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RAFT Polymerization with Triphenylstannylcarbodithioates (Sn-RAFT)

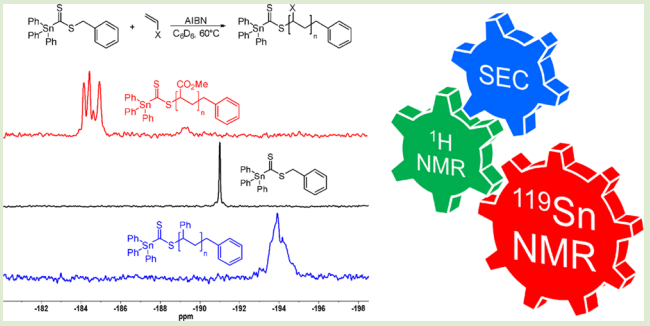
Ihor Kulai,[†,‡] Oleksii Brusylovets,[‡] Zoia Voitenko,[‡] Simon Harrisson,[†] Stéphane Mazières,[†] and Mathias Destarac*[,†]

[†]IMRCP, UMR 5623, Université de Toulouse, 118, route de Narbonne F-31062 Toulouse, Cedex 9, France

[‡]Taras Shevchenko National University of Kyiv, Department of Chemistry, 64/13, Volodymyrska Street, Kyiv, Ukraine 01601

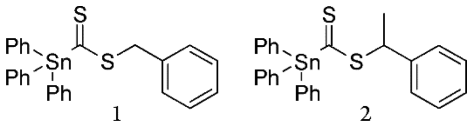
Supporting Information

ABSTRACT: A new range of tin-based reversible addition−fragmentation chain-transfer (RAFT) agents is described and evaluated for the polymerization of acrylamides, methyl acrylate and styrene. These organometallic compounds are highly reactive reversible transfer agents which allow an efficient control of the polymerization of substituted acrylamide monomers, whereas RAFT control for methyl acrylate and styrene polymerization is contaminated by side reactions at prolonged reaction times. ^{119}Sn NMR is shown to be an informative instrument for the monitoring of Sn-RAFT-mediated polymerizations.



Reversible deactivation radical polymerization (RDRP)[1] offers a wide range of possibilities for the design of complex polymer architectures.[2−7] Reversible addition−fragmentation chain transfer (RAFT) polymerization is a form of RDRP that originated in the mid-1990s,[8,9] while the use of thiocarbonylthio RAFT agents of general structure R-S(C═S)Z appeared in 1998.[10,11] Since then, hundreds of RAFT agents with this structure have been developed.[12] Generally, these compounds are categorized according to their Z group, including dithioesters (Z = alkyl or aryl),[13,14] xanthates (Z = OR),[15] trithiocarbonates (Z = SR),[16,17] and dithiocarbamates (Z = NRR′).[18,19] Each of these categories is suited to a specific, and often limited, class of monomers. Interestingly, there are few examples of RAFT agents designed using other heteroelements such as fluorine,[20] phosphorus,[21−25] and selenium[26,27] at the α position of the thiocarbonylthio group. The introduction of a magnetic nucleus connected directly to thiocarbonyl group allows the use of heteronuclear NMR techniques to monitor the polymerization.[24−26] One of the advantages of this approach is the development of "orthogonal" probes to determine the consumption of the RAFT agent, its stability, the stability of the polymer chain end, and the yield of postpolymerization transformations using separate information channels. This addresses the weaknesses of ^{1}H or ^{13}C NMR, which are not convenient for complex systems such as polymers because of overlapping signals and low signal intensities, respectively.[28,29] We synthesized triphenylstannylcarbodithioates **1** and **2** (Chart 1) and evaluated their use as RAFT agents. This allowed us to investigate the effect of the triphenyltin Z-group on the activity of the RAFT agents and to monitor the polymerization by ^{119}Sn NMR spectroscopy.

Chart 1. Triphenylstannylcarbodithioate RAFT Agents



Organotin chemistry has been strongly developed over the last century, mainly because the derived molecules are highly active biologically and have a rich free-radical chemistry.[30,31] Organotin-based reactants in free-radical polymerization have been studied to a much lesser extent by comparison. Polymers based on tributyltin acrylate and tributyltin methacrylate are highly biotoxic and are used as antifouling paints.[32,33] A polystyrene-supported tributyltin hydride has been developed as a nonpolluting organotin reagent for synthesis.[34] Triphenylstannylcarbodithioate **1** has been reported as a ligand for transition metal complexes; ^{119}Sn NMR was used, in combination with other analytic methods, to follow its coordination.[35] Therefore, we proposed compounds **1** and **2** as RAFT agents, which could also act as NMR probes to monitor the RAFT polymerization and aid further investigation of its mechanism.

