Study of the Reaction between Nitroxide-Terminated Polymers and Thiuram Disulfides. Toward a Method of Functionalization of Polymers Prepared by Nitroxide Mediated Free "Living" Radical Polymerization

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ABSTRACT: Nitroxide-terminated polystyrenes resulting from "living" free radical polymerization processes have been "functionalized" by combination reaction with thiuram disulfide compounds, i.e., tetraethyl thiuram disulfide (**3a**), and *N*,*N*′-diethyl-*N*,*N*′-bis{2-((trimethylsilyl)oxy)ethyl} thiuram disulfide (**3c**). The quantitative substitution of the nitroxide moiety by the dithiocarbamate group has been characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, MALDI-TOF mass spectrometry, ESI mass spectrometry, and LSI mass spectrometry. The reaction has also been studied on a model compound.

Introduction

In a manner similar to anionic "living" polymerization, the nitroxide-mediated "living" radical polymerization[1] of olefins leads to the formation of polymers with narrow polydispersities and allows a perfect control of the molecular mass of the polymer obtained. In the radical process, the living character is a consequence of the fast reversible combination reaction of a growing polymer radical with a stable nitroxide radical to form an adduct; i.e., an alkoxyamine, which is a "dormant" species (cf. Scheme 1).

The "living" free radical polymerization of olefins, using either nitroxide control or atom transfer (ATRP), is considered as a potentially more powerful process than the "living" ionic polymerization[2] because of both the wide range of polymerizable monomers and the less drastic experimental conditions. Moreover, this method has been successfully applied to the macromolecular engineering of architecturally controlled polymers.[3]

Anionic "living" polymerization processes may also be involved in the synthesis of *ω*-functional polymers. For example, the living end of polystyrene prepared by anionic polymerization may be converted to an alcoholate end by reaction with ethylene oxide (this is the first step of Schulz and Milkovich's method[4] for the synthesis of polystyrene macromonomers). Thus, it was interesting to study a free radical process allowing the same reaction pattern, i.e., the quantitative substitution of the nitroxide moiety of *ω*-alkoxyamine type polymers by another chemical species carrying some functional group (cf. Scheme 2).

A speculative scheme for such a substitution is the addition to the alkoxyamine-terminated polymers of an organic species leading to an irreversible combination with the polymer radical coming from the thermal homolysis of the polymer chain end, the temperature being high enough to dissociate the alkoxyamine group. If the combination reaction of the new group is irreversible, such an addition might result in a quantitative substitution of the nitroxide moiety.

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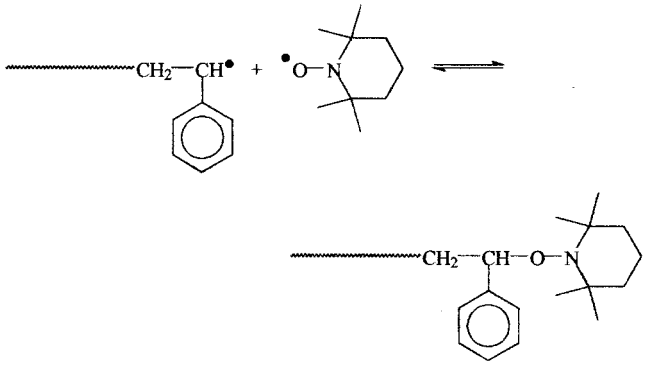
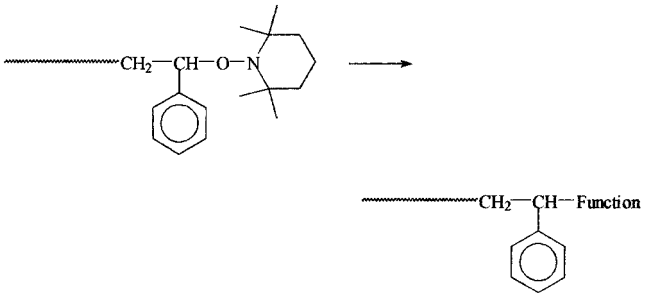
Scheme 1. Equilibrium between Active and Dormant Species in Nitroxide-Mediated "Living" Polymerization



Scheme 2. Substitution of the Nitroxide Moiety of *ω*-Alkoxyamine Type Polymers



Thiuram disulfides are known to behave as iniferters, i.e., are able to act in radical polymerization media as initiators, transfer agents, and termination agents.[5] The termination reaction is the consequence of the formation of dithiocarbamate radicals in the reaction medium because of either the thermal homolysis of the S−S bond of the thiuram disulfide or the transfer reaction of alkyl radicals onto the S−S bond (cf. Scheme 3).

In a photopolymerization process, this system may be considered as "living"[6] because of the reversible combination between alkyl radicals and dithiocarbamate radicals. But, in thermal polymerization, the reversibility of such a combination reaction seems to be very

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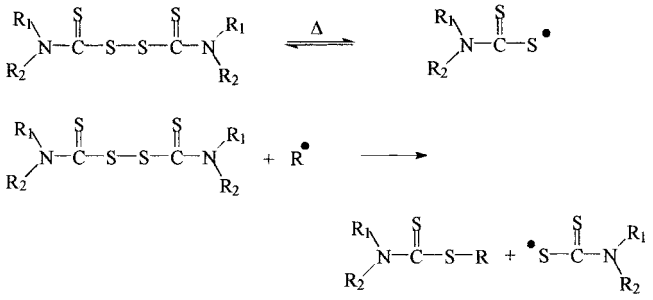
Scheme 3. Formation of Dithiocarbamate Radical with Thiuram Disulfides



