MALDI-TOF Mass Spectrometry Analysis of TEMPO-Capped Polystyrene

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ABSTRACT: Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of polystyrenes prepared by 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)-mediated living free radical polymerization has been performed using two different matrices. A complete assignment of the observed peaks could be proposed, owing to the experimental resolution which allowed us to display the isotopic distribution. With the 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol)/silver trifluoroacetate system, a major part of the charged chains undergoes gas phase fragmentation during the analysis. This phenomenon, only minor for conventionnally prepared polystyrene, is particularly enhanced when the chains contain a TEMPO-based alkoxyamine end group. In contrast, the dead chains with no alkoxyamine end group are properly detected. When using the 2,5-dihydroxybenzoic acid (DHB) matrix without added salt, only protonation occurs involving the alkoxyamine functionality. Only the TEMPO-capped polystyrene chains are observed and no fragmentation occurs; the dead chains which have no protonation site are not detected. This still allows determination of the nature of the polymer headgroup and gives an insight into the initiation mechanism. Thermally self-initiated polystyrene in the presence of TEMPO contains predominantly a 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl headgroup. When dibenzoyl peroxide (BPO) is used as an initiator at 130 °C in the presence of TEMPO ([TEMPO]/[BPO] = 1.2), both benzoyloxy and 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl headgroups are detected. When an alkoxyamine initiator is used, only the fragment derived from this initiator is observed and the extent of thermal initiation seems to be reduced by comparison with the use of dibenzoyl peroxide initiator. These results can be explained by the enhanced formation of 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl radical in the presence of free TEMPO.

Introduction

Living/controlled free radical polymerization (LFRP)[1] has received, during the last 5 years, increasing interest based upon the expectation that this process might be an alternative to the living ionic polymerizations which require very drastic experimental conditions (i.e., low temperature, thorough elimination of moisture and impurities). Indeed, this technique has the advantage of being easy to carry out since the only essential purification is the elimination of oxygen. The most widespread possibility to achieve livingness (or at least control of the polymerization) is based on an equilibrium between the active macromolecular radical and a dormant covalent counterpart which can be either an alkoxyamine (nitroxide-mediated LFRP)[1,2] or an alkyl halide (atom transfer radical polymerization).[1,3]

TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) is the most widely used nitroxide and is mainly applied for the controlled polymerization of styrenic monomers. This stable radical is able to efficiently scavenge the carbon-centered radicals, and the reaction is reversible. For the polymerization of styrene, temperatures higher than 120 °C are required. In that case, polymerization was shown to be "living" with constant concentration of propagating radicals, linear increase of M_n with monomer conversion, and relatively narrow molar mass distribution. This was true when either TEMPO was added to a conventional polymerization medium (composed of monomer and of a radical initiator)[1,2] or when a preformed alkoxyamine was used as a unimolecular initiator.[1,4] At high temperatures, however, the thermally self-initiated polymerization of styrene cannot be avoided and was shown to play a key role in the polymerization kinetics.[5] It was reported that when only styrene and TEMPO were mixed at $T > 120$ °C, LFRP could be achieved.[6,7] A period of inhibition was first observed (also called "incubation" period by the authors), the duration of which increased when the initial concentration of TEMPO was raised.[7] During this period, no polymer could be recovered. Then, polymerization started at a rate similar to that usually measured in TEMPO-mediated LFRP of styrene and had the characteristics of a living polymerization. Three different species could be isolated during the "incubation" period: the 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl−TEMPO adduct (D-TEMPO, **1**), the 1-phenylethyl−TEMPO adduct (PE-TEMPO, **2**), and to a minor extent, the bis-TEMPO adduct (**3**) (Scheme 1). Their respective proportions were not reported. It was only mentioned that for the reaction of 200 equiv of styrene with TEMPO at 130 °C ([TEMPO] = 0.05 mol/L in bulk styrene), the major constituent was **1** and the minor one was **3** after 3.5 h. After being isolated and fully characterized, the TEMPO adducts **1** and **2** proved to be efficient initiators for the LFRP of styrene. In contrast, the bis-adduct **3** gave poorly controlled polymerization. From those results, it was concluded that efficient unimolecular initiators were formed "in situ" during the "incubation" period and could initiate a living polymerization.

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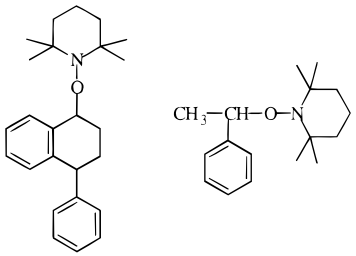
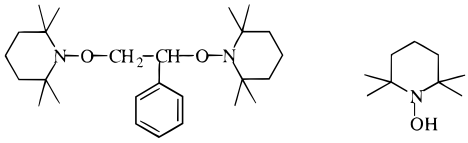
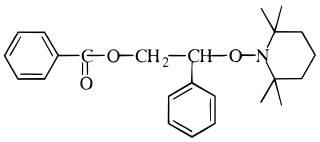
Scheme 1



1 (D-TEMPO) **2 (PE-TEMPO)**



3 **4**



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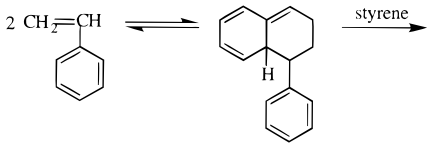
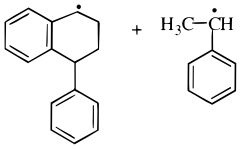
Scheme 2



