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A Multidisciplinary Approach to the Use of Pyridinyl Dithioesters and Their *N*-Oxides as CTAs in the RAFT Polymerization of Styrene. Not the Chronicle of a Failure Foretold

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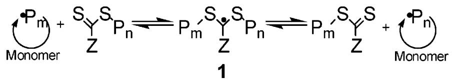
ABSTRACT: The efficiency of three isomeric pyridinyl dithioesters and their *N*-oxides as chain transfer agents in the RAFT (reversible addition fragmentation chain transfer) polymerization of styrene was tested. *Ortho* (dithiopicolinates), *meta* (ditionicotinates), and *para* (dithioisonicotinates) isomers controlled the polymerization of styrene although with some retardation with respect to dithiobenzoates. The retardation, which was even greater for the *N*-oxides, was attributed to excessive stabilization of the dormant radical species intermediate in the RAFT process by the heteroaromatic rings as inferred from the measured reduction potentials of the compounds. Styrene polymerization was actually blocked at very low conversion in the case of the dithioisonicotinate *N*-oxide, and on the basis of ESR (electron spin resonance) studies it is suggested that in this case the dormant radical may actually act as a scavenger of the propagating radical. Although the knowledge beforehand of the reduction potential of a given CTA (chain transfer agent), from which the stability of the dormant radical it would form during the RAFT process could be estimated, might in principle allow one to foretell its performance, such predictions must be considered with caution.

Introduction

Reversible addition fragmentation chain transfer (RAFT) polymerization based on the use of dithioesters ZC(S)SR as chain transfer agents (CTAs) has recently emerged as one of the most promising controlled radical polymerization processes because of its versatility, as it can handle the presence of a variety of different functional monomers and it requires relatively mild operating conditions.[1−5] The key steps of the RAFT process as shown in Scheme 1 are the thiophilic addition of the propagating radical to the thiocarbonyl group of the dithioester and the fragmentation of the sulfur−carbon bond of the resulting spin adduct to restitute a dithioester and a propagating radical.

Scheme 1



For the RAFT process to be efficient, the R residue of the CTA must be a good leaving group, e.g. 2-cyanoprop-2-yl, cumyl, benzyl;[6] besides, the spin adduct **1** must be a relatively stable radical, its formation, i.e. the addition of the propagating radical to the dithioester, being competitive with propagation.[7,8] On the other hand, an excessive stability of **1** would result in a slow fragmentation reaction and hence in an undesired retardation of the polymerization.[9−12] The stability of the spin adduct **1** is therefore critical for the efficiency of the RAFT process and can be modulated by changing the nature of the residue Z. Indeed, electron-withdrawing Z groups make radicals **1** longer-lived due to the captodative effect, i.e. stabilization due to the simultaneous presence of electron-donating and electron-accepting substituents bound to the radical center,[13,14] whereas the radical stabilization effect of lone pair donors Z groups is reduced. It was recently demonstrated that, in RAFT radicals, Z groups that are strong lone pair donors and weak sigma acceptors (such as $-NR_2$) remain as neat radical stabilizing substituents, but those that are weaker lone pair donors and stronger sigma acceptors (such as −OR) have a negligible radical stabilization effect and (in some cases) even a destabilizing effect, due to their sigma withdrawing properties.[15] A Z phenyl group is sufficient to stabilize radicals **1**, so that tertiary dithiobenzoates are good CTAs in the polymerization of MMA or styrene.[1,2] A similar, actually slightly stronger stabilizing effect is exerted by the phosphoryl group of phosphoryl dithioformates [$(EtO)_2P(O)C(S)SR$] that have also been successfully exploited as controlling agents in the polymerization of styrene.[16] In addition, phosphoryl dithioformates proved particularly useful for ESR studies of the polymerization process.[17]

Following the recent report of the synthesis of the previously unknown *N*-oxides of some pyridinyl dithioesters,[18] we were prompted to investigate whether the electron-withdrawing effect of the heteroaromatic ring might render these compounds susceptible of being good CTAs. We report here on the polymerization controlling

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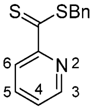
ability of benzyl 2-dithiopicolinate (**2**), benzyl dithionicotinate (**3**), benzyl dithioisonicotinate (**4**), and of their corresponding *N*-oxides (**5**−**7**). We also report on the redox properties of compounds **2**−**7**, of methyl 2-dithiopicolinate (**8**), and of methyl dithioisonicotinate *N*-oxide (**9**) that have been investigated for the sake of comparison as well as on the ESR characterization of their radical anions and of some spin adducts modeling the radical species involved in the RAFT polymerization process.



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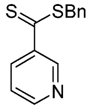

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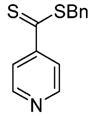

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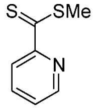

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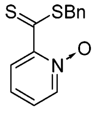

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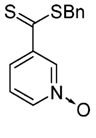

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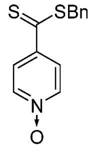

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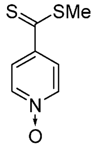

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Experimental Section

Materials and Methods. α,α-Azoisobutyronitrile (Fluka, 98%), benzyl bromide (Aldrich, 98%), bromomethane (Aldrich, 99.5%), copper(I) bromide (Aldrich), dimethylmercury (Aldrich, 95%), 4,4′-dinonyl-2,2′-dipyridyl (Aldrich, 97%), di-*tert*-butyl peroxide (BPO, Fluka, 95%), manganese(0) carbonyl (Aldrich, 98%), tetrabutylammonium perchlorate (Fluka, >99%), tetrabutylammonium tetrafluoroborate (Fluka, >99%), triphenylgermanium hydride (Aldrich), and tris(trimethylsilyl)silane (Aldrich, 97%) were commercially available. Styrene (99%) was purchased from Aldrich and washed with 3 × 100 mL of 2.0 M sodium hydroxide and 3 × 100 mL of water, dried with anhydrous sodium sulfate, stored at 5 °C, and eventually distilled under vacuum prior to use. Compounds **8** and **9** were prepared as previously described.[18] Acetonitrile (ACN), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), tetrahydrofuran (THF), and all other solvents (Aldrich) were dried and distilled as necessary.

The reactions were monitored by TLC (thin layer chromatography) using silica plates. The products were purified by flash chromatography and crystallized when needed. NMR spectra were recorded with a Bruker DPX250 spectrometer (^{1}H, 250 MHz; ^{13}C, 62.9 MHz) using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. High-resolution mass spectra were recorded with a QTOF Micro Waters spectrometer in the positive-ion electrospray-ionization mode.

Synthesis of Dithioesters. Compounds **2**−**7** were synthesized according to a general procedure whereby potassium *tert*-butoxide was added to a mixture of the appropriate benzenesulfonylmethylpyridine[19−21] or benzenesulfonylmethylpyridine *N*-oxide[22] and elemental sulfur in THF. The resulting reaction mixture was further reacted with benzyl bromide and eventually chromatographed on silica gel. Upon removal of the solvent, the pure dithioesters **2**−**7** were isolated.