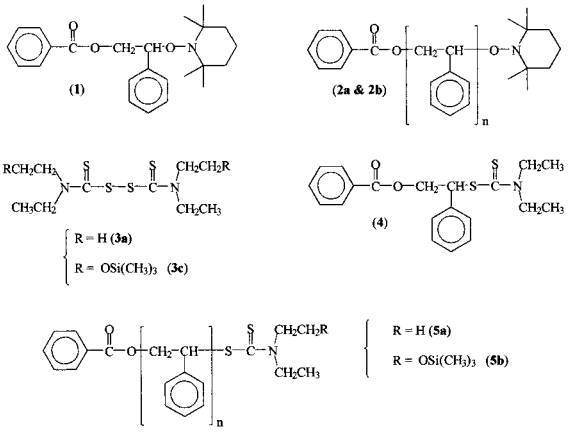
low (cf. Scheme 4), and consequently, the *thermal* polymerization of vinyl type monomers in the presence of a thiuram disulfide iniferter is not considered as a "living" process.

Thus, a nitroxide-terminated polymer heated in the presence of a thiuram disulfide might lead to the substitution of the nitroxide moiety by a dithiocarbamate group (cf. Scheme 5). However, as pointed out by a referee, if the combination reaction between alkyl radicals and dithiocarbamate radicals is not totally irreversible, then the substitution of the nitroxide moiety by a dithiocarbamate moiety is not quantitative. In such a case, the extent of the substitution depends on the difference of dissociation rates between these two species (and results from an equilibrium).

Endo et al. have found some "living" nature in the thermal polymerization of styrene in the presence of disulfides[7] attributed to the dissociation of the C−S bond. For example, the dissociation energy is ca. 217 kJ/mol in the case of $C_6H_5CH_2-SCH_3$. This value may be compared to the calculated dissociation energy of alkoxyamine groups,[8] ranging from 60 to 160 kJ/mol. In a recent studies, Fukuda et al.[9] have experimentally determined an apparent value of 124 kJ/mol for the dissociation energy of nitroxide-terminated polystyrene. From these values, the substitution can be expected to be *quasi* quantitative.

The thiuram disulfide compound may be designed to carry some functional group, as is the case for **3c**, i.e.,

Chart 1. Studied Compounds



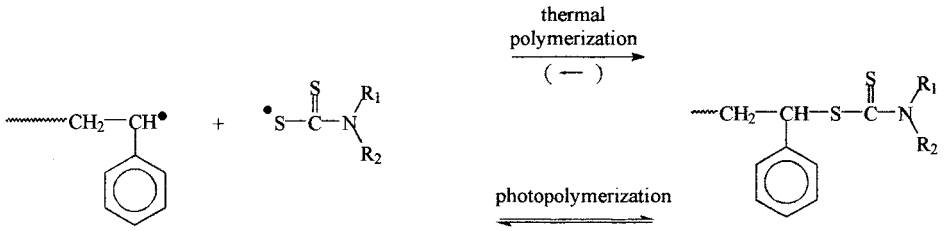
the 2-((trimethylsilyl)oxy)ethyl fragment being considered as a precursor of a 2-hydroxyethyl function. Thus, the reaction shown in the Scheme 5 may be considered as a method of functionalization of nitroxide-mediated free radical polymers. This paper deals with the study of such systems.

The samples obtained were characterized by size exclusion chromatography (SEC), matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), electrospray ionization mass spectrometry (ESI MS), liquid secondary ions mass spectrometry (LSI MS), and ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

Experimental Section

The different species studied are shown in the Chart 1. The polymers studied were nitroxide-terminated polystyrenes prepared by Hawker's method,[10] i.e., the synthesis of an alkoxyamine initiator (**1**), the 1-benzoyl-2-phenyl(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane, followed by the polymerization of styrene[11] in the presence of **1**. According to this procedure, two polystyrene samples **2a** and **2b** were prepared. The only difference between the two samples is the molar mass average (cf. Table 1).

Scheme 4. Combination of Polymer Radicals with Dithiocarbamate Radical



Scheme 5. Substitution of Nitroxide Moieties by Dithiocarbamate Groups

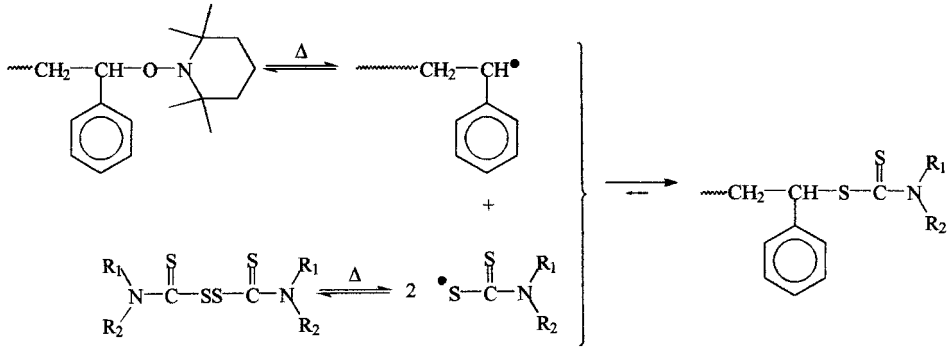


Table 1. Characterization of Nitroxide-Terminated Polymers 2a and 2b

run	[styrene]/[**1**]	monomer conversion ρ	Dpn[a] theoretical[c]	Dpn SEC	PI[b] SEC	Dpn ^{1}H NMR[d]
2a	109	0.18	20	27	1.1	25
2b	109	0.16	17	25	1.1	24

[a] Dpn: average number of the degree of polymerization. [b] PI: polydispersity. [c] Calculated as ρ[Styrene]/[**1**]. [d] Calculated from the ratio of the number of hydrogen atoms carried by both BPO−CH_2− and −CH(C_6H_5)−O−N═ fragments to C_6H_5 (BPO included).