Triphenylstannylcarbodithioates **1** and **2** were prepared according to a slightly modified literature method,[35] which involves a nucleophilic attack on carbon disulfide by triphenylstannyl anion and subsequent alkylation with the corresponding substituted benzyl bromide. The reaction

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Table 1. Macromolecular Characteristics of Various Polymers Synthesized by Sn-RAFT Mediated Polymerization

entry	monomer (conc. (M))	Sn-RAFT (conc. (mM))	AIBN conc. (mM)	t (h)	$M_{n\,th}$[a] (kDa)	M_n[b] (kDa)	$Đ$[c]	conv.[d] (%)
1	NIPAM[e] (4.94)	**1** (33.5)	6.8	2	5.20	5.05	1.02	27.9
2	NIPAM (4.94)	**1** (33.5)	6.8	3	11.85	15.65	1.03	67.9
3	NIPAM (4.94)	**1** (33.5)	6.8	4	13.40	15.80	1.06	77.0
4	NIPAM (4.94)	**1** (33.5)	6.8	5	15.25	19.50	1.09	88.3
5	TOA[e] (2.12)	**1** (20.0)	2.0	3.5	2.30	3.10	1.28	9.0
6	TOA (2.12)	**1** (20.0)	2.0	5.5	10.85	10.15	1.10	53.1
7	TOA (2.12)	**1** (20.0)	2.0	6.25	14.80	14.65	1.12	73.3
8	TOA (2.12)	**1** (20.0)	2.0	7	17.90	17.80	1.10	89.3
9	TOA[e] (2.12)	**2** (15.0)	2.0	4.75	7.60	8.85	1.05	27.1
10	TOA (2.12)	**2** (15.0)	2.0	5.1	14.65	16.60	1.04	54.1
11	TOA (2.12)	**2** (15.0)	2.0	6.25	19.85	20.85	1.11	74.1
12	TOA (2.12)	**2** (15.0)	2.0	8	23.65	23.15	1.11	88.7
13	TOA[e] (1.32)	**1** (25.1)	5.1	7	8.55	7.77	1.09	83.0
14	TOA[e] (1.26)	PTOA-**1** (7.9)	0.8	3	13.95	14.20	1.49	21.2
15	TOA (1.26)	PTOA-**1** (7.9)	0.8	6	19.20	20.70	1.48	39.3
16	TOA (1.26)	PTOA-**1** (7.9)	0.8	9	24.55	24.50	1.41	57.6
17	TOA (1.26)	PTOA-**1** (7.9)	0.8	13	31.10	33.40	1.35	80.0
18	MA[f] (11.1)	**2** (49.1)	4.9	1.5	4.40	4.40	1.07	20.0
19	MA (11.1)	**2** (49.1)	4.9	3	9.30	10.60	1.11	45.0
20	MA (11.1)	**2** (49.1)	4.9	4.5	13.55	16.80	1.13	67.0
21	MA (11.1)	**2** (49.1)	4.9	6	18.20	21.90	1.25	91.0
22	St[f] (8.70)	**1** (46.6)	4.7	6	2.00	2.40	1.37	7.4
23	St (8.70)	**1** (46.6)	4.7	13	3.80	6.15	1.34	16.7
24	St (8.70)	**1** (46.6)	4.7	24	6.10	17.70	1.40	28.6
25	St (8.70)	**1** (46.6)	4.7	48	9.50	30.85	1.37	46.0

[a] $M_{nth} = ([M]_0/[\text{Sn-RAFT}]_0) \times (\text{conv.}) \times M_w(M) + M_w(\text{Sn-RAFT})$. This expression assumes complete consumption of the CTA and a negligible contribution of the initiator-derived chains. [b] Determined by SEC, see Supporting Information for details. [c] $Đ = M_w/M_n$ [d] Monomer conversion was determined by ^{1}H NMR. [e] 1,4-Dioxane solution, 60 °C. [f] In bulk, 60 °C.

sequence is depicted in Scheme S1; yields are fair to good. After purification, the Sn-RAFT agents were free of additional organotin species (by ^{119}Sn NMR) and at high degree of purity.