Benzyl 2-Dithiopicolinate, 2. Potassium *tert*-butoxide (3.36 g, 30 mmol) was added under stirring to a mixture of 2-benzenesulfonylmethylpyridine (2.33 g, 10 mmol) and elemental sulfur (0.96 g, 30 mmol) in THF (100 mL). During the addition the color of the mixture changed to dark brown. After stirring the reaction mixture up to 12 h benzyl bromide (5.13 g, 30 mmol) was added dropwise, and stirring continued for 1 h. The solvent was then removed under reduced pressure; the residue was dissolved in methylene chloride (10 mL) and chromatographed on silica gel. Upon removal of the solvent, the pure dithioester **2** was isolated. Dark red solid, mp 35 °C. Yield 88%. ^{1}H NMR (CDCl$_3$): δ = 4.54 (s, 2H, SC**H**$_2$), 7.18−7.47 (m, 6H, C$_6$**H**$_5$ + C**H**^{Py}), 7.78 (td, 1H, *J* = 9.5, *J* = 1.6, C**H**^{Py}), 8.33 (d, 1H, *J* = 8.1, C**H**^{Py}), 8.59 (dt, 1H, *J* = 4.6, *J* = 0.7, C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 41.6 (S**C**H$_2$), 122.2, 126.8, 127.6, 2 × 128.6, 2 × 129.4, 135.0, 136.9, 147.9, 156.4 (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 226.1 (**C**═S). HRMS: (MH$^+$) calcd 246.0411, found 246.0393.

Benzyl Dithionicotinate, 3. Pink solid, mp 29 °C. Yield 91%. ^{1}H NMR (CDCl$_3$): δ = 4.67 (s, 2H, SC**H**$_2$), 7.08−7.67 (m, 6H, C$_6$**H**$_5$ + C**H**^{Py}), 8.22 (dt, 1H, *J* = 8.0, *J* = 2.0, C**H**^{Py}), 8.73 (dd, 1H, *J* = 4.8, *J* = 1.4, C**H**^{Py}), 9.16 (d, 1H, *J* = 2.1, C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 42.4 (S**C**H$_2$), 123.1, 127.9, 2 × 128.2, 2 × 129.3, 134.2, 134.4, 140.1, 147.0, 152.7 (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 224.1 (**C**═S). HRMS: (MH$^+$) calcd 246.0411, found 246.0400.

Benzyl Dithioisonicotinate, 4. Red paste. Yield 89%. ^{1}H NMR (CDCl$_3$): δ = 4.56 (s, 2H, SC**H**$_2$), 7.18−7.34 (m, 5H, C$_6$**H**$_5$), 7.70 (d, 2H, *J* = 6.1, C**H**^{Py}), 8.65 (d, 2H, *J* = 6.1, C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 42.3 (S**C**H$_2$), 2 × 120.1, 128.0, 2 × 128.8, 2 × 129.3, 134.2, 150.0, 2 × 150.4, (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 224.9 (**C**═S). HRMS: (MH$^+$) calcd 246.0411, found 246.0396.

Benzyl 2-Dithiopicolinate *N*-Oxide, 5. Potassium *tert*-butoxide (3.36 g, 30 mmol) was added under stirring to a mixture of 2-benzenesulfonylmethylpyridine *N*-oxide[22] (2.49 g, 10 mmol) and elemental sulfur (0.96 g, 30 mmol) in THF (100 mL). During the addition the color of the mixture changed to dark brown. After stirring the reaction mixture up to 12 h benzyl bromide (5.13 g, 30 mmol) was added dropwise, and stirring continued for 1 h. The solvent was then removed under reduced pressure, and the residue was dissolved in methylene chloride (10 mL) and chromatographed on silica gel. Upon removal of the solvent, the pure dithioester **5** was isolated. Dark red paste. Yield 84%. ^{1}H NMR (CDCl$_3$): δ = 4.51 (s, 2H, SC**H**$_2$), 7.15−7.40 (m, 7H, C$_6$**H**$_5$ + 2 × C**H**^{Py}), 8.08 (m, 1H, C**H**^{Py}), 8.21 (m, 1H, C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 43.9 (S**C**H$_2$), 125.6, 126.9, 128.1, 128.5, 2 × 129.1, 2 × 129.9, 134.6, 140.5, 149.4 (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 216.8 (**C**═S). HRMS: (MH$^+$) calcd 262.0360, found 262.0349.

Benzyl Dithionicotinate *N*-Oxide, 6. Dark pink solid, mp 64 °C. Yield 95%. ^{1}H NMR (CDCl$_3$): δ = 4.59 (s, 2H, SC**H**$_2$), 7.22−7.35 (m, 6H, C$_6$**H**$_5$ + C**H**^{Py}), 7.78 (d, 1H, *J* = 8.1, C**H**^{Py}), 8.30 (d, 1H, *J* = 6.4, C**H**^{Py}), 8.77 (s, 1H, C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 42.4 (S**C**H$_2$), 123.6, 125.4, 126.9, 128.2, 2 × 128.9, 2 × 129.3, 133.8, 137.2, 141.0, 142.8 (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 219.5 (**C**═S). HRMS: (MH$^+$) calcd 262.0360, found 262.0341.

Benzyl Dithioisonicotinate *N*-Oxide, 7. Dark red solid, mp 57 °C. Yield 74%. ^{1}H NMR (CDCl$_3$): δ = 4.59 (s, 2H, SC**H**$_2$), 7.18−7.38 (m, 5H, C$_6$**H**$_5$), 7.93 (d, 2H, *J* = 7.4, 2 × C**H**^{Py}), 8.13 (d, 2H, *J* = 7.4, 2 × C**H**^{Py}). ^{13}C NMR (CDCl$_3$): δ = 42.3 (S**C**H$_2$), 2 × 123.3, 128.1, 2 × 128.8, 2 × 129.3, 2 × 134.1, 138.8, 138.9 (**C**$_6$H$_5$ + **C**$_5$H$_4$N), 219.3 (**C**═S). HRMS: (MNa$^+$) calcd 284.0180, found 284.0161.

Synthesis of Polystyryl Bromide. A solution comprising styrene (5.68 mL, 49.0 mmol), copper(I) bromide (70.6 mg, 0.53 mmol), 4,4′-dinonyl-2,2′-dipyridyl (403.6 mg, 1 mmol), and 1-phenylethyl bromide (0.34 mL, 2.5 mmol) was prepared and transferred to an ampule that was subsequently degassed by three freeze−evacuate−thaw cycles, sealed, and heated at 110 °C for 7 h in a thermostated oil bath. The conversion was estimated to be 67.7% through a comparison of the integrals of the NMR doublets centered at 5.35 and 5.75 ppm (2H, PhCH═C**H**$_2$) and at 6.4−7.4 ppm (5H, **Ph**CH═CH$_2$). The solution was diluted in chloroform, precipitated in methanol, and filtered. Gel permeation chromatography (GPC) analysis gave M_n 1205 and M_w/M_n 1.1.