The thiuram disulfide compounds used were tetraethyl thiuram disulfide (**3a**) and *N*,*N*′-diethyl-*N*,*N*′-bis{2-((trimethylsilyl)oxy)ethyl} thiuram disulfide (**3c**).

Materials. Commercially available styrene and benzoyl peroxide (BPO, Aldrich) were purified by standard methods. Tetraethyl thiuram disulfide (**3a**), TEMPO and trimethylsilyl chloride were purchased from Aldrich and used as received. Silica gel for flash chromatography was Merck Kieselgel 60 (70−230 mesh).

Instruments. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded in solution with a Bruker AM300 (300 MHz) spectrometer. ^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker AM300 spectrometer, using the carbon signal of the solvent as the internal standard. SEC characterizations were carried out on a Waters chromatograph connected to a multi angle LS detector (Wyatt). THF was used as the solvent. MALDI-TOF-MS experiments were conducted using a VOYAGER ELIT from Perseptive Biosystem equipped with a N_2 laser ($\lambda = 337$ nm). The matrix was made of 1,8,9-anthracenetriol containing silver trifluoroacetate. The weight concentration of the polymer was 0.1%. The spectra were recorded in linear and reflectron modes over the range m/z 800−7000. ESI MS: Polymer samples were investigated using a VG Platform from Micromass, equipped with a monoquad as the analyzer. The spectra were acquired over the range m/z 400−3000 at different cone voltages (100, 140, and 180 V). The solvent was methanol containing 2×10^{-4} mol·L^{-1} NaI or dichloromethane/methanol/formic acid mixture. LSI MS: The apparatus used was a ZAB 2 SEQ from Micromass. Ionization was obtained with Cs^+ LSI. Polymer samples were dissolved in dichloromethane, and the solvent was nitrobenzyl alcohol. Mass spectra were acquired over the range m/z 360−3600.

Synthesis

1. Preparation of the alkoxyamine initiator **1** was conducted as described by Hawker et al.[10]

Polymers Samples 2a and 2b. 1 (0.2 g, 0.5 mmol) was added to 5.95 g (57.2 mmol) of styrene. The reaction was immersed in an oil bath at 130 °C and kept under nitrogen for 2 h.

3b. The *N*,*N*′-bis(2-hydroxyethyl)-*N*,*N*′-diethyl thiuram disulfide was prepared according to a procedure described elsewhere.[12]

3c. To a solution of 3.3 g (30.48 mmol) of trimethylsilyl chloride in 5 mL of THF was added 3.1 g (30.48 mmol) of triethylamine. The solution was stirred for 10 min. Then, 5 g (15.24 mmol) of **3b** in 10 mL of THF was added dropwise. The reaction was allowed to proceed overnight. After filtration, the solvent was evaporated and the residue washed with water, dried over $MgSO_4$, and purified by flash chromatography (1:1 heptane/dichloromethane) to afford a yellow oil (m = 4.5 g, 62%).

^{1}H NMR ($CDCl_3$): δ 0.09 (s, 18H, CH_3), 1.24 (t, 3H, CH_3), 1.45 (t, 3H, CH_3), 3.92−4.14 (m, 12H, CH_2).

Study of the Substitution. Reaction between 1 and 3a (Model Compound). To a solution of **3a** [199 mg (0.67 mmol)] in 10 mL of xylene was added dropwise 330 mg (0.87 mmol) of **1** in 20 mL of xylene. The reaction was allowed to proceed for 5 h at 140 °C. After cooling, the solution was evaporated to dryness and purified by flash chromatography eluting with 2:1 heptane/dichloromethane to give **4** as a yellow oil (130 mg, 40%).

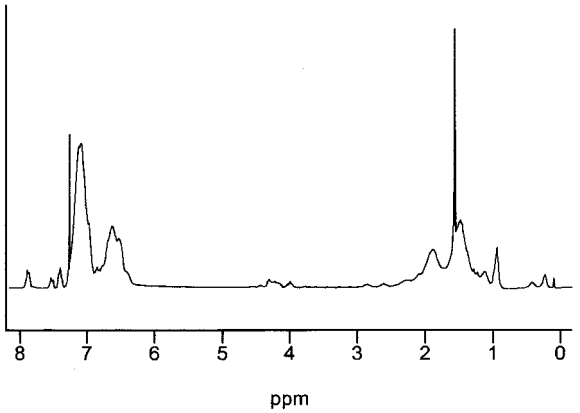


Figure 1. ^{1}H NMR spectrum of **2a**.

^{1}H NMR ($CDCl_3$): δ 1.27 (t, 6H, CH_3), 3.68−3.85 (m, 2H, CH_2), 3.90−4.15 (m, 2H, CH_2) 4.81 (d, 2H, CH_2), 5.72 (t, 1H, CH), 7.20−7.65 (m, 8H, ArH), 7.90−8.15 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ 11.58, 12.65, 46.84, 49.82, 54.12, 66.51, 126.78, 127.89, 128.34, 128.67, 128.95, 129.46, 139.99, 138.02, 166.19, 193.23.

Anal. Calcd for $C_{18}H_{23}NSO_2$: C, 68.1; H, 7.3; O, 10.1; N, 4.4; S, 10.1 Found: C, 67.5; H, 6.9; N, 4.1; O, 9.8; S, 10.3.

Reaction between 2a and 3a. To a solution of 21.1 mg (0.07 mmol) of **3a** in 10 mL of xylene was added 400 mg (0.14 mmol) of **2a** in 20 mL of xylene. The reaction was immersed in an oil bath for 20 h under a nitrogen atmosphere at 140 °C. After cooling, the solution was evaporated to dryness and the polymer **5a** was purified by precipitation (twice) in methanol and dried overnight under vacuum (m = 199 mg, 0.066 mmol, 44%).