DH

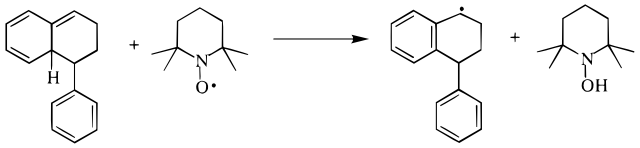


D• **PE•**

In the absence of radical scavenger, the accepted Mayo mechanism of thermal autopolymerization of styrene[8] involves a reaction between a Diels−Alder styrene dimer (**DH**) and a molecule of styrene leading to the initiating radicals **D•** and **PE•** (see Scheme 2). Moad et al.[9] described the isolation and characterization of the species formed upon heating styrene at 100 °C in the presence of TEMPO ([TEMPO] = 0.05 mol/L in bulk styrene). They recovered three species: **1** (45%), **3** (10%) and the hydroxylamine **4** (44%). The 1-phenylethyl−TEMPO adduct **2** was not observed. Interestingly, the consumption of TEMPO was found to be approximately 20 times faster than the known rate of thermal initiation in the absence of any added scavenger. To explain these results, the authors proposed that TEMPO was able to react with **DH** to lead to **D•** and **4** by hydrogen abstraction (Scheme 3). The radical **D•** was trapped by TEMPO to lead to **1.** The formation of the minor product **3** was explained by the reaction of styrene with two molecules of TEMPO.

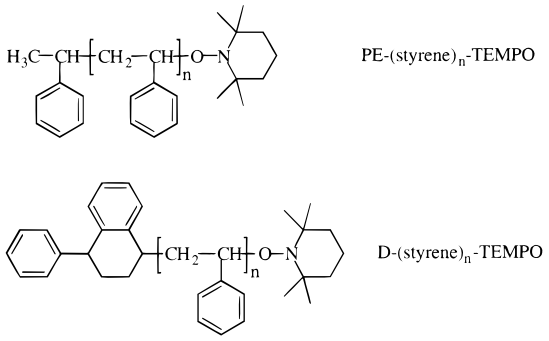
On the basis of the results of Devonport,[7] the TEMPO-mediated LFRP of styrene in the absence of added initiator leads to the two TEMPO-capped polystyrene chains resulting from the two different initiating radicals, as shown in Scheme 4. However, according to the mechanism of Moad,[9] the species initiated by **PE•** should be present in negligible amount. All these conclusions were drawn from the analysis of the potentially initiating species formed in the medium before the very beginning of the polymerization. However, only the direct analysis of the polymers might give conclusive information about their real structure and particularly the nature of their headgroup. The ^{1}H and ^{13}C NMR analyses of self-initiated polystyrene in the presence of TEMPO was recently reported.[10] It confirmed the results of Moad et al.[9] demonstrating that **D•** is the main initiating species since only the 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl headgroup could be detected, whereas no methyl headgroup coming from 1-phenylethyl was observed.

Scheme 3



DH **TEMPO** **D•** **4**

Scheme 4



Another technique able to provide such information (for polymers and not only for short oligomers) is the MALDI-TOF-MS analysis (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry). Besides the potential interest for determination of the accurate molar mass, it is a powerful tool for closer insight into the polymer structure.[11,12] Indeed, with a separation better than 1 atomic mass unit, it allows discrimination between various structures. Mass spectrometry analyses of polystyrene prepared by TEMPO-mediated LFRP were previously reported.[13] The authors described the analysis of TEMPO-capped polystyrene samples by MALDI-TOF-MS, by ESI-MS (electrospray ionization mass spectrometry), and by L-SIMS (liquid secondary ion mass spectrometry). Polymerization was initiated either by dibenzoyl peroxide (BPO) in the presence of TEMPO or by the alkoxyamine unimolecular initiator **5** (Scheme 1). MALDI-TOF mass spectra (dithranol matrix with silver trifluoroacetate) showed a broader distribution than could be expected from size exclusion chromatography measurements. Several ion distributions were displayed, among which only two have been assigned. They reportedly correspond to the following cationized polymers: $[BO-(styrene)_n-BO, Ag]^+$ and $[BO-(styrene)_n-CH=CH-C_6H_5, Ag]^+$, where BO is the benzoyloxy fragment coming from the initiation by BPO. No series with the TEMPO-based alkoxyamine end group could be evidenced by this technique. In contrast, using ESI-MS and L-SIMS, quite different

Table 1. Experimental Conditions for Styrene LFRP Carried out at 130 °C and SEC Characterization of the Polystyrene Samples

ref	[BPO] (mol L^{-1})	[CSA] (mol L^{-1})	[**2**] (mol L^{-1})	[TEMPO] (mol L^{-1})	time (h)	ρ (%)	M_n	M_w	I_p
PS1	0.050	0.010	0	0.060	2.5	4.4	1470	1630	1.11
PS2	0	0.010	0	0.060	4.0	4.4	1790	2020	1.13
PS3	0	0	0	0.060	6.0	6.0	1730	1930	1.11
PS4	0	0	0.030	0.001	6.0	18.8	4530	5600	1.23

results were provided, since the main observed series were $[BO-(styrene)_n-TEMPO, metal]^+$ and $[BO-(styrene)_n-TEMPO, H]^+$ respectively. From these observations, the main conclusion was that prompt fragmentations of the chains could occur in the MALDI source.[13] They were responsible for the absence of the cationized TEMPO-capped polystyrene in the mass spectra as well as for the formation of the cationized $[BO-(styrene)_n-BO, Ag]^+$ series which was not produced by ESI-MS and L-SIMS. Thus, none of the used mass spectrometry techniques could lead to a definitive characterization of the different macromolecular structures or to the determination of their relative amounts in the polymer.