Electrochemistry. All the cyclic voltammetry experiments were carried out at 20 ± 1 °C in ACN using tetrabutylammonium tetrafluoroborate as supporting electrolyte in a water thermostated cell. The working electrode was either a gold−platinum or a glassy carbon disk (φ = 1 mm) and was carefully polished before each set of voltammograms with a 1 μm diamond paste and ultrasonically rinsed in absolute ethanol. Similar electrochemical patterns were obtained in either case, indicating that the reduction processes were not considerably dependent on the nature of the electrode. The electrochemical instrumentation consisted of a Tacussel GSTP4 programmer and a home-built potentiostat equipped with a positive feedback compensative device.[23] The data were acquired with a

Table 1. Formal Potentials ($E°$) of 2−9 and Some Reference Compounds in Acetonitrile vs SCE (Saturated Calomel electrode)

compd	$E°$/V	lifetime/s	compd	$E°$/V	ref
2	−1.140	0.1−0.3			
3	−1.150	0.4−0.7	MeC(S)SMe	∼−1.65	32
4	−1.018	>20	$(EtO)_2P(O)CH_2C(S)$-SMe	−1.64	33
5	−1.008	0.1−0.2	PhC(S)SMe	−1.32	34
6	−1.005	0.1−0.2	$(EtO)_2P(O)C(S)SMe$	−1.10	35
7	−0.927	10−20	$(EtO)_2P(S)C(S)SMe$	−1.04	35
8	−1.186	5−10	MeO(O)CC(S)SMe	−0.88	36
9	−0.987	>20			

310 Nicolet oscilloscope. The counter electrode was a Pt wire and the reference electrode an aqueous saturated calomel electrode (SCE) with a salt bridge containing the supporting electrolyte. The SCE was checked against the ferrocene/ferricinium couple (considering a formal potential $E° = +0.45$ V/SCE in ACN) before and after each experiment. On the basis of repetitive measurements, absolute errors on potentials were found to be ca. ±10 mV.

ESR Experiments. ESR spectra were recorded with an upgraded Bruker ER200D/ESP300 spectrometer equipped with a dedicated data station for the acquisition and manipulation of the spectra, a standard variable temperature device, a NMR gaussmeter for the calibration of the magnetic field, and a frequency counter for the determination of g-factors that were corrected with respect to that of perylene radical cation in concentrated sulfuric acid. Computer simulations of the spectra were obtained using a software[24] based on a Monte Carlo minimization procedure.

The radical anions from **2**−**9** were obtained either by reduction of the appropriate compound with potassium *tert*-butoxide (^{t}BuOK) in DMSO or by electrochemical reduction. This was carried out using an Amel Instruments 2051 potentiostat and a flat cell (50 × 9.5 × 1.5 mm) inserted inside the cavity of the ESR spectrometer and equipped with a platinum gauze (cathode) and a platinum wire (anode). In these experiments the dithioesters (ca. 10^{-2} M) were dissolved in dry DMSO or ACN containing $^nBu_4NClO_4$ (10^{-1} M) as supporting electrolyte.

In a typical experiment of radical addition, a Suprasil quartz tube (i.d. 4 mm) containing a thoroughly argon purged benzene or *tert*-butylbenzene solution of dithioester **7** or **9** (ca. 10^{-3} M), and the appropriate radical precursors were irradiated with the light from a 1 kW high-pressure mercury lamp inside the cavity of the ESR spectrometer and, when necessary, heated. Methyl and benzyl radicals were obtained by thermolysis or photolysis of dimethylmercury or by photolysis of methyl or benzyl iodide in the presence of manganese(0) carbonyl. The polystyryl radical was similarly obtained by photolysis of the corresponding bromide in the presence of manganese(0) carbonyl. Silyl and germyl radicals where instead generated by photolysis of the corresponding organometallic hydride in the presence of di-*tert*-butyl peroxide.

RAFT Polymerization of Styrene. A master batch of 20 mL (175 mmol) of styrene, 5.6 mg (34.1 μmol) of AIBN, and 45.6 mg (0.186 mmol) of **2**−**4** or 48.8 mg (0.186 mmol) of **5**−**7** was prepared, and aliquots of 3 mL were placed in polymerization ampules. The ampules were degassed by freeze and thaw cycles, sealed under nitrogen, and heated at the appropriate temperature. At the end of the reaction, each ampule was quenched in cold water and the reaction mixture diluted with methylene chloride. The polymer was then precipitated into methanol, washed with methanol, and purified by precipitation from methylene chloride into methanol. The polymer was dried on silica gel in vacuo for several hours. Conversion of styrene was estimated by weighting the obtained polymer. Several polystyrene samples were synthesized this way performing the polymerizations at either 60 or 80 °C for different reaction times. As a typical example, 3.0 mL (26 mmol) of styrene were reacted with 6.84 mg (28 μmol) of **4** and 0.85 mg (5.1 μmol) of AIBN at 60 °C for 30 h, giving sample **4/2** (see Table 4) with a yield of 7.6%. Number-average molar mass and polydispersity index resulted in $M_n = 17\,300$ and $M_w/M_n = 1.37$. As a further example, 3.0 mL (26 mmol) of styrene was reacted with 7.32 mg (28 μmol) of **7** and 0.85 mg (5.1 μmol) of AIBN at 60 °C for 30 h, giving sample **7/1** (see Table 5) with a yield of 1.0%. Number-average molar mass and polydispersity index resulted in $M_n = 5900$ and $M_w/M_n = 1.21$.

DFT (Density Functional Theory) Calculations. DFT calculations employing the B3LYP functional[25,26] were carried out to compute the hyperfine splitting (hfs) constants of the radical species $\mathbf{4}^{\bullet-}$, $\mathbf{9}^{\bullet-}$, **11**, **21**, and **22** using the GAUSSIAN98 system of programs.[27] Unrestricted wave functions were used to describe radical species. Geometries and hfs constants were obtained employing a valence double-ζ basis set supplemented with standard polarization[28,29] and diffuse[29,30] functions on heavy atoms (6-31+G*). At this level of theory the radical anions $\mathbf{4}^{\bullet-}$ and $\mathbf{9}^{\bullet-}$ were computed to be thermodynamically stable with respect to electron loss while the radical dianions **21** and **22** were computed to be not only thermodynamically but also kinetically unstable. However, addition of standard diffuse functions to heavy atoms to better describe the negatively charged species provides reliable results in this particular case (delocalized π dianion radicals) since inspection of the electronic distribution in the singly occupied MO shows that the diffuse atomic functions are less populated than the valence atomic functions. That is, the wave function does not describe an anion interacting with a free electron.[31]

Results

Electrochemical Reduction. The electrochemical behavior of compounds **2**−**9** was investigated by cyclic voltammetry (CV). The reduction of **4**, **7**, **8**, and **9** was a monoelectronic process reversible at any potential scan rate, resulting in the formation of the radical anions $\mathbf{4}^{\bullet-}$, $\mathbf{7}^{\bullet-}$, $\mathbf{8}^{\bullet-}$, and $\mathbf{9}^{\bullet-}$. As for the other derivatives, the reduction process, also monoelectronic, depended on the scan rate (v) being reversible at $v > 1$ V s^{-1} (**2** and **6**), $v > 2$ V s^{-1} (**5**), and $v > 10$ V s^{-1} (**3**). From these scan rates the lifetime of the different radical anions could be estimated (see Table 1). These are very persistent species, with lifetimes ranging from some tenths of a second for *ortho* and *meta* derivatives to over 10 s for the *para* isomers, their chemical stability not being affected when replacing a methyl for a benzyl group or when switching from pyridine derivatives to the corresponding *N*-oxides. The reduction potentials

