styrene)$_{o+p}$-A]$_2$+Na]$^+$, where A = X or I, at 1669.8 *m/z*, 1636.7 *m/z*, 1603.7 *m/z* for $m + n + o + p = 9$, 1674.8 *m/z*, 1641.8 *m/z* for $m + n + o + p = 10$ (according to the number of X and I groups in the macromolecules); (3) Intermediate radicals terminated with a hydrogen atom (absent in ESI mass spectrum): [X-(styrene)$_m$-S-CH(Ph)-S-(styrene)$_n$-X+Na]$^+$ expected at 1628 *m/z* for $m + n = 12$, [X-(styrene)$_m$-S-CH(Ph)-S-(styrene)$_n$-I+Na]$^+$ at 1699 *m/z* for $m + n = 13$, [I-(styrene)$_m$-S-CH(Ph)-S-(styrene)$_n$-I+Na]$^+$ at 1666 *m/z* for $m + n = 13$.

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(64) As suggested by one of the reviewers, this also comes from the fact that the ESI-TOF instrumentation employs orthogonal acceleration of ions that pass a hexapole focusing lens. RF fields skew molecular weight distributions. In contrast, MALDI-TOF instrumentation employs linear extraction and acceleration of the ions, and MALDI-generated ions traverse the TOF tube without passing a quadrupolar field. As a result, MALDI-TOF ion distributions are more representative of actual molecular weight distributions.

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MA8013788