To evaluate the ability of the novel RAFT agents to induce RDRP, we polymerized a selection of more-activated monomers, namely, *N*-ispropropylacrylamide (NIPAM), *N*-*tert*-octyl acrylamide (TOA), methyl acrylate (MA), and styrene (St), using Sn-RAFT agents at 60 °C with AIBN as thermal initiator. The reactant concentrations were chosen so that the theoretical number-average molar mass (M_n) of the polymer was about 20 kDa at 100% monomer conversion or 40 kDa in the case of chain extension with TOA. Selected conversion−time data, macromolecular characteristics (M_n, $Đ$) and reactant concentrations are collected in Table 1.

Sn-RAFT agents were ineffective in the polymerization of less activated monomers. Indeed, Sn-RAFT **1** totally inhibits the polymerization of vinyl acetate, vinyl pivalate, and *N*-vinyl caprolactam. This result is similar to those obtained with RAFT agents, such as dithioesters, which give highly stabilized intermediate radicals.[36]

Polymerizations of *N*-alkyl acrylamides were conducted in 1,4-dioxane solution (entries 1−12, Table 1). Significant induction periods were observed, about 1.5 h in the case of NIPAM/**1** system (Figure S7), 3 h for TOA/**1** (Figure S10), and 4.5 h for TOA/**2** (Figure S13). Such behavior is also observed in polymerizations mediated by dithiobenzoates and has been explained by slow initialization of the RAFT agent.[37] M_n values are in good agreement with theoretical predictions and tend to increase linearly during the polymerization (Figures S8, S11, and S14), demonstrating the efficiency of Sn-RAFT agents. Dispersity values are consistently low throughout polymerization, with values close to 1.10 at high monomer conversion. This behavior suggests high chain transfer constants (at least 10) for both the RAFT agents and the dormant polymer chains. These features are illustrated by overlays of size-exclusion chromatography (SEC) chromatograms of polymer samples (Figures S9, S12, and S15).

A chain extension of PTOA-**1** macro-Sn-RAFT agent, prepared using Sn-RAFT **1** (entry 13, Table 1), was also performed (entries 14−17, Table 1). No retardation was observed in this case (Figure S16), typical for macro-RAFT agents.[38] M_n values are well correlated with theoretical predictions and increase linearly, while the dispersity initially increases from 1.09 (starting macro-Sn-RAFT agent) to 1.49 and then gradually decreases to 1.35 at 80% conversion (Figure 1a). These features are illustrated by SEC traces of the polymer samples in Figure 1b.

The bulk polymerization of MA (entries 18−21, Table 1) also shows characteristics of controlled RAFT polymerization. The inhibition period is almost negligible (Figure S17). The evolution of M_n with MA conversion is nearly linear, with a slight upward curvature during the second half of the polymerization, while dispersity increases from 1.07 to 1.25 (Figure 2a). A slight shouldering at high monomer conversions is observed in the size exclusion chromatograms, explaining the increase in $Đ$ (Figure 2b). The additional peak is about twice the M_p of the main peak and can be attributed to chain combination at high reaction times.

Bulk polymerization of St (entries 22−25, Table 1) shows no induction period (Figure S18) and exhibits the features of a RDRP only at low monomer conversion. After 6 h of reaction, M_n values are close to theory, with a relatively low dispersity of