5a: ^{1}H ($CDCl_3$) δ 1.20−2.40 (m, 85H, CH_3, CH_2, CH), 3.60−3.66 (m, 2H, CH_2N), 3.75−4.11 (m, 2H, CH_2N), 4.15−4.35 (m, 2H, CH_2O), 6.35−7.65 (m, 128H, ArH), 7.83−7.95 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 11.75, 12.63, 40.47, 41.94−46.6 (m), 55.50, 64.00, 65.05, 125.60, 125.76, 126.20, 126.57, 126.8−129.58 (m), 145.21−146.13 (m), 166.38, 194.35.

Reaction between 2b and 3c. The same procedure between **2b** and **3c** affords the polymer **5b**.

5b: ^{1}H ($CDCl_3$) δ 0.10 (s, 9H, CH_3), 1.20−2.85 (m, 65H, CH_3, CH_2, CH), 3.75−4.45 (m, 8H, CH_2N, CH_2O), 6.13−7.54 (m, 108H, ArH), 7.85−7.92 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 1.10, 29.78, 40.54−46.07 (m), 59.60, 70.50, 125.75−129.55 (m), 130.92, 132.89, 145.39, 166.35, 195.31.

Results and Discussion

Both polymer samples **2a** and **2b** were prepared according to Hawker's procedure.[10] This method was preferred to the method described by Georges et al.,[1c] i.e., the polymerization of styrene initiated by BPO in the presence of an excess of TEMPO, because of the better control of both the molar mass and polydispersities of the polystyrene formed, especially for low molar mass polystyrenes. The difference is the result of a better control allowed by Hawker's procedure at the very beginning of the polymerization that can be attributed to the "persistent radical effect" discussed by Fisher.[13] According to this author, and the studies of Gnanou et al.[14] and Hawker et al.,[15] the functionality of the formed polymer, in terms of percentage of polymer chains terminated by the alkoxyamine group, might be very close to one.

The polymer samples **2a** and **2b** have been characterized by SEC (cf. Table 1). The ^{1}H NMR spectrum of these polymers are identical to the spectra published by Hawker et al. (cf. Figure 1).

Table 2. Characterization Of Dithiocarbamate-Terminated Polymers 5a and 5b

run	polymer recovered (wt %)	Dpn[a] SEC	PI[b] SEC	Dpn ^{1}H NMR	Dpn MALDI-TOF MS
5a	44	31	1.2		
5b	31	29	1.1	29[c]	26[d]

[a] Dpn: average number of the degree of polymerization. [b] PI: polydispersity. [c] Calculated from the ratio $(CH_3)_3Si$ to C_6H_5 (BPO included). [d] Calculated from the series A in the MALDI-TOF spectrum.

SEC Analysis of Polymers 5a and 5b. Due to the slight solubility of the polymer samples into methanol, the yield of the reactions between nitroxide-terminated polystyrene and thiuram disulfides was ca. 40% in terms of weight percentage of polymer recovered. In fact, the low molar mass part of such a sample is more soluble in methanol than the high part. This behavior explains the slight increase of both the number and the weight average molar masses of **5a** and **5b** compared to **2a** and **2b,** respectively (cf. Table 2). However, such precipitation cannot be avoided because of the necessity to remove all traces of thiuram disulfide and/or nitroxide species in the recovered polymer.

The SEC trace shows only one peak. In particular, the possible formation of polymer species showing a molar mass twice the molar mass of **2a** or **2b,** as the consequence of some hypothetical recombination between the polymer radicals, can be totally excluded.

^{1}H NMR and ^{13}C NMR Analysis of 4. The ^{1}H NMR spectrum of the model compound **4** is reported in the Experimental Section. This spectrum shows clearly the disappearance of the signals located at 0.76, 1.00, 1.27 (singlet), and 1.37 ppm, respectively, attributed to the methyl groups attached to the nitroxide moiety, and the formation of signals at 3.73 and 4.0 ppm attributed to the CH_3-CH_2-N hydrogen atoms, and 1.27 ppm (triplet) attributed to the CH_3-CH_2-N hydrogen atoms, respectively, i.e., all of them being carried by the dithiocarbamate moiety.

The comparison between the ^{13}C NMR spectra of **1** and **4** shows a new signal located at 193 ppm, which has been attributed to the *C*═S carbon.

IR Analysis of 4. The comparison of the IR spectra of **1** and **4** shows many differences. The most significant is the formation of a strong sharp peak located at 1418 cm^{-1}. Such a signal, also observed in the case of **3a**, has been assigned to the C═S stretching band.

^{1}H NMR Analysis of Polymers 5a and 5b. As in the spectrum of **4**, the ^{1}H NMR diagrams of both polymers **5a** and **5b** do not show any signal that can be attributed to alkoxyamine groups. Thus, the reactions between both **2a** to **3a** and **2b** to **3c** lead to the quantitative cleavage of the nitroxide moieties.

However, in the case of the system **2a/3a** the substitution of the nitroxide group by the dithiocarbamate group is not proved, because of the lack of identification of hydrogen signals resulting from this latter group, the expected range and intensity of such signals being not favorable.

This is not the case with the system **2b/3c**. The spectrum (cf. Figure 2) shows a strong signal at δ 0.10 ppm, which can be unambiguously attributed to the nine hydrogen atoms of the trimethylsilyl group located on the dithiocarbamate moiety. Moreover, the ratio between this signal and the signals of the hydrogen atoms located on the polymer chain allows the determination of the molar mass of this polymer, which is in good agreement with the SEC characterization (cf. Table 2).