Table 2. ESR Hyperfine Splitting Constants (a) and g Factors (g) for Radical Anions Obtained by Reduction of Compounds 2−9[a]

compd	solvent	a_2	a_3	a_4	a_5	a_6	a_X	g
2	acetonitrile	0.148 (1N)	0.101	0.673	0.054	0.234	0.093 (2H)	2.0076_3
3	dimethyl sulfoxide	0.413	0.124 (1N)	0.580	0.099	0.282	n.r.[b]	2.0074_9
4	acetonitrile	0.305	0.048	0.272 (1N)	0.048	0.305	0.044 (2H)	2.0081_1
5	hexamethylphosphoramide	0.394 (1N)	0.107	0.883	0.141	0.455	0.315 (1H + 1H)	2.0074_3
6	dimethyl sulfoxide	0.398	0.172 (1N)	0.620	0.070	0.269	n.r.[b]	2.0075_8
7	dimethyl sulfoxide	0.335	0.115	0.496 (1N)	0.115	0.335	0.055 (2H)	2.0079_1
8	acetonitrile	0.140 (1N)	0.089	0.670	0.050	0.233	0.154 (3H)	2.0079_3
9	dimethyl sulfoxide	0.329	0.107	0.513 (1N)	0.107	0.329	0.114 (3H)	2.0081_1

[a] Hyperfine splitting constants in mT. [b] Not resolved.

Table 3. ESR Hyperfine Splitting Constants (*a*) and *g* Factors (*g*) for Radical Adducts to Compounds 7 and 9 at Room Temperature in Benzene[a]

compound/radical	spin adduct	$a_{2,6}$	$a_{3,5}$	a_4	a_X	a_Y	g
7/Me	**10**	0.385	0.180	0.394 (1N)	0.112 (2H)	0.109 (3H)	2.0052_4
7/CH_2Ph	**11**	0.388	0.177	0.395 (1N)	0.033 (2H)	0.033 (2H)	2.0049_9
7/$Si(SiMe_3)_3$	**12**	0.398	0.178	0.408 (1N)	n.r.[b]		2.0053_2
7/$GePh_3$	**13**	0.375	0.170	0.400 (1N)	n.r.		2.0052_9
7/polystyryl	**14**	0.384	0.179	0.395 (1N)	0.054 (2H)	n.r.	2.0050_9
9/Me	**15**	0.384	0.168	0.402 (1N)	0.089 (3H)	0.089 (3H)	2.0050_3
9/CH_2Ph	**16**	0.384	0.179	0.397 (1N)	0.113 (3H)	0.112 (2H)	2.0052_5
9/$Si(SiMe_3)_3$	**17**	0.396	0.173	0.402 (1N)	0.094 (3H)		2.0041_6
9/$GePh_3$	**18**	0.392	0.180	0.395 (1N)	0.129 (3H)		2.0041_7
9/polystyryl	**19**	0.386	0.173	0.395 (1N)	≤0.040 (3H)		2.0047_9

[a] Hyperfine splitting constants in mT. [b] Not resolved.

Table 4. Molar Mass, Polydispersity Index, and Conversion Data for Polystyrene Samples Prepared via AIBN-Initiated Polymerization of Styrene with Dithioesters 2−4

dithioester/ sample	T/°C	time/h	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	conv/%
2/1	60	14	15.0	17.6	1.17	6.9
2/2	60	20	18.4	23.1	1.25	7.8
2/3	60	30	25.7	34.6	1.34	14.1
2/4	60	40	36.5	49.5	1.35	16.0
2/5	80	4	20.8	26.7	1.28	11.7
2/6	80	8	21.4	27.9	1.30	14.8
2/7	80	14	28.4	39.6	1.39	22.4
2/8	80	20	32.9	50.1	1.50	20.9
2/9	80	30	34.0	49.1	1.40	24.4
3/1	60	14	9.5	11.1	1.15	6.4
3/2	60	20	14.1	16.5	1.17	10.6
3/3	60	30	24.3	33.7	1.38	14.2
3/4	60	40	32.3	49.3	1.52	23.3
3/5	80	4	13.7	16.5	1.20	10.5
3/6	80	8	20.1	24.1	1.19	17.2
3/7	80	14	23.2	28.3	1.21	20.6
3/8	80	20	30.3	39.9	1.31	24.8
3/9	80	30	36.6	49.4	1.35	28.9
3/10	80	40	39.2	64.1	1.63	32.5
4/1	60	14	6.3	8.1	1.27	1.0
4/2	60	30	17.3	23.8	1.37	7.6
4/3	60	40	25.3	37.4	1.40	10.6
4/4	60	65	41.8	69.8	1.60	14.3
4/5	80	4	18.9	22.7	1.20	7.8
4/6	80	8	19.8	25.8	1.30	8.7
4/7	80	14	22.9	31.8	1.39	10.7
4/8	80	20	24.8	35.2	1.42	13.4
4/9	80	30	30.1	42.1	1.4	15.6

Table 5. Molar Mass, Polydispersity Index, and Conversion Data for Polystyrene Samples Prepared via AIBN-Initiated Polymerization of Styrene with Dithioesters 5−7

dithioester/ sample	T/°C	time/h	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	conv/%
5/1	60	20	8.2	13.0	1.58	1.5
5/2	60	30	16.0	24.0	1.50	4.3
5/3	60	41	22.9	41.4	1.80	6.9
5/4	60	60	30.0	58.0	1.90	11.5
5/5	80	4	10.5	22.2	2.00	5.0
5/6	80	8	17.0	33.0	1.90	7.0
5/7	80	14	20.5	38.8	1.89	11.3
5/8	80	20	37.8	51.1	1.80	13.0
5/9	80	30	33.6	76.8	2.20	17.4
5/10	80	40	41.4	86.0	2.00	18.6
6/1	60	30	15.9	21.6	1.35	4.8
6/2	60	40	20.1	31.5	1.56	5.7
6/3	60	65	28.5	48.5	1.70	9.0
6/4	60	105	72.3	125.0	1.72	19.9
6/5	80	4	6.3	8.0	1.28	1.0
6/6	80	8	11.8	16.2	1.37	6.0
6/7	80	14	13.5	19.3	1.42	7.9
6/8	80	20	25.8	43.1	1.67	10.9
6/9	80	40	44.5	98.7	2.20	22.7
7/1	60	30	5.9	7.0	1.21	1.0
7/2	60	40	9.6	12.6	1.30	1.5
7/3	60	65	15.0	21.7	1.40	2.2
7/4	60	105	42.6	70.0	1.64	9.0
7/5	80	4	4.6	6.0	1.27	1.1
7/6	80	8	9.1	11.3	1.24	1.5
7/7	80	14	12.1	17.3	1.42	5.2
7/8	80	20	21.9	33.0	1.50	7.3
7/9	80	30	28.3	44.3	1.56	10.5
7/10	80	40	33.7	81.6	2.00	20.6

determined for the different compounds are collected in Table 1 along with those reported in the literature for some reference derivatives. Although for some of the compounds additional reduction waves were detected at more negative potentials, the full electrochemical behavior of compounds **2**−**9** was not investigated as only their first reduction potential values (that is, the potentials corresponding to the formation of their radical anions) were pertinent to the present study.