In the present work, MALDI-TOF mass spectrometry of various polystyrenes obtained by TEMPO-mediated LFRP have been performed. They were initiated at $T = 130$ °C either by BPO, by the alkoxyamine **2**, or by the previously described thermal mechanism only. The main objectives were to study the influence of the target preparation and of the desorption conditions on the MALDI-TOF mass spectra and to identify the structure of the polymer in relation with the nature of the initiator.

Experimental Section

Polystyrene Synthesis. Styrene was distilled before use. 2,2,6,6-Tetramethyl piperidine-N-oxyl (TEMPO, 98% purity), dibenzoyl peroxide (BPO, 97% purity), and camphorsulfonic acid (CSA, 98% purity) were used as provided by Aldrich. The 1-phenylethyl−TEMPO adduct **2** [2,2,6,6-tetramethyl-1-(1-phenethyloxy)piperidine] was synthesized and purified according to the procedure described by Howell.[14] The solutions of the various additives in styrene (5−10 g) were degassed by freeze−thaw cycles under vacuum. The tubes were sealed off and then immersed in an oil bath thermostated at 130 °C. After polymerization, the content of each tube was poured under stirring into an excess of methanol. The polymers were isolated by filtration, washed with methanol, and dried. Styrene conversion (ρ) was determined by gravimetry. The experimental conditions are summarized in Table 1.

Size Exclusion Chromatography (SEC). SEC was performed using a Waters apparatus working at room temperature with stabilized tetrahydrofuran (THF) eluent at a flow rate of 1 mL min^{-1} and equipped with four PL-gel 10μ columns (100, 500, 10^3, and 10^4 Å). A differential refractive index detector was used and molar masses were derived from a calibration curve based on polystyrene standards.

MALDI-TOF Mass Spectrometry. MALDI-TOF-MS was performed using a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflector modes. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polystyrene solutions (2−5 g L^{-1}) were prepared in THF. The matrices, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol) and 2,5-dihydroxybenzoic acid (DHB), were also dissolved in THF (10 and 15 g L^{-1}, respectively). The polystyrene solution (10 μL) was mixed with 50 μL of the matrix solution. In the case of dithranol/polystyrene solution, 10 μL of a silver trifluoroacetate solution (2 g L^{-1} in THF) was added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems.

Results and Discussion

Dithranol/Silver Trifluoroacetate Matrix. The polystyrene samples presented in Table 1 were analyzed by MALDI-TOF-MS using two different matrices. First, the dithranol/silver trifluoroacetate system was used since it is known to be well-suited for the analysis of polystyrene.[15] Spectra are shown in Figure 1 for the different samples. Unexpectedly, none has a single narrow molar mass distribution, although the MALDI-TOF mass spectra should be very close to the SEC chromatograms for the molar mass (MM) and molar mass distribution (MMD) ranges of the studied polystyrenes. As reported by Jasieczek et al.[13] for similar compounds, complex distributions generally broader than expected are observed with an important tailing toward the lower m/z values. For the four studied samples (**PS1**, **PS2**, **PS3**, and **PS4**), several ion series can be distinguished, each of them corresponding to polystyrene chains cationized by Ag^+ with various headgroups and end groups (repeat unit 104.06 u). For a given series and a given degree of polymerization, the multiplicity of the signal results from the isotopic distribution. The multiplicity can provide additional information about the chemical composition of the polymer (one or several species), and this can be deduced by comparing the distribution of the natural isotopic cluster to the theoretical one for a single species (Figure 2).

An attempt to assign the series is derived on the basis of MM calculations for the various possible structures. These calculations are presented in Table 2 for a selected molar mass region, between 1450 and 1500 u. The headgroup can be a benzoyloxy fragment (BO, coming from initiation by BPO) or a function resulting from self-initiation (4-phenyl-1,2,3,4-tetrahydro-1-naphthyl, **D**, or 1-phenylethyl, **PE**). The most probable end group is the TEMPO-based alkoxyamine. However dead chains can be formed by irreversible termination between two propagating radicals, leading essentially to recombination products in the case of polystyrene.[16] Therefore, such chains bear either the same or two different initiator fragments at each end. Irreversible termination can also occur by TEMPO-induced β-hydrogen elimination leading to unsaturated chain end (endo unsaturation).[17] Furthermore, a transfer reaction of a hydrogen atom from the Diels−Alder dimer **DH**[17,18] or from the hydroxylamine **4**[19] to the propagating radical can also occur, leading to chains with a saturated end group. Fragmentation during the MALDI-TOF analysis leading to polystyrene with a methylene end group was observed by Zammit[16] and this end group is also considered here.