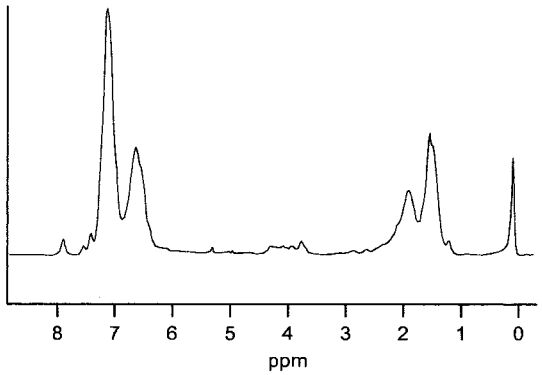


Figure 2. ^{1}H NMR spectrum of **5b**.

As in the spectrum of **4**, the ^{13}C NMR spectra of both **5a** and **5b** show a signal located at 195 ppm, being attributed to the C═S carbon.

IR Analysis of Polymers 5a and 5b. As it is the case for the model compound **4**, both the IR spectra of **5a** and **5b** show a sharp peak located at 1415 cm^{-1}, attributed to the stretching band of the C═S bond.

Discussion of NMR and IR Characterizations. In all cases (**4**, **5a**, **5b**), NMR and IR characterizations are in good agreement with the expected substitution of the nitroxide moiety by the dithiocarbamate group. However, the NMR or IR signals resulting from the dithiocarbamate fragment contained in polymers **5a** and **5b** could also be attributed to some traces of **3a** or **3c** in the recovered polymer, despite the careful precipitation of these polymer samples. For this reason, the presence of the dithiocarbamate fragment at the polymer chain end must be proved by mass spectrometry.

Mass Spectrometry. In these studies, the benzoyloxy moiety is noted BPO, the nitroxide moiety is noted TEMPO, the *N*,*N*-diethyldithiocarbamate moiety is noted NDE, and the *N*-2-((trimethylsilyl)oxy)ethyl-*N*-ethyldithiocarbamate moiety is noted NTSE, respectively.

MALDI-TOF MS. MALDI-TOF of the three products **2b**, **5a**, and **5b** were investigated in both reflectron and linear modes. The reflectron mode providing a higher flight path allows a better resolution. The spectra were surprisingly the same, offering the same distributions, although it has been proved by ^{1}H NMR that they had different structures. The weakness of the bounding between the last styrene residue of the polymer chain and the further heteroatom (O or S) is well-known, thus **2b**, **5a**, and **5b** are probably subjected to fragmentation during ionization, providing the cleavage and the loss of a fragment corresponding to the polymer chain end. This behavior has already been observed by Haddelton et al.[16] in the case of nitroxide-terminated polystyrene, i.e., **2b**.

Therefore, the MS spectra of the polymers appear similar, independent of the nature of the chemical group located at the polymer chain end. Thus, MALDI-TOF MS does not seem to be adapted to the characterization of such products, in the experimental conditions chosen. Nevertheless, three principle series have been assigned in both linear and reflectron modes, for Dp ranging from 9 to 50, as $[BPO-(sty)_n-CH=CHC_6H_5 + Ag]^+$, series A; $[BPO-(sty)_n-BPO + H]^+$, series B; $[BPO-(sty)_n-BPO + Na]^+$, series C; and $[(sty)_{n+1}-CH=CHC_6H_5 + Ag]^+$, series D, respectively. Series D corresponds to the

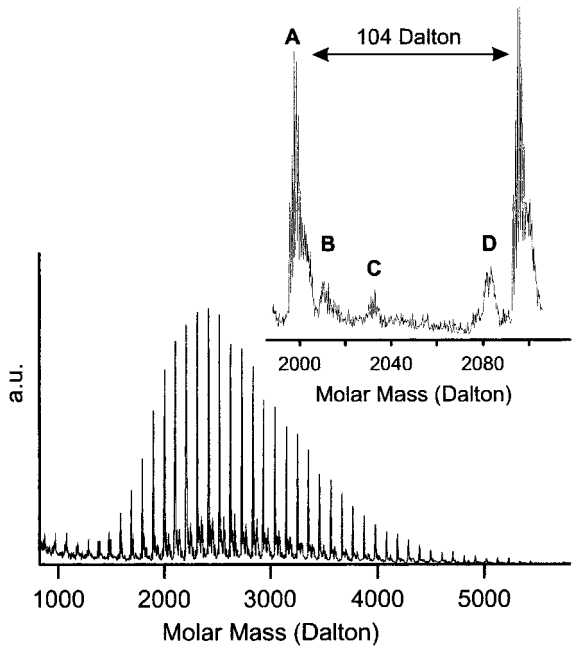


Figure 3. MALDI-TOF spectrum of polymer **5a**.

next homologue of series A but subjected to a fragmentation with a loss of 122 Da, i.e., a BPO residue. Series C is the less important series, the alkali metal ion coming probably from the glassware, and thus, its presence is variable (it is not observed in the MS spectrum of **2b**). Series A has been used to calculate the molar mass number average of the sample **5b** (cf. Table 2 and Figure 3). The molar mass average determined by MALDI is slightly lower than the values obtained by both SEC and NMR analyses. As discussed by Davis et al.,[17] the comparison between SEC and MALDI data shows that MALDI generally underestimates the high molar mass tail in a polymer distribution. The origin of these differences is very various. In the present case, the difference may be attributed to the ionization efficiency and/or the detector response at higher mass.

ESI MS. ESI MS of the samples gives results different from those obtained by MALDI-TOF MS. The spectra of the polymers are quite different, suggesting that ESI MS seems to be more adapted to the study of such samples than MALDI-TOF MS. As is known from the literature, various parameters such as solvent, nature, and concentration of added cations and cone voltage strongly influence the ionization and the desorption efficiency from the droplets.[18] The experimental conditions must be adapted to each sample. In the present study, two solvents were tried: (a) (dichloromethane/methanol 50/50 mixture with 1% formic acid) and (b) methanol with the presence of NaI (2×10^{-4} M).