The reduction potentials proved only slightly sensitive to the relative position of the dithioester group and the nitrogen atom, the *para* isomers exhibiting somewhat lower values than the *ortho* and *meta* derivatives. Also, replacing a methyl for a benzyl group as R residue (e.g. switching from **2** to **8** or from **7** to **9**) resulted in an almost unnoticeable increase of the reduction potential which, all in all, seems to be mostly dictated by the dithioester function. According to sensible expectations, the reduction potentials of *N*-oxides **5**−**7** were slightly less negative than those of the corresponding compounds **2**−**4**.

ESR Studies. When compounds **2**−**9** were reduced electrochemically at room temperature inside the cavity of the ESR spectrometer at potentials close to those collected in Table 1, spectra were recorded (see Figure 1) that were attributed to the corresponding radical anions, the ESR spectral parameters of which are collected in Table 2. The chemical reduction of the compounds (treatment with ^{t}BuOK in DMSO or HMPA) led to the detection of the same ESR spectra.

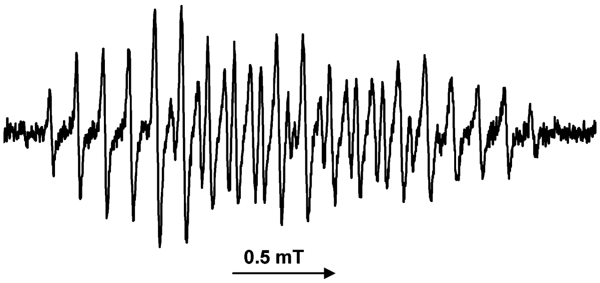


Figure 1. ESR spectrum observed by electrochemical reduction at room temperature of compound **9** in dimethyl sulfoxide containing $^nBu_4ClO_4$ (0.1 M) as supporting electrolyte.

An increase of the applied potential during the reduction of compounds **2** and **4** and of the correspond-

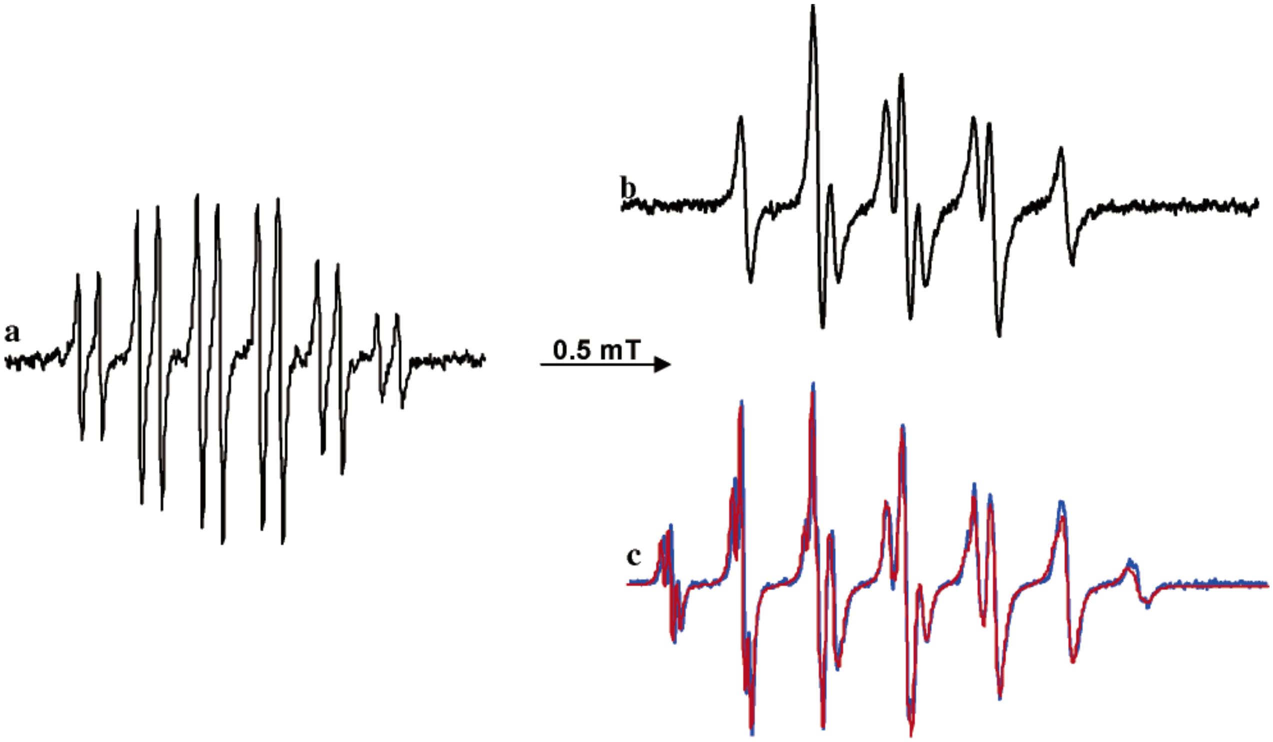
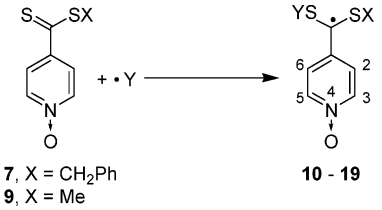


Figure 2. ESR spectra observed upon prolonged electrochemical reduction of compound **2** or **5** (a, radical **20**), **4** (b, radical **21**), and **7** (c, radicals **21** and **22** in a 45.3% and 54.7% amount, respectively; blue, experimental; red, simulation).

Scheme 2



ing *N*-oxides **5** and **7** led to the observation of new signals that eventually replaced the initially observed spectra of the radical anions. In the case of **2** and **5**, the same spectrum was eventually observed which exhibited the following spectral parameters: $a_H = 0.08$ mT, $a_H = 0.230$ mT, $a_N = 0.233$ mT, $a_H = 0.455$ mT, $g = 2.0080_0$ (see Figure 2a). In the case of compound **4** the spectrum of the radical anion was replaced by the spectrum shown in Figure 2b, which is due to a radical species where the unpaired electron is coupled with two sets of equivalent hydrogen atoms and a nitrogen ($a_N = 0.335$ mT, $a_{2H} = 0.013$ mT, $a_{2H} = 0.272$ mT, $g = 2.0081_6$). Similar treatment of **7** led instead to the observation of the spectrum in Figure 2c that was in fact the superimposition of the signals from two radicals. One was the same observed with dithioester **4**, whereas in the other the unpaired electron was again coupled with two sets of equivalent hydrogen atom and a nitrogen, but with different coupling constant ($a_N = 0.601$ mT, $a_{2H} = 0.027$ mT, $a_{2H} = 0.268$ mT, $g = 2.0081_6$).