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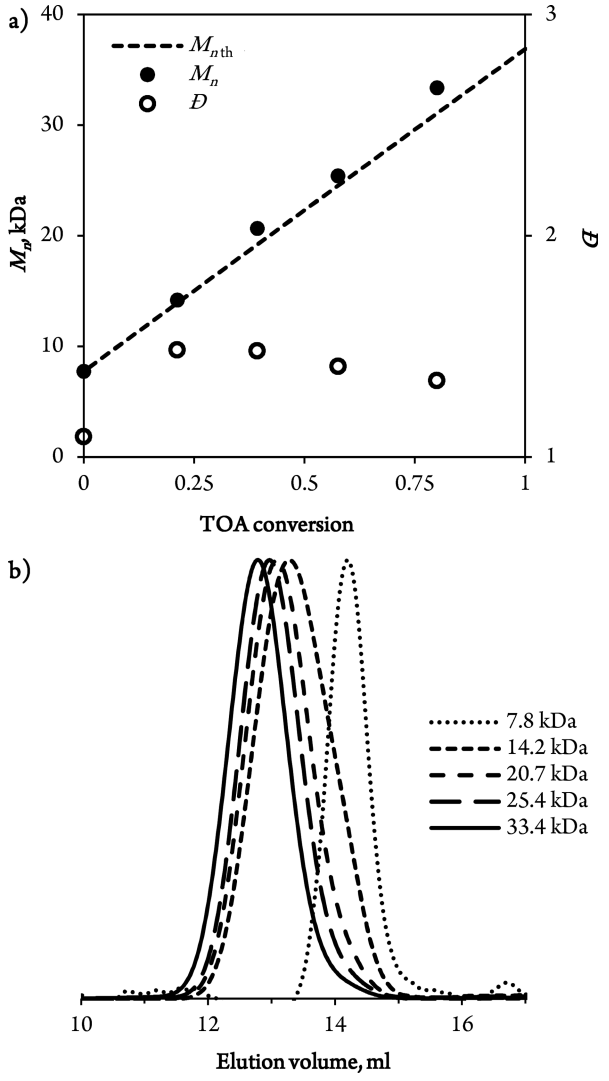

Figure 1. (a) Evolution of M_n and Đ during the chain extension of PTOA-**1** 7.8 K; (b) Overlay of SEC chromatograms for the chain extension of PTOA-**1** 7.8 K (entries 13−17, Table 1).

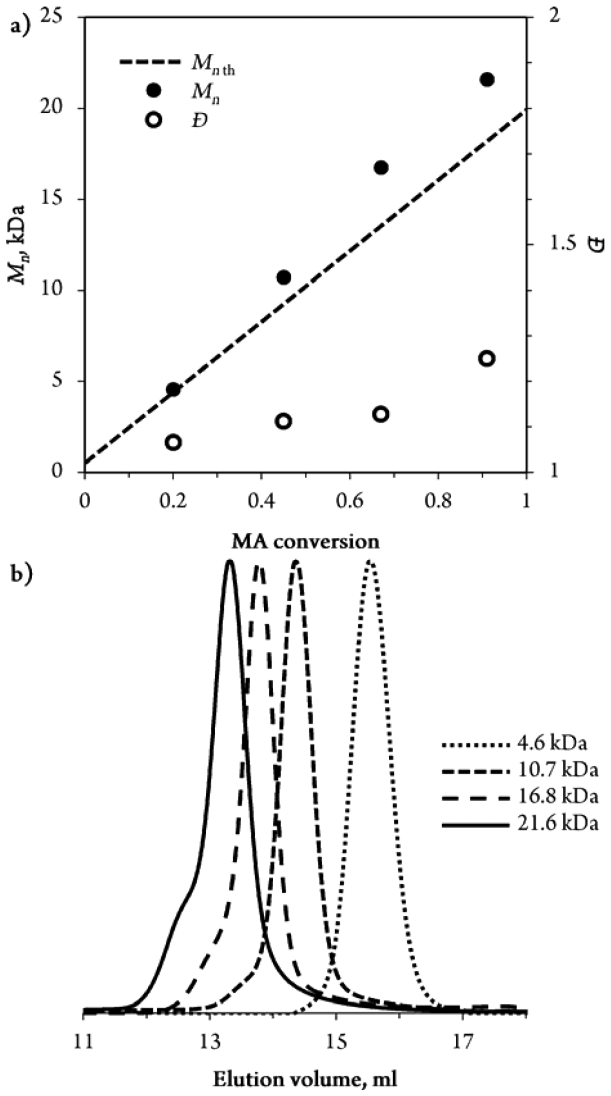

Figure 2. (a) Evolution of M_n and Đ during the polymerization of MA mediated by Sn-RAFT **2**; (b) Overlay of SEC chromatograms for the polymerization of MA mediated by Sn-RAFT **2**.