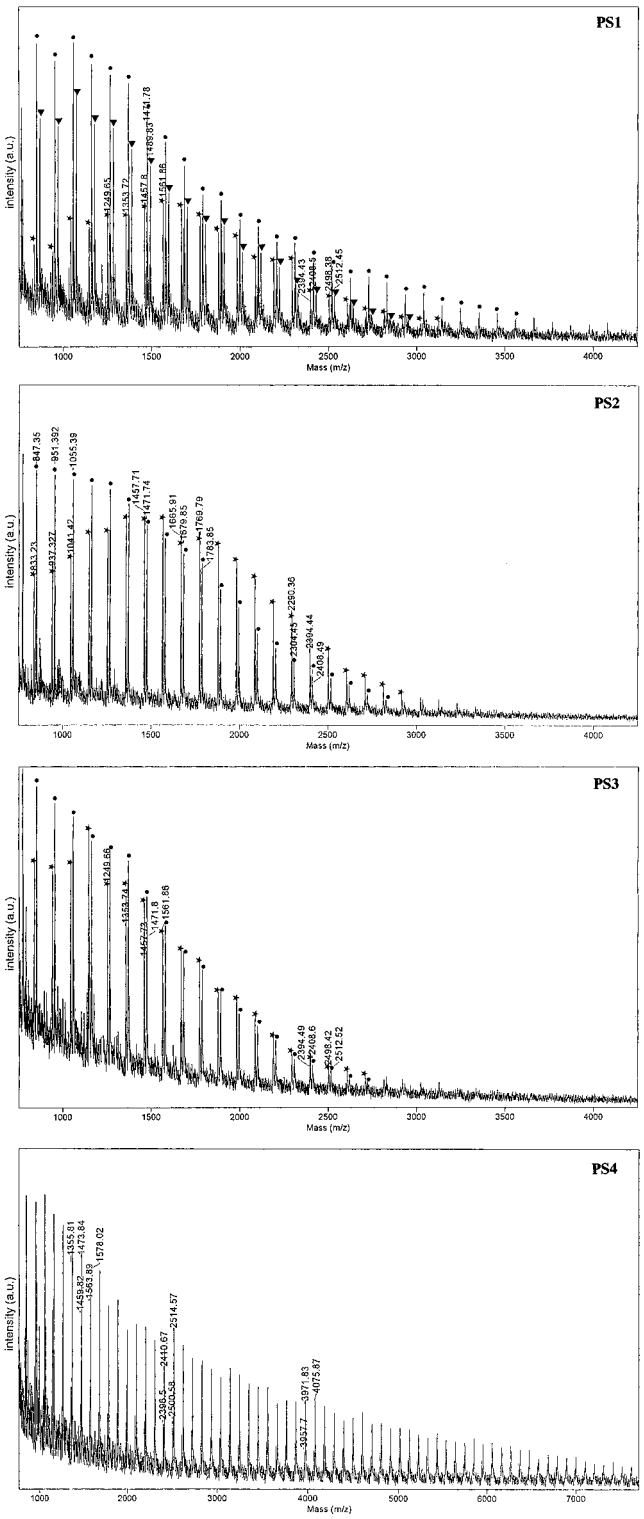


Figure 1. MALDI-TOF mass spectra (reflector mode) obtained with dithranol/silver trifluoroacetate matrix for the four polystyrenes **PS1**, **PS2**, **PS3** and **PS4**: ★, series **a** ; ●, series **b**; ▼, series **c**.

The molar mass values for the experimentally observed series are reported in Table 3 and compared with the theoretical values of Table 2. For the four analyzed samples, the main conclusion is that no series corresponds to TEMPO-capped polystyrene, which is in good agreement with the previously reported results of Jasieczek et al.[13] obtained under similar experimental conditions. Concerning the **PS1** sample, three main

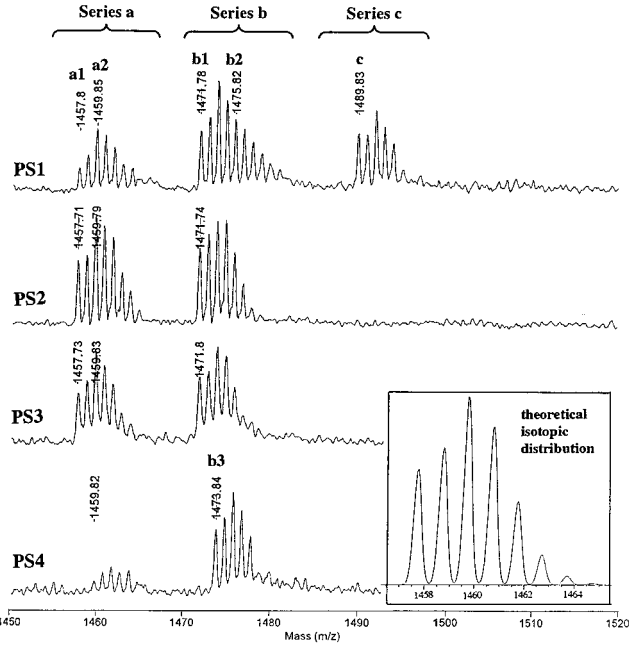


Figure 2. MALDI-TOF mass spectra (reflector mode) obtained with dithranol/silver trifluoroacetate matrix for the four polystyrenes **PS1**, **PS2**, **PS3** and **PS4**. Expansions between $m/z = 1450$ and 1520 u. Theoretical isotopic cluster calculated for $[D-(styrene)_{10}-CH=CH-C_6H_5, Ag]^+$.