As outlined in Scheme 2, compounds **7** and **9** were also subjected to addition by free radicals generated in situ. Thus, **7** and **9** were thermally or photoreacted with dimethylmercury, methyl, benzyl, or polystyryl bromide and manganese(0) carbonyl, tris(trimethylsilyl)silane or triphenylgermanium hydride, and BPO. The spin adducts of the in situ generated free radicals were characterized by ESR spectroscopy, and their spectral parameters are collected in Table 3.

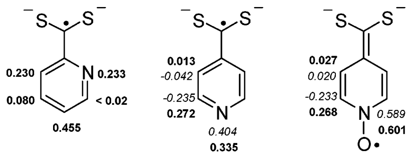
RAFT Polymerization of Styrene. Several polystyrene samples were synthesized by performing RAFT-controlled polymerizations at either 60 or 80 °C, as described in the Experimental Section. Number-average molar mass and polydispersity index values are collected in Tables 4 and 5 along with reaction yields. The resulting polymer samples exhibited a pale red-pinkish color due to the presence of the terminal dithioester group of the controlling agent. In all cases size exclusion chromatography (SEC) curves were shifted toward higher values along the molar mass scale with increasing reaction time, this increase in the molar mass being the expected trend for a controlled polymerization process.

An increase of the polydispersity index value with time was also common to all samples. This behavior is similar to that already observed in the case of benzyl diethoxyphosphoryldithioformate[15] and collides with that exhibited by benzyl dithiobenzoate,[1,17] the latter compound being a better RAFT controlling agent than the former.

Discussion

We have already pointed out in the introductory section that the relative stability of the radicals of general structure **1** is a critical factor in determining the efficiency of a RAFT process involving a particular chain transfer agent. Because radicals **1** have two electron-donating thioalkyl groups linked to the radical carbon center, their stability is bound to increase with the electron-withdrawing ability of the third residue Z due to capto-dative stabilization.

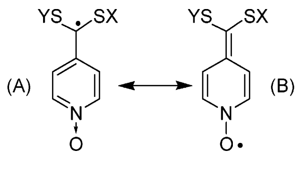
In this light, it should be possible to predict the ability of a given dithioester ZC(S)SR to act as a RAFT mediator on the basis of its reduction potential, which is expected to lower as the electron-withdrawing ability of Z increases.



20 **21** **22**

Figure 3. Experimental and DFT (density functional theory) calculated (italic) hyperfine splitting constants for radical dianions **20**−**22**.

Scheme 3



10 - 19

X = Me, CH_2Ph; Y = Me, CH_2Ph, $Si(SiMe_3)_3$, $GePh_3$, Polystyryl

From the data collected in Table 1 it emerges that compounds **2**−**9** have reduction potentials in the range −0.9 to −1.2 V vs SCE, thus indicating that the electron-withdrawing ability of the pyridinyl residues and of their *N*-oxides is in between that of a phenyl group and that of a methoxycarbonyl group and is comparable to that of a phosphoryl or thiophosphoryl residue. Indeed, thanks to this stabilizing effect, the ESR spectra of the radical anions from compounds **2**−**9** could be readily observed (see Figure 1), as it had already been the case for the radical anions of several phosphoryl dithioformates.[35] It should also be noticed that the radical anions $\mathbf{2}^{\bullet-}$−$\mathbf{9}^{\bullet-}$ were observed independently of the relative position of the heterocyclic nitrogen and the dithioester function: this would indicate that direct conjugation between the thiocarbonyl group an the nitrogen atom is not essential to stabilization, which is not unexpected as the radical anions of simple dithiobenzoates have also been long since detected by ESR.

Although similar and less negative reduction potentials would be expected for the *ortho* and *para* derivatives with respect to the *meta* isomers, the values reported in Table 1 indicate that in fact *ortho* and *meta* derivatives exhibit similar values that are slightly more negative than those of the corresponding *para* isomers. This finding may reflect some steric interaction that would push the dithioester group out of the plane of the aromatic ring in the *ortho* derivatives, thus reducing conjugation with respect to the *para* isomers.

DFT calculations at UB3LYP/6-31+G* level were performed for the radical anions from two of the examined dithioestersand the predicted hfs constants ($a_2 = -0.295$ mT, $a_3 = 0.065$ mT, $a_N = 0.261$ mT, $a_5 = 0.055$ mT, $a_6 = -0.272$ mT, $a_{2H} = -0.016$ mT for $\mathbf{4}^{\bullet-}$ and $a_2 = -0.370$ mT, $a_3 = 0.172$ mT, $a_N = 0.472$ mT, $a_5 = 0.192$ mT, $a_6 = -0.372$ mT, $a_{3H} = 0.104$ mT for $\mathbf{9}^{\bullet-}$) were found to be in very good agreement with the experimentally measured values.

As for the identification of the species responsible for the spectra observed upon prolonged treatment of **4** and **7**, we believe these species to be the radical dianions **21** and **22** resulting by loss of a benzyl fragment from the corresponding radical anions followed by further reduction in situ (see Figure 3). This assignment was substantiated by DFT calculations at the UB3LYP/6-31+G* level that predicted for **21** and **22** coupling constants in very good agreement with those found experimentally.

On a similar basis, we identify as radical **20** the species responsible for the final spectrum observed in the electrochemical reduction of compounds **2** and **5**. The observation of **20** upon reduction of **5** and of **21** upon reduction of **7** indicates that deoxygenation must also take place at some stage.

The observation of such radical dianions in the reduction of dithioesters is not unprecedented. Indeed, the radical dianion $(EtO)_2P(O)C(S)S^{\bullet 2-}$ was previously detected in the chemical or electrochemical reduction of diethoxyphosphoryl dithioformates $(EtO)_2P(O)C(S)SR$.[35]

The stabilizing action of the heteroaromatic rings should make the spin adducts resulting from radical addition to dithioesters **2**−**9** persistent enough to readily allow their ESR detection. In the present study radical addition experiments were only carried out with compounds **7** and **9** that, in view of their symmetric structure, were expected to afford spin adducts with simple ESR spectra. Thus, generation of methyl, benzyl, silyl, germyl, and polystyryl radicals in the presence of these compounds led to the ESR detection of the corresponding spin adducts **10**−**19**, for which a mesomerism can be viewed between structures **A** and **B** (see Scheme 3).

Also in this case, DFT calculations predicted hfs constants ($a_{2,6} = -0.421$ mT, $a_{3,5} = 0.288$ mT, $a_N = 0.305$ mT, $a_{X,Y}(2H) = 0.069$ mT for **11**) in substantial agreement with experiment. Calculations also indicated a significant contribution of structure **B**, formally a divinyl nitroxide, to the mesomeric system. It should however be pointed out that, although the nitrogen splitting values for radicals **10**−**19** do meet expected values for unsaturated nitroxides,[37] their *g*-factors slightly lower than expected also indicate that the contribution of mesomeric structure **A** cannot be disregarded.

In view of their "favorable" reduction potentials and hence of the relative stability of their spin adducts, compounds **2**−**7** were tested as CTAs in the RAFT polymerization of styrene. Compounds **8** and **9** were instead disregarded because the methyl residue is not a suitable leaving group. The results (see Tables 4 and 5) indicated control of the polymerization of styrene by all the examined compounds, although with different performances.