1.37 (entry 22, Table 1). Unexpectedly, for longer reaction times, a strong upward deviation from linearity was observed on M_n-conversion evolution profiles (Figure S19), while dispersities remained nearly constant throughout polymerization. SEC demonstrates significant peak broadening at intermediate monomer conversions (Figure S20). Additionally, the intensity of the pink coloration, which is an indicator of the thiocarbonylthio fragment, decreased over the course of the polymerization. This phenomenon can be attributed to the thermal decomposition of the dithioformate fragment, as has been reported for other classes of RAFT agents.[39]

To understand better the transformations of the triphenylstannylcarbodithioate fragment over the course of polymerization we have employed ^{119}Sn NMR. Polymerizations of MA and St were performed in NMR tubes at 60 °C in C_6D_6 solution with AIBN as thermal initiator. As the natural abundance of ^{119}Sn is only 8.59% and its receptivity is 220 times less than for ^{1}H,[28] we have modified the initial concentrations of reagents to obtain an acceptable quality of spectra. Detailed information about reagent concentrations, conversion−time data and macromolecular characteristics of obtained polymers are listed in Tables S1 and S2. The combination of ^{1}H and ^{119}Sn NMR (Figures S25 and S30) monitoring allowed us to obtain detailed kinetic profiles for the monomer and RAFT conversion, respectively (Figures S21 and S26), and measure the transfer constants (Figures S22 and S27) as 15.0 for the MA/**1** system and 18.4 for St/**1** respectively.

The MA polymerization in C_6D_6 follows the same tendencies as the bulk MA polymerization: excellent control over M_n until 63% monomer conversion and upward curvature at higher conversions (Figure S23) with appearance of a high molecular weight shoulder in the SEC (Figure S24). Figure 3 depicts the overlay of ^{119}Sn NMR spectra of Sn-RAFT **1** and St and MA crude polymerization mixtures. It shows the consumption of Sn-RAFT **1** whose signal at −191.0 ppm gradually disappears during polymerization, with concomitant appearance of complex signals at −184−185 ppm for PMA-**1** and −193−195 ppm for PSt-**1**, which correspond to the Sn-RAFT fragment located at the polymer chain end. Similar NMR signals were observed in the ^{31}P NMR spectra of the polymers prepared starting from P-RAFT agents[24,25] and are due to the atactic character of RAFT polymers, which are composed of numerous stereoisomers. ^{119}Sn NMR also revealed side peaks,

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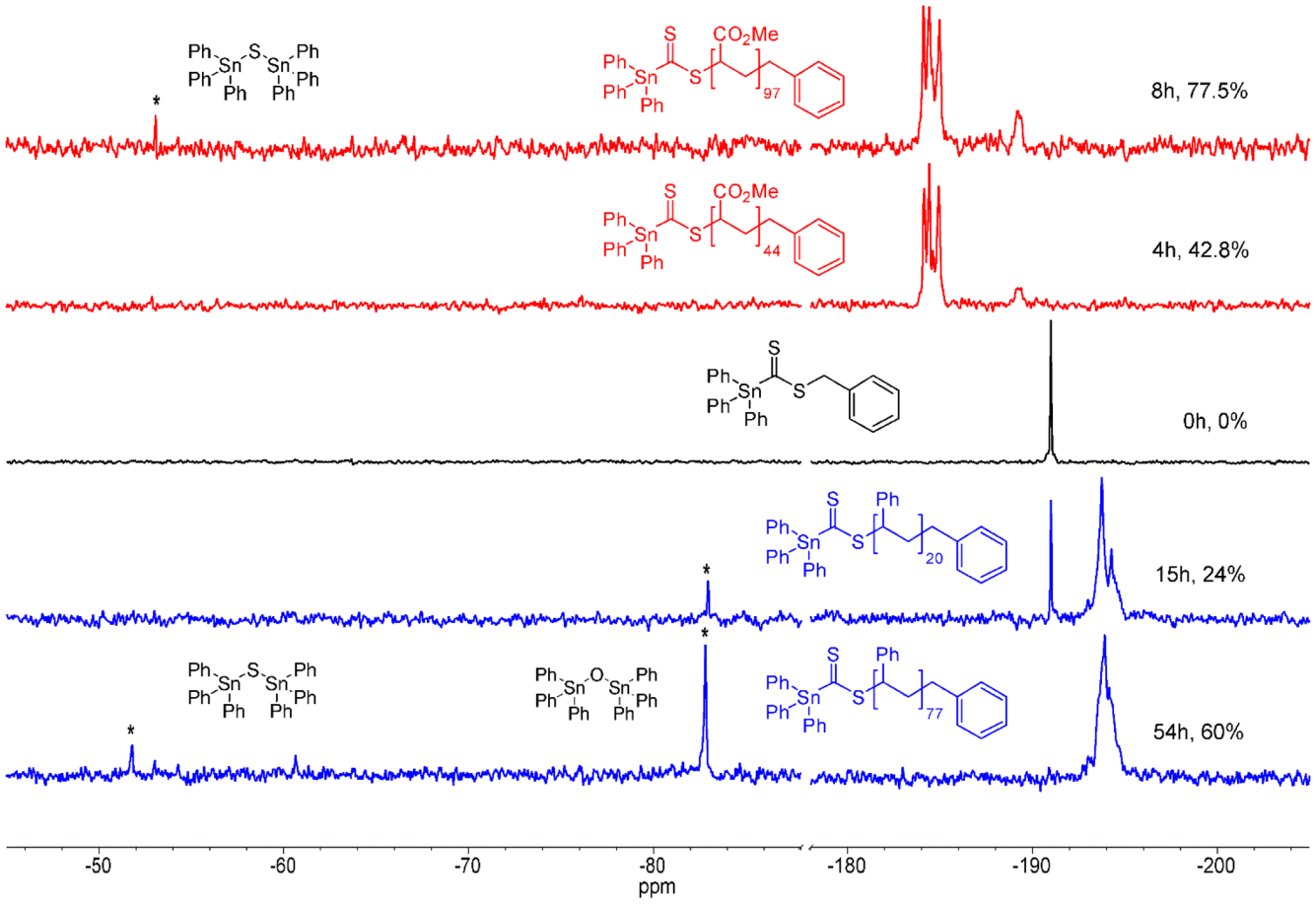