2b. In a first attempt, **2b** was studied in methanol with Na^+ addition. The predominant species observed are $[BPO{-}(sty)_n{-}TEMPO]^+$, i.e., corresponding to M^+, and not MNa^+ or MH^+ as expected. The observation of M^+ is quite surprising, because of the presence of cations in the solvent, i.e., leading usually to the formation of the cationized species,[16] unless the formation of this species depends on the nature of the cations.[19] On the contrary, of some results reported by Haddelton et al.,[16] the series $[BPO{-}(sty)_n{-}CH{=}CHC_6H_5 + \text{cation}]^+$ is not observed. Thus, methanol seems not adapted to the analysis of **2b**.

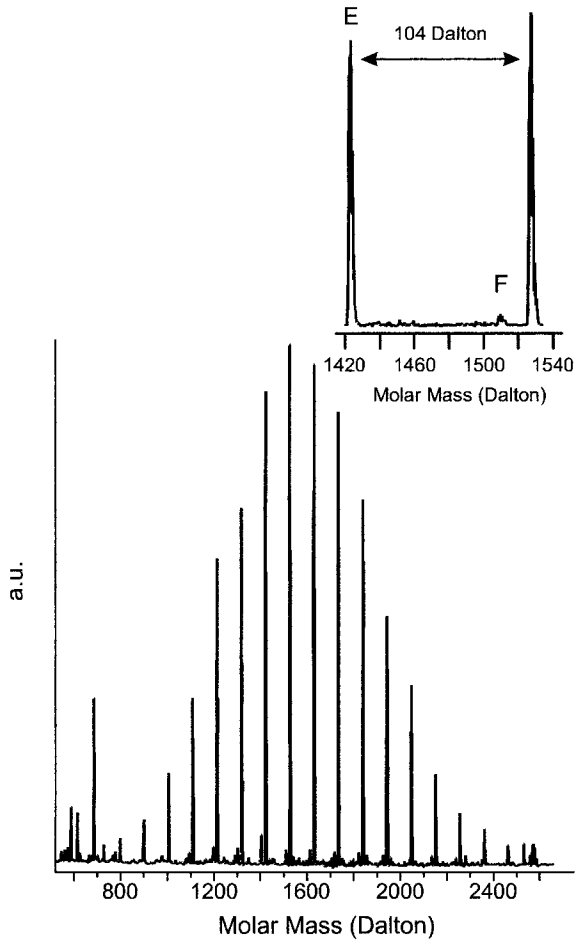


Figure 4. ESI MS spectrum of polymer **2b**.

Table 3. Comparison of Experimental versus Theoretical Mass for the ESI MS Spectrum of 2b in Dichloromethane/Methanol/Formic Acid Solvent Mixture

peak	origin	formula	theor mass (Da)	exptl mass (Da)
E	$BPO{-}(sty)_{11}{-}TEMPO, H^+$	$C_{104}H_{111}O_3N$, H	1422.8	1422.8
F	$(sty)_{13}{-}TEMPO, H^+$	$C_{113}H_{122}ON$, H	1510.0	1509.3

With the dichloromethane/methanol/formic acid solvent mixture, the expected $[BPO{-}(sty)_n{-}TEMPO, H]^+$ is observed (cf. Table 3 and Figure 4), series E, with a Dp ranging from 4 to 20 for a cone voltage of 120 V. Another minor series (series F) is observed and corresponds to $[(sty)_n{-}TEMPO, H]^+$, which corresponds to the loss of the BPO residue (122 Da). The intensity of these series slightly increases with increasing cone voltage, indicating that the series F is the product of fragmentation.[20] As already described in the literature,[18] slight modifications of the relative abundance of the various oligomers with exit capillary voltage is observed. Varying this voltage from 80 to 120 V resulted in an increase of the higher oligomers. Various hypotheses can be made to explain these changes, such as the neutralization by loss of cations though collisions in the interface, which occurs preferentially for low-mass compounds.[18]

5a. ESI MS experiments (cf. Table 4 and Figure 5) were conducted in methanol with Na^+ addition and confirm the structure of **5a**. In fact, a series (series J) with a mass distribution of 104 has been found, ranging from 1645 to 2789 Da (DP from 13 to 24), and corre-

Table 4. Comparison of Experimental versus Theoretical Mass for the ESI MS Spectrum of 5a in Methanol with Addition of NaI (2×10^{-4} M)

peak	origin	formula	theor mass (Da)	exptl mass (Da)
J	BPO—$(sty)_{17}$—NDE, Na^+	$C_{148}H_{151}O_2NS_2$, Na	2061.1	2062.5
K	BPO—$(sty)_{17}$—NDE, Na^+ loss of CH_3 and CH_2CH_3	$C_{145}H_{143}O_2NS_2$, Na	2017.0	2016.9
	BPO—$(sty)_{17}$—$TEMPO^+$	$C_{152}H_{159}O_3N$	2046.2	not observed

Table 5. Comparison of Experimental versus Theoretical Mass for the ESI MS Spectrum of 5b in Methanol with Addition of NaI (2×10^{-4} M)

peak	origin	formula	theor mass (Da)	exptl mass (Da)
G	BPO—$(sty)_{14}$—NTSE, Na^+	$C_{127}H_{135}O_3NS_2Si$, Na	1836.9	1838.1
H	BPO—$(sty)_{14}$—NTSE, Na^+ loss of CH_2CH_3	$C_{125}H_{130}O_3NS_2Si$, Na	1807.9	1809.3
I	BPO—$(sty)_{14}$—NTSE, Na^+ loss of CH_3	$C_{126}H_{132}O_3NS_2Si$, Na	1821.9	1824.0
	BPO—$(sty)_{15}$—$TEMPO^+$	$C_{136}H_{143}O_3N$	1838.1	observed?