Figure 4 shows the trend of the number-average molar mass M_n and the polydispersity index M_w/M_n as a function of time at 60 °C for the polystyrene samples prepared with dithioesters **2**−**7** and with benzyl dithiobenzoate, **23**, as a comparison. As it can be seen, M_n increases linearly with time in all cases, as is expected for properly controlled polymerization processes. It should however be noted that while the increase of M_n in the case of the three pyridinyl derivatives **2**−**4** is comparable to that observed with dithiobenzoate **23**, it becomes much slower for the pyridinyl *N*-oxides **5** and **6** and even more so for **7**. An examination of Figure 4 also reveals that the polydispersity index, although initially rather good for all the heteroaromatic CTAs, increases as the polymerization proceeds whereas a decrease of M_w/M_n is expected for a well-behaved RAFT agent, similarly to that observed with **23**.

A comparison between **23** and dithioesters **4** and **7** makes more evident the different behavior of the heteroaromatic compounds as RAFT agents. Figure 5a shows the SEC curves observed for polystyrene samples

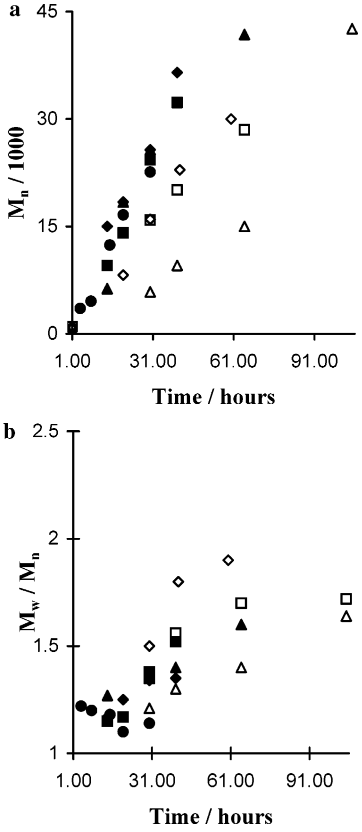


Figure 4. Plot of the number-average molar mass M_n (a) and polydispersity index (b) as a function of time for the AIBN-initiated polymerization of styrene with RAFT agents **2** (◆), **3** (■), **4** (▲), **5** (◇), **6** (□), **7** (△), and **23** (●) at 60 °C.

obtained when using the three RAFT CTAs. It can be seen that in the three cases the curves are fairly narrow corresponding to a polydispersity index of 1.20, 1.25, and 1.15 for **4**, **7**, and **23**, respectively, and that there is a decrease of M_n in the opposite order.

The different behavior of dithioesters **4**, **7**, and **23** is also evident when the ratio between M_n and the yield is plotted as a function of time (Figure 5b). In the case of the *N*-oxide **7** the ratio that represents the maximum attainable molecular mass decreases rather steeply. In the case of the pyridinyl dithioester **4** the value of the ratio is smaller and decreases more slowly, whereas for compound **23** the value is fairly constant and close to 100 000, a value that corresponds to a degree of polymerization of 1000, which is similar to the molar ratio between styrene and the RAFT agents used in the polymerizations.

Even more revealing is the trend of the polymerization yield with time for the three CTAs that is shown in Figure 6. It can be seen that the polymerization process slows down significantly when replacing **23** with **4** and virtually comes to a halt when compound **7** is used.

It is well established that a critical factor determining the rate of RAFT polymerization is the rate of fragmentation of the "dormant" radical species (**1** in Scheme 1) and hence its stability. As already mentioned, the captodative effect plays a very important role in the stabilization of this species. From the reduction potentials reported in Table 1 it is evident that the extent of captodative stabilization should be greater for pyridinyl dithioesters than for dithiobenzoates, and this may result in a lower fragmentation rate of **1** and in a slower

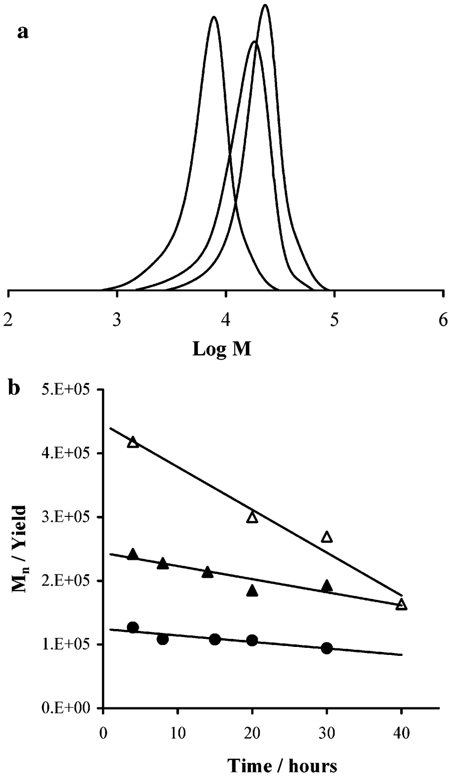


Figure 5. SEC (size exclusion chromatography) curves (a) and variation of the ratio M_n/yield with time (b) for polystyrene samples obtained at 80 °C after 30 h using compounds **4** (central trace and ▲), **7** (leftmost trace and △), and **23** (rightmost trace and ●) as RAFT agents.

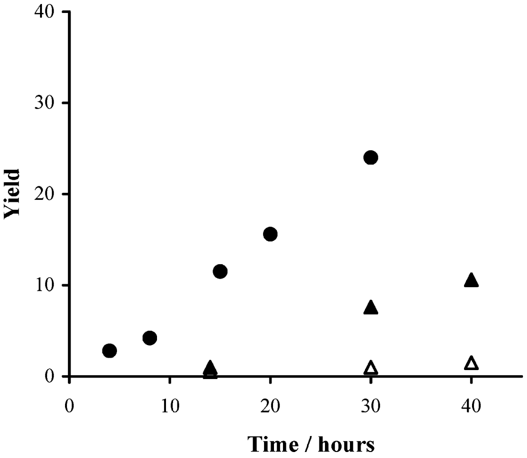
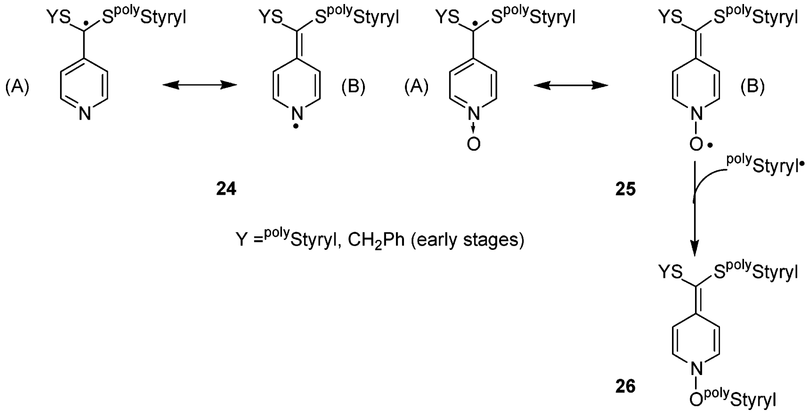


Figure 6. Plot of yield vs time for the AIBN-initiated polymerization of styrene at 60 °C using **4** (▲), **7** (△), and **23** (●) as RAFT transfer agents.

overall polymerization process. On the other hand, the difference between the reduction potentials of the pyridinyl dithioesters (e.g., **4**) and those of the corresponding *N*-oxides (e.g., **7**) seems too small to account for the dramatic reduction of the polymerization observed when using the latter compounds as RAFT agent. Additional effects other than the simple difference in capto-dative stabilization must then be taken into account.