Figure 3. Overlay of ^{119}Sn NMR spectra for the polymerization of MA (Table S1) and St (Table S2) mediated by Sn-RAFT **1** in NMR tubes. *Peaks marked with asterisk correspond to products of thermal degradation.

two of which appeared during MA polymerization and two during St polymerization. During both polymerizations, a small fraction of bis(triphenyltin)sulfide arising from chain end degradation was formed at prolonged reaction times, as evidenced by the presence of a narrow signal at −53 ppm.[40] During MA polymerization, ^{119}Sn NMR showed the formation of a peak that was assigned to the MA:**1** monoadduct at −186 ppm at low reaction times (Figure S25) and its disappearance after about 20% conversion.

An additional broad peak, characteristic of a Sn-containing fragment born by the polyacrylate chain, was observed at −189 ppm. The very close chemical shift to that of the regular Sn-RAFT chain end suggested us that it may correspond to a similar triphenyltin RAFT group, possibly bonded to a different moiety than an acrylate unit.

In the case of St polymerization, deviation in control over M_n appears after 24% conversion and is accompanied by the appearance of an additional peak in the ^{119}Sn NMR spectrum at −82.9 ppm (Figure 3). Its intensity rises over the course of polymerization in parallel with the deterioration in the polymerization control. The sharpness of this peak suggests the formation of a low molar mass product resulting from chain end degradation, and its observed chemical shift most closely resembles that of $(Ph_3Sn)_2O$ (−83.1 ppm).[41]

These results demonstrate that some degradation of the Sn-RAFT reactive end-group takes place over prolonged reaction times at 60 °C. Such lability can be explained by the influence of triphenylstannyl group on the reactivity of the thiocarbonylthio group.[42] These problems may be overcome by running Sn-RAFT polymerizations at lower temperature and for limited reaction times.

To conclude, we have synthesized two related organometallic triphenylstannylcarbodithioate compounds and evaluated their performance as RAFT agents in the polymerization of various monomers. As expected from the presence of the electron-donating triphenylstannyl group, Sn-RAFT agents are highly reactive, mediating the RAFT polymerization of more-activated monomers but totally inhibiting the polymerization of less-activated monomers. Finally, the described triphenylstannyl-carbodithiates are very similar to dithiobenzoates, both in their pink coloration and in their reactivity in RAFT polymerization. This suggests that the electron-rich triphenylstannyl group has a similar radical-stabilizing effect to that of the phenyl group. ^{119}Sn NMR was shown to be a useful method to monitor Sn-RAFT polymerization, and provided important information on the chain transfer kinetics of Sn-RAFT, chain-end fidelity of RAFT end-groups, and observation of side reactions with, in some cases, identification of the formed byproducts. Further studies are in progress to investigate the side reactions observed in polymerizations of St and MA with the help of organotin model compounds and deeper ^{119}Sn NMR investigations. The thermal stability of triphenylstannylcarbodithioates, the mechanism of their thermal degradation, and the effect of carrying out the polymerization at low temperature will be the subject of further investigations.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental information, Scheme S1, Tables S1 and S2, and Figures