series are observed, **a**, **b**, and **c** (Figure 1). Series **a** is the only one exhibiting a symmetrical and narrow MMD ($M_n = 1630$, $M_w = 1800$, $I_p = 1.1$ as given by the MALDI-TOF-MS). The monoisotopic peak of this series is at $m/z = 1457.80$ u (series **a1**). According to Table 2, this might correspond to the two following isomeric forms: Ag^+-cationized self-initiated polystyrene with **D** headgroup and endo unsaturation or **D** end group. Comparison of the natural isotopic cluster with the theoretical isotopic distribution (Figure 2) shows the possible existence of another minor series at $m/z = 1459.85$ u (series **a2**). This could correspond to the Ag^+-cationized self-initiated chains with **PE** or **D** headgroup and respectively endo unsaturated or saturated end group. The possible series at $m/z = 1461.72$ u corresponding to $[PE-(styrene)_n-PE, Ag]^+$ or to $[PE-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$ cannot be significantly evidenced. In this general series **a**, the headgroup comes from thermal self-initiation and the end groups are the usual ones arising from irreversible termination processes such as recombination or disproportionation, β-hydrogen elimination, and H transfer from **DH**. Series **b** and **c**, in contrast to series **a**, have a significant tailing toward the lower m/z values. They could correspond to species originating, at least partially, from prompt fragmentation during the MALDI processes. The monoisotopic peak of the isotopic cluster of series **b** at $m/z = 1471.78$ u corresponds to Ag^+-cationized self-initiated polystyrene with a **D** group at the head and a methylene exo double bond at the end (**b1**). However, the high multiplicity of this cluster cannot be explained by the isotopic distribution of **b1** alone. Another type of macromolecule with a slightly higher MM (+4 u, $m/z = 1475.82$, series **b2**) exists which could be reasonably assigned to BPO-initiated polystyrene, terminated either by an unsaturation or by a **D** end group. The two other expected series at $m/z = 1473.73$ u and $m/z = 1477.68$ u have not been significantly identified. The last series **c** represents a single distribution (good agreement between the natural iso-

Table 2. Theoretical Molar Mass of Ag^+-Ionized Polystyrene (Monoisotopic Peak) for the Various Possible Structures

assumed possible structure	termination process	n	calcd MM of the monoisotopic peak (u)
initiation with BPO			
$[BO-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	irreversible decomposition of the alkoxyamine (β hydrogen elimination) and/or disproportionation	11	1475.68
$[BO-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$	irrreversible termination by H transfer from DH and/or disproportionation	11	1477.68
$[BO-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	degradation of the polystyrene chain during the analysis	11	1489.69
$[BO-(styrene)_n-TEMPO, Ag]^+$	reversible capping with TEMPO	11	1528.76
		10	1424.70
thermal initiation with PE			
$[PE-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	irreversible decomposition of the alkoxyamine (β hydrogen elimination) and/or disproportionation	11	1459.72
$[PE-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$	irreversible termination by H transfer from DH and/or disproportionation	11	1461.72
$[PE-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	degradation of the polystyrene chain during the analysis	11	1473.73
$[PE-(styrene)_n-TEMPO, Ag]^+$	reversible capping with TEMPO	11	1512.80
		10	1408.74
thermal initiation with D			
$[D-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	irreversible decomposition of the alkoxyamine (β hydrogen elimination) and/or disproportionation	10	1457.72
$[D-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$	irreversible termination by H transfer from DH and/or disproportionation	10	1459.72
$[D-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	degradation of the polystyrene chain during the analysis	10	1471.73
$[D-(styrene)_n-TEMPO, Ag]^+$	reversible capping with TEMPO	10	1510.79
		9	1406.73
recombination products			
$[BO-(styrene)_n-BO, Ag]^+$		11	1493.65
$[BO-(styrene)_n-D, Ag]^+$		10	1475.68
$[BO-(styrene)_n-PE, Ag]^+$		11	1477.68
$[D-(styrene)_n-D, Ag]^+$		9	1457.72
$[D-(styrene)_n-PE, Ag]^+$		10	1459.72
$[PE-(styrene)_n-PE, Ag]^+$		11	1461.72

Table 3. MALDI-TOF Experimental Molar Masses of the Ag^+-Ionized Polystyrenes (Dithranol/Silver Trifluoroacetate Matrix)

value of the monoisotopic peak (u) for the experimentally observed series	identified series	polystyrene samples in which the series was identified	assumed possible structure	n
1457.80	**a1**	**PS1, PS2, PS3**	$[D-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	10
			$[D-(styrene)_n-D, Ag]^+$ [a]	9
1459.85	**a2**	**PS4, (PS1, PS2, PS3)**	$[PE-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	11
			$[D-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$ [a]	10
1471.78	**b1**	**PS1, PS2, PS3**	$[D-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	10
1473.84	**b3**	**PS4**	$[PE-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	11
1475.82	**b2**	**PS1**	$[BO-(styrene)_n-CH=CH-C_6H_5, Ag]^+$	11
			$[BO-(styrene)_n-D, Ag]^+$ [a]	10
1489.83	**c**	**PS1**	$[BO-(styrene)_n-CH_2C(C_6H_5)=CH_2, Ag]^+$	11

[a] Least probable structure.

topic cluster and the theoretical isotopic distribution). The monoisotopic peak of the cluster at $m/z = 1489.83$ u corresponds most probably to the Ag^+-cationized polystyrene initiated by BPO and bearing a methylene end group. The recombined polymer with a benzoyloxy fragment at each end (calculated $m/z = 1493.65$ u) is not observed.

Concerning the **PS2** and **PS3** polystyrenes which were thermally self-initiated, only the series **a1**, **a2**, and **b1** are observed (Figures 1 and 2). All the signals which were previously assigned to BPO-initiated chains have obviously disappeared from the MALDI mass spectra. Spectra of **PS2** and **PS3** are similar with each other, which indicates that the added acid, CSA, has no effect on the structure of the polymer.