Focusing the attention on the "dormant" radicals **1**, the remarkable difference between those derived from pyridinyl dithioesters and those from the corresponding *N*-oxides (indicated in Scheme 4 as **24** and **25**, respectively) cannot go unnoticed.

Scheme 4



As already stressed above and at variance with radical **24**, radical **25** can be viewed as a diunsaturated nitroxide, which makes the contribution of mesomeric structure **B** more relevant than in the case of **24**. This is also supported by DFT calculations on the structurally related radical **10**. Because of the well-known ability of nitroxides to couple with alkyl radicals, radical **25** might then act as a trap for the growing polystyryl radical to give alkoxyamine **26**, thereby hampering the polymerization process. True enough, under appropriate conditions the formation of **26** may be a reversible process, and indeed the reversible coupling of relatively stable nitroxides with growing polymer radicals is also largely used to control radical polymerization, the process being known as NMP (nitroxide-mediated polymerization).[38,39] Fragmentation of the oxygen−carbon bond in **26** requires more drastic conditions, i.e. higher temperatures, than necessary for the cleavage of the sulfur−carbon bond in **25** or, more generally in the dormant radicals **1**; actually, when polymerization of styrene in the presence of **7** was carried out at temperatures $T > 110$ °C, a higher yield was obtained but the polydispersity index was very poor, i.e. greater than 2.

Indirect support of this explanation may be provided by the higher yields observed when replacing **7** with *N*-oxides **5** and **6**. Indeed, the nitroxidic structure is not possible for the "dormant" adduct of the *meta*-dithioester, and although possible for that of the *ortho*-derivative **5**, its formation might be prevented by steric factors.

Concluding Remarks

The greater electron-withdrawing ability of the pyridinyl and pyridinyl *N*-oxide residue with respect to that of phenyl results in lower reduction potentials for the heteroaromatic dithioesters than for dithiobenzoates. The radical anions of these compounds as well as their spin adducts resulting via thiophilic addition of free radicals were readily observed by ESR thanks to the stabilizing effect exerted by the pyridinyl and pyridinyl *N*-oxide residues that is similar to, or slightly greater than, that of phosphoryl and thiophosphoryl groups.

Pyridinyl dithioesters control the radical polymerization of styrene, although with a poorer control of the molar mass distribution as compared to benzyl dithiobenzoate and with an evident retardation. This may be related to the rate of bond dissociation and re-formation with respect to the propagation rate. Pyridinyl *N*-oxide dithioesters, on the other hand, are not suitable as RAFT CTAs as they stop the polymerization at a few percent of conversion. A tentative explanation of the inefficiency of these last compounds involves termination through coupling between the propagating radical and an in situ generated nitroxide. Thus, the failure of dithioisonicotinate *N*-oxide **7** in acting as an efficient RAFT mediator should not be attributed to excessive stabilization of the intermediate radical **1** and could not be foretold on the basis of its reduction potential.

References and Notes

(1) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 9801478 A1 980115, Jan 25, 1998.
(2) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krsitina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(3) Quinn, J. F.; Rizzardo, E.; Davis, T. P. *Chem. Commun.* **2001**, 1044−1045.
(4) Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402−408.
(5) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283.
(6) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.
(7) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, J. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.
(8) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243−245.
(9) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11*, 823−835.
(10) Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026−3029.
(11) Coote, M. L.; Radom, L. *J. Am. Chem. Soc.* **2003**, *125*, 1490−1491.
(12) Coote, M. L. *Macromolecules* **2004**, *37*, 5023−5031.
(13) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 7−932.
(14) Viehe, H. G.; Janousek, Z.; Merényi, R. *Acc. Chem. Res.* **1985**, *18*, 148−154.
(15) Coote, M. L.; Henry, D. J. *Macromolecules* **2005**, *38*, 1415−1433.
(16) Laus, M.; Papa, R.; Sparnacci, K.; Alberti, A.; Benaglia, M.; Macciantelli, D. *Macromolecules* **2001**, *34*, 7269−7275.
(17) Alberti, A.; Benaglia, M.; Laus, M.; Macciantelli, D.; Sparnacci, K. *Macromolecules* **2003**, *36*, 736−740.
(18) Abrunhosa, I.; Gulea, M.; Masson, S. *Synthesis* **2004**, 928−934.
(19) Trost, B.; Braslau, R. *J. Org. Chem.* **1988**, *53*, 532−537.
(20) Grierson, D. S.; Bettiol, J.-L.; Buck, I.; Husson, H.-P.; Rubiralta, M.; Diez, A. *J. Org. Chem.* **1992**, *57*, 6414−6421.
(21) Crispino, G.; Breslow, R. *J. Org. Chem.* **1992**, *57*, 1849−1855.
(22) Jarvis, B. B.; Marien, B. A. *J. Org. Chem.* **1977**, *42*, 2676−2680.
(23) Garreau, D.; Savéant, J.-M.; Stella, L. *Electroanal. Chem.* **1972**, *35*, 309−331.

(24) Lucarini, M.; Luppi, B.; Pedulli, G. F.; Roberts, B. P. *Chem.—Eur. J.* **1999**, *5*, 2048−2054.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(28) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

(29) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; De Frees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654−3665.

(30) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.

(31) Guerra, M. *J. Phys. Chem. A* **1999**, *103*, 5983−5988.

(32) Mayer, R.; Scheihauer, S.; Kunz, D. *Chem. Ber.* **1966**, *99*, 1393−1413.

(33) Alberti, A.; Guerra, M.; Hapiot, P.; Lequeux, T.; Macciantelli, D.; Masson, S. *Phys. Chem. Chem. Phys.* **2005**, *7*, 250−257.

(34) Voss, J.; von Bulov, C.; Drews, T.; Mischke, P. *Acta Chem. Scand., Ser. B* **1983**, *37*, 519−525.

(35) Alberti, A.; Benaglia, M.; Hapiot, P.; Hudson, A.; Le Coustumer, G.; Macciantelli, D.; Masson, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1908−1913.

(36) Iwai, K.; Takemura, F.; Furue, M.; Nozakura, S.-I. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 763−767.

(37) Forrester, A. R. In *Landolt-Börnstein*, New Series, Group II; Fischer, H. Ed.; Springer-Verlag: Berlin, 1989; Vol. 17, Part d2.

(38) Moad, G.; Anderson, A. G.; Krstina, J.; Moad, C. L.; Rizzardo, E.; Spurlinig, T. H.; Thang, S. H. In *Controlled Radical Polymerzation*; ACS Symposium Series No. 685; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1997; pp 332−360.

(39) *Advances in Controlled/Living Radical Polymerisation*; ACS Symposium Series No. 854; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2003.

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