Table 6. Comparison of Experimental versus Theoretical Mass for the LSI MS Spectrum of 2b

peak	origin	formula	theor mass (Da)	exptl mass (Da)
L	BPO—$(sty)_{18}$—TEMPO, H^+	$C_{160}H_{167}O_3N$, H	2151.3	2152.6

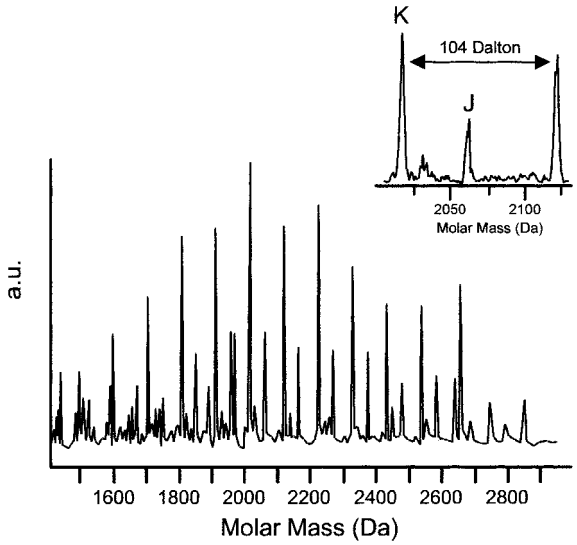


Figure 5. ESI MS spectrum of polymer **5a**.

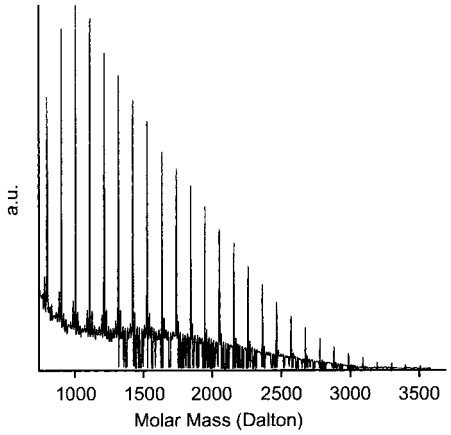


Figure 6. LSI MS spectrum of polymer **2b** (series L).

sponding to [BPO—$(sty)_n$—NDE + $Na]^+$. Another distribution is identified (series K) corresponding to a loss of 44 Da from the series J. This series increases with cone voltage and becomes predominant for high cone voltage (180 V). These observations suggest[20] that the series K is obtained by fragmentation from the series J. No peak corresponding to **2b**, i.e., M^+ in these experimental conditions, is observed, confirming the quantitative substitution expected.

5b. Unfortunately, the ESI MS of **5b** cannot prove the quantitative substitution of the nitroxide moiety. For example, the species [BPO—$(sty)_{14}$—NTSE + $Na]^+$, whose theoretical mass is expected at 1836.9 Da, is observed at 1838.1 Da (cf. Table 5). However, this value corresponds also to the theoretical molecular mass of **2b** with a DP equal to 15, i.e., M^+ in the experimental conditions. Thus, due to the bad resolution of this experiment, no conclusion about the structure of **5b** is obtained by ESI MS, even if the quantitative substitution has been proved by ^1H NMR.

For the three compounds **2b**, **5a**, and **5b** studied in methanol with Na^+ addition, at low *m*/*z*, two other series with mass distributions of 150 and 82 Da, peculiarly abundant as cone voltage is decreased, are attributed to the presence of traces of some contaminant during the sample preparation, because they do not appear on the spectrum of **2b** in the dichloromethane/methanol/formic acid solvent mixture.

Thus, ESI MS experiments confirm the structure of the compounds **2b** and **5a**, showing the role of experimental factors such as the nature of the solvent and the cone voltage.

LSI MS. 2b. In this case, the protonated species [BPO—$(sty)_n$—TEMPO + $H]^+$ were observed, with the presence of minor series, confirming the correct structure of the polymer (cf. Table 6 and Figure 6).

5a and 5b. In both cases, the protonated species [BPO—$(sty)_n$—NDE + $H]^+$ and [BPO—$(sty)_n$—NTSE + $H]^+$, respectively, were observed. These results confirm the expected structure of the polymer, with the presence of minor series (cf. Tables 7 and 8 and Figures 7 and 8).

Discussion of MS Characterizations. The particular behavior of **2b, 5a, and 5b** in MALDI-TOF has to be noted. This behavior seems to be attributed to the weakness of the C—O and C—S bonds, respectively, between the polymer and both the nitroxide and the dithiocarbamate chain end. ESI MS spectra are compatible with the expected structure of the three compounds and show the influence of the experimental conditions on the ionization efficiency. Finally, LSI MS appears to be adapted to the study of the structure of

Table 7. Comparison of Experimental versus Theoretical Mass for the LSI MS Spectrum of 5a

peak	origin	formula	theor mass (Da)	exptl mass (Da)
M	BPO—$(sty)_{18}$—NDE, H^+	$C_{156}H_{159}O_2NS_2$, H	2143.2	2144.7
N	?			2160.1
O	BPO—$(sty)_{19}$—NDE, H^+ loss of CH_2CH_3	$C_{162}H_{162}O_2NS_2$, H	2218.2	2219.0
P	BPO—$(sty)_{19}$—NDE, H^+ loss of CH_3	$C_{163}H_{164}O_2NS_2$, H	2232.2	2232.7
(L)	BPO—$(sty)_{18}$—TEMPO, H^+	$C_{160}H_{167}O_3N$, H	2151.3	not observed