The polystyrene **PS4** was initiated by the preformed alkoxyamine **2** (PE-TEMPO). Two main ion series can be evidenced as seen in Figures 1 and 2. As reported in Table 3 and according to Table 2, the first and less intense one (monoisotopic peak of the isotopic cluster at $m/z = 1459.82$ u) most probably corresponds to chains with a **PE** headgroup that are terminated by an endo unsaturation (series **a2**). Due to the low intensity of the cluster, no conclusion can be drawn about the presence or absence of the ion series corresponding to the recombination product $[PE-(styrene)_n-PE, Ag^+]$ or to the saturated compound $[PE-(styrene)_n-CH_2CH_2-C_6H_5, Ag]^+$, both expected at $m/z = 1461.72$ u. However, if existing, those series would be in proportion lower than **a2**. The second observed series (monoisotopic peak at $m/z = 1473.84$ u) which is a single cluster, might correspond to polystyrene initiated by **PE** and bearing a methylene end group (series **b3**). Thus, the polystyrene **PS4** has a **PE** headgroup, owing to the initiation by the PE-TEMPO alkoxyamine, and its end groups correspond to either irreversible termination during the synthesis or degradation during the analysis (which leads to the most intense peak). The possible **D** headgroup arising from self-initiation and observed in **PS2** and **PS3** cannot be evidenced. This will be discussed at the end of the section.

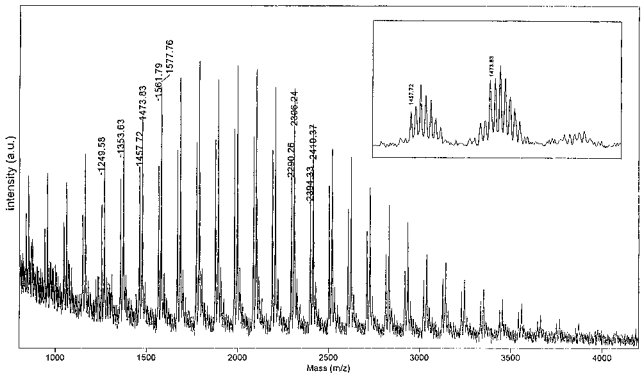


Figure 3. MALDI-TOF mass spectrum (reflector mode) obtained with dithranol/silver trifluoroacetate matrix for the **PS2** sample after heating at 130 °C during 24 h. $M_n = 2100$; $M_w = 2400$; $I_p = 1.14$ (same MMD for both observed series).

Those experimental results show that, with the dithranol/silver trifluoroacetate matrix, the MALDI-TOF-MS analysis of polystyrene does not allow a simple and reliable interpretation. This comes essentially from the fragmentation of the chains supposed to occur near the chains end during the MALDI processes (series **b1, b3**, and **c**). This situation is most probably responsible for the formation of a methylene end group instead of the hypothetic $[BO-(styrene)_n-BO, Ag]^+$ structure which was proposed by Jasieczek et al.[13] Under similar experimental conditions, Zammit et al.[16] have observed the formation of such fragments in the analysis of polystyrenes conventionally initiated by azobisisobutyronitrile, but this was only a minor phenomenon. Fragmentation of polystyrene chains has also been reported by Craig[20] in the FD of polystyrene. Since no polymer with a TEMPO-based alkoxyamine end group is detected by the MALDI-TOF technique (although it should be the main structure), it might be reasonable to consider that decomposition of those chains is very favorable. Consequently, the degraded chains might mainly correspond to the initially TEMPO-capped polystyrene. However, the exact mechanism of their fragmentation is not yet fully understood.

Evidence of the unstability of TEMPO-capped polystyrene chains under our MALDI experimental conditions has been provided by the study of **PS2** after heating this polymer at 130 °C in an oven during 24 h. Two series exhibiting a narrow and symmetrical MMD are observed in the MALDI mass spectrum of the resulting polymer when using the dithranol/silver trifluoroacetate matrix (Figure 3). The series **a1** (monoisotopic peak of the isotopic cluster at $m/z = 1457.72$ u) is still observed, but the series **b1** attributed to gas-phase fragmentations has been shifted to another series (monoisotopic peak of the cluster at $m/z = 1473.83$ u) assigned to polystyrene with a phenyl ketone end group. Such species have been shown to arise upon heating TEMPO-capped polystyrene in the presence of oxygen (homolysis of the alkoxyamine end group and further oxidation).[21] Thus, in the absence of the TEMPO-based alkoxyamine end group, gas-phase chain fragmentation could not be evidenced any more.

In contrast to series **b1**, **b3** and **c**, the series **a1**, **a2** and **b2** correspond to nondegraded polymer. In those cases, the absence of the TEMPO end group is the result of irreversible termination reactions which cannot be completely suppressed during the polymerization process. It would be obviously very difficult to quantify their proportion in the polymer on the single basis of the MALDI-TOF mass spectra presented in Figure 1. Possible structures were proposed for those dead chains (Table 3). Combination of the information provided by the analysis of the four different samples now enables us to propose a better assignment. The absence in the MALDI mass spectra of the recombination products $[BO-(styrene)_n-BO, Ag]^+$ and $[PE-(styrene)_n-PE, Ag]^+$ is an indication that this mode of termination is not favored. Thus, the best assignment for series **a1** is $[D-(styrene)_n-CH=CH-C_6H_5, Ag]^+$ instead of $[D-(styrene)_n-D, Ag]^+$ and the best assignment for series **b2** is $[BO-(styrene)_n-CH=CH-C_6H_5, Ag]^+$ instead of $[BO-(styrene)_n-D, Ag]^+$. For **PS4**, the best assignment for series **a2** is $[PE-(styrene)_n-CH=CH-C_6H_5, Ag]^+$. Therefore, it appears that the dead chains have most probably an endo unsaturation at the end indicating that β-hydrogen abstraction is the favored chain breaking event. For polymers **PS1**, **PS2**, and **PS3**, series **a2** has a very low intensity; the absence of any other saturated chains in the polymers could indicate that $[D-(styrene)_n-CH_2-CH_2-C_6H_5, Ag]^+$ is not the best assignment, but $[PE-(styrene)_n-CH=CH-C_6H_5, Ag]^+$ is. For both proposed attributions, however, the involved reactions (i.e., transfer from DH or from the hydroxylamine and thermal initiation with **PE**$^\bullet$) are not far from being negligible, at least at low conversion.