Table 8. Comparison of Experimental versus Theoretical Mass for the LSI MS Spectrum of 5b

peak	origin	formula	theor mass (Da)	exptl mass (Da)
Q	BPO—$(sty)_{19}$—NTSE, H^+	$C_{167}H_{175}O_3NS_2Si$, H	2335.3	2337.0
R	BPO—$(sty)_{20}$—NTSE, H^+ loss of $OSi(CH_3)_3$	$C_{172}H_{174}O_2NS_2$, H	2350.3	2353.5
S	?			2367.9
T	?			2384.0
U	BPO—$(sty)_{20}$—NTSE, H^+ loss of CH_3	$C_{174}H_{180}O_3NS_2Si$, H	2424.3	2425.9
(L)	BPO—$(sty)_{20}$—TEMPO, H^+	$C_{176}H_{183}O_3N$, H	2359.4	not observed

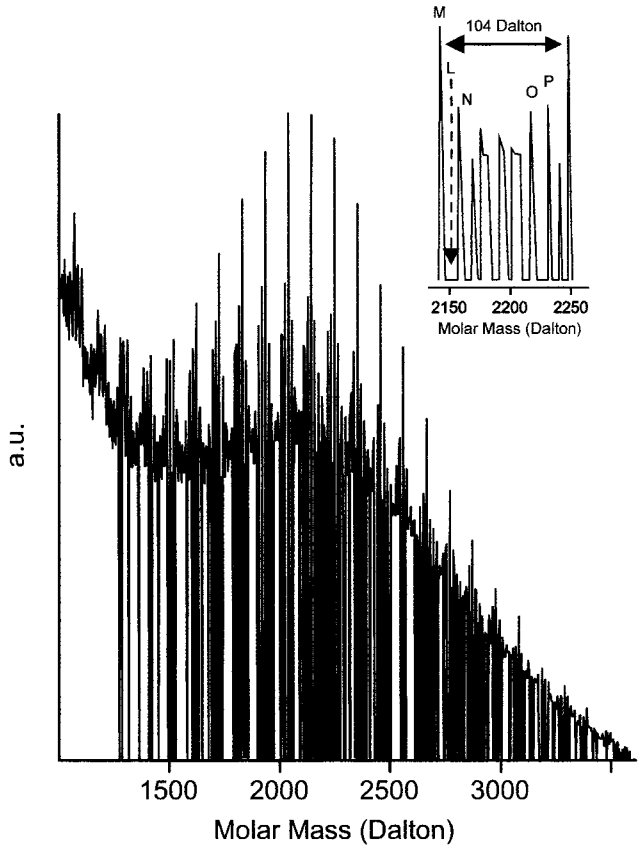


Figure 7. LSI MS spectrum of polymer **5a**.

such polymers, although some fragmentations occur. The pathways of these fragmentations have not yet been explained.

However, the expected structures of the polymer samples, i.e., resulting from the substitution of the nitroxide group by a dithiocarbamate fragment have been clearly identified. Moreover, the spectra of both **5a** and **5b** did not show any peaks that can be attributed to **2b** (or **2a**); i.e., such a substitution seems to be quantitative (cf. Figures 7 and 8). As expected in the Introduction, whatever the rate of dissociation of the C—S bond between the polymer backbone and the dithiocarbamate moiety, it is low enough compared to the dissociation rate of the C—O bond of the alkoxyamine group to be neglected.

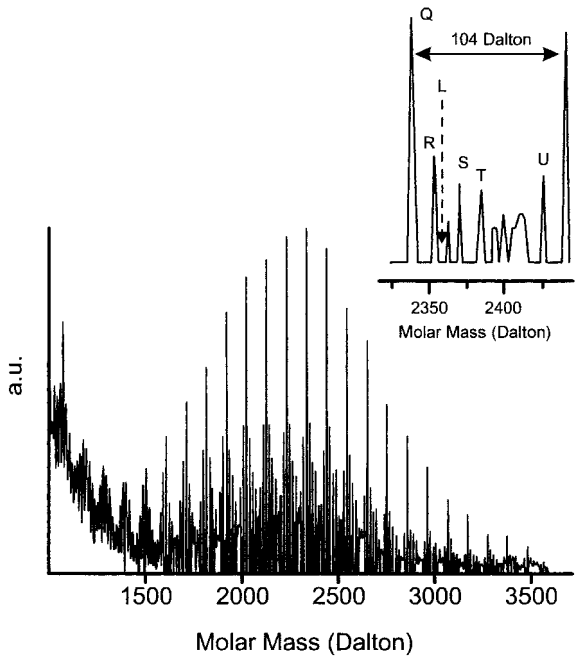


Figure 8. LSI MS spectrum of polymer **5b**.

Conclusion

The reaction of nitroxide-terminated polymers with thiuram disulfide compounds leads to the quantitative substitution of the nitroxide moiety by a dithiocarbamate group. This substitution can be shown by ^1H NMR and IR spectroscopy and clearly identified by LSI MS, which appears to be the best MS method for the characterization of polymers bearing chain end functional groups linked to the polymer chain by both C—O or C—S bonds.

This type of reaction can be considered as a new method for the functionalization of polymers, in the way that any functional group linked to the N atom of the thiuram disulfide compound is linked to the polymer chain end after the substitution. However, the functionalization discussed in the present article is of little practical interest because of the possible direct synthesis of dithiocarbamate-terminated polymers by "living" photopolymerization. Other chemical species with the same reaction pattern, but leading to the formation of more interesting functional polymers, are presently under investigation.

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