Table 4. Theoretical Molar Mass of Protonated TEMPO-Capped Polystyrene with Various Initiating Groups

structure	n	calcd MM of the monoisotopic peak (u)
$[BO-(styrene)_n-TEMPO, H]^+$	11	1422.86
$[D-(styrene)_n-TEMPO, H]^+$	10	1404.89
$[PE-(styrene)_n-TEMPO, H]^+$	11	1406.90

DHB Matrix. To avoid polymer degradation and make the interpretation easier, a different analytical procedure was applied. The more acidic DHB matrix was used without any added salt in order to selectively protonate the alkoxyamine end group. Using such conditions, the dead chains which have irreversibly lost their TEMPO capping agent during the synthesis cannot be ionized and should disappear from the MALDI mass spectra. Therefore, this method is not suited to analyze the nature of the end groups but still allows determination of the various headgroups. In other words, it is well-suited to give information on the nature of the true initiator. In Table 4, the three different structures of the protonated TEMPO-capped polystyrenes are summarized by considering the initiation by either BPO or by thermally formed radicals (potentially **D**$^\bullet$ and **PE**$^\bullet$). In all the MALDI mass spectra, narrow MMD can be evidenced, indicating that no fragmentation has occurred and, as expected, all the detected chains correspond to TEMPO-capped polystyrene with various headgroups (Figure 4). This confirms that the previously mentioned absence of TEMPO was the consequence of the analytical conditions only. The **PS2** and **PS3** samples, which have been polymerized without any added initiator, exhibit only one apparent ion series corresponding to a single MMD, since the natural isotopic clusters perfectly fit with the theoretical distribution for a single species (Figure 5). This series may be assigned to $[D-(styrene)_n-TEMPO, H]^+$. Concerning the polymer **PS1**, two series with similar abundances are detected. The first one corresponds to

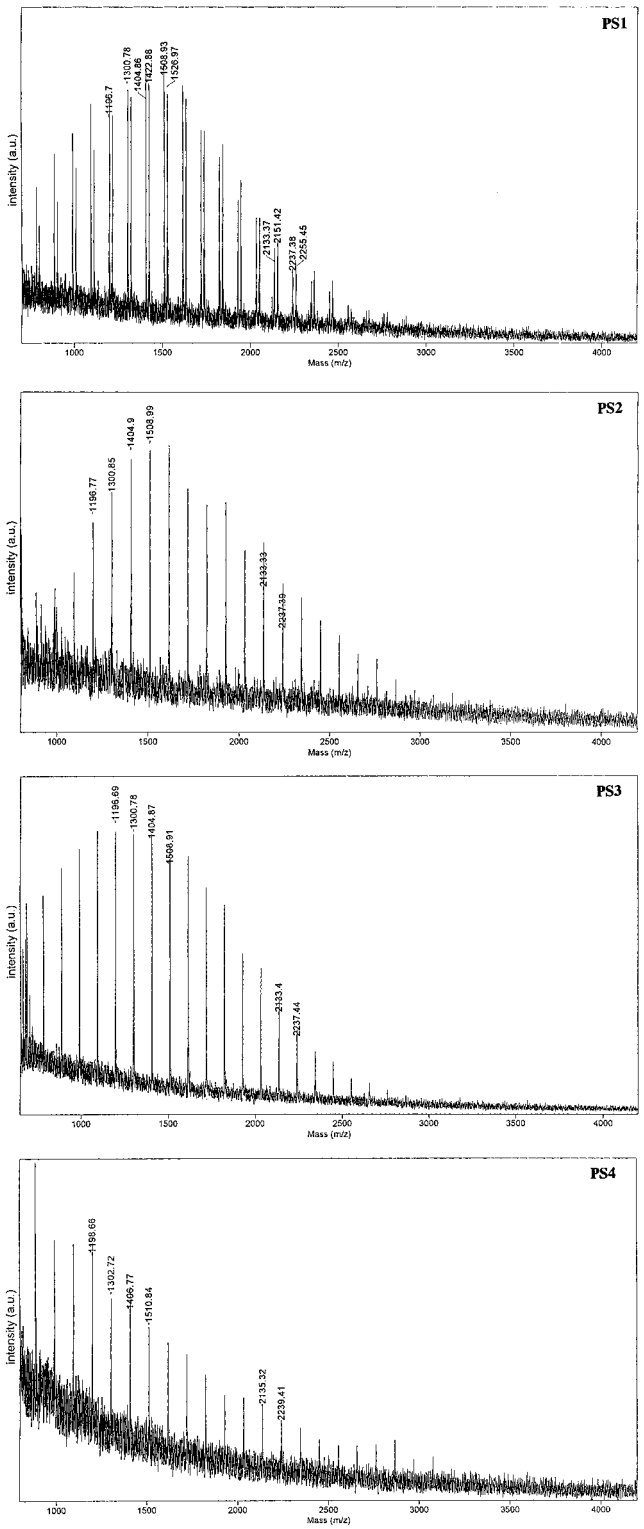


Figure 4. MALDI-TOF mass spectra (reflector mode) obtained with DHB matrix for the four polystyrenes **PS1**, **PS2**, **PS3** and **PS4**. **PS1:** $M_n = 1590$; $M_w = 1740$; $I_p = 1.09$ (same MMD for both series). **PS2**: $M_n = 1710$; $M_w = 1940$; $I_p = 1.13$. **PS3**: $M_n = 1400$; $M_w = 1670$; $I_p = 1.19$. **PS4**: not calculated (too broad distribution).

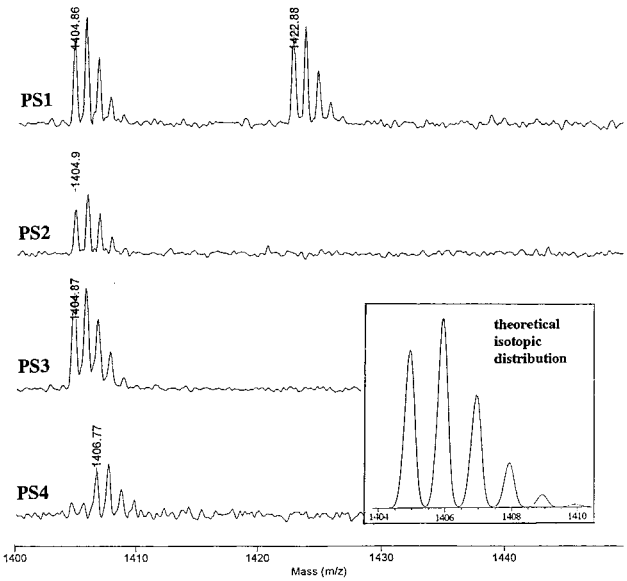


Figure 5. MALDI-TOF mass spectra (reflector mode) obtained with DHB matrix for the four polystyrenes **PS1**, **PS2**, **PS3** and **PS4**. Expansions between $m/z = 1400$ and 1450 u. Theoretical isotopic cluster calculated for [D−(styrene)$_{10}$−TEMPO, H]$^+$.

self-initiated polymer [D−(styrene)$_n$−TEMPO, H]$^+$ and the second one to BPO-initiated polymer [BO−(styrene)$_n$−TEMPO, H]$^+$. The polymer **PS4** has only one distribution with a shift of two units toward the higher m/z values with respect to polymers **PS2** or **PS3**. It corresponds to [PE−(styrene)$_n$−TEMPO, H]$^+$. Only a weak trace of the peaks corresponding to [D−(styrene)$_n$−TEMPO, H]$^+$ can be observed.

Since there is only one end group possibility and no fragmentation during the analysis, these results provide interesting information about the nature of the initiating groups in the polystyrene chains and can be related to the experimental conditions applied for the synthesis. The self-initiated polystyrenes (**PS2** and **PS3**) bear a **D** fragment at the head and no **PE** fragment. This is in perfect agreement with the recently reported NMR investigations[10] and confirms the mechanism proposed by Moad.[9] When BPO is used as an initiator in the presence of TEMPO, two different headgroups can be evidenced: the expected benzoyloxy fragment and **D**. When the unimolecular initiator PE-TEMPO is used, only the **PE** headgroup is observed and initiation by **D**$^\bullet$ is found to be negligible. Therefore, in the presence of free TEMPO at the beginning of the polymerization, the formation of the initiating species **D**$^\bullet$ is favored, owing to the fast reaction of the Diels−Alder dimer **DH** with the nitroxide. Even when a conventional initiator is added, the proportion of chains initiated by **D**$^\bullet$ may be high; it probably depends on the respective concentrations of BPO and TEMPO. In contrast, in the absence of a sufficient concentration of free TEMPO at the beginning of the polymerization, the formation of the initiating species **D**$^\bullet$ is very slow, resulting from the Mayo mechanism only, i.e., the reaction of **DH** with styrene. Therefore, the use of an alkoxyamine unimolecular initiator leads to a polymer with better structural integrity and is probably the best-suited method to achieve head functionalization of the polymer and controlled architectures.

Conclusion

MALDI-TOF mass spectrometry of TEMPO-capped polystyrene has been performed using two different matrices. With the dithranol/silver trifluoroacetate system, the TEMPO-capped polystyrene chains undergo gas phase fragmentation during the analysis. The mechanism of such fragmentation remains not fully

unsderstood and is still under investigation. Nevertheless, a complete assignment of the observed peaks could be proposed, owing to the experimental resolution, which allowed us to display the isotopic distribution. In contrast to TEMPO-capped chains, the dead chains are properly detected. They most probably have an endo unsaturation at the end, which means that the main termination reaction is the β-hydrogen abstraction. When using the DHB matrix without added salt, protonation occurs involving the alkoxyamine end functionality. Only the TEMPO-capped polystyrene chains are observed and no fragmentation occurs; the dead chains which have no protonation site are not detected. This still allows one to determine the nature of the polymer headgroup and to give an insight into the initiation mechanism. Particularly, it is shown that self-initiated polystyrene in the presence of TEMPO has essentially a 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl headgroup. This is in agreement with the mechanism previously proposed by Moad that TEMPO is able to abstract an hydrogen from the styrene Diels−Alder adduct, leading to the 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl initiating radical. This initiation exists also when BPO is used as an initiator in conjunction with TEMPO, but it is considerably reduced with an alkoxyamine unimolecular initiator.

Combination of both analytical conditions allowed us to provide a picture of the polymer structure, in relation with the experimental conditions of polymerization. However, the MALDI-TOF-MS analysis would be improved if all the species could be quantitatively detected without discrimination under the same analytical conditions. By modifying the alkoxyamine end group into a more stable species (oxidation into phenyl ketone) the MALDI-TOF MS analysis becomes possible, as was reported by Malz.[21] However, a direct analysis of the raw polymer without any chemical modification would give more reliable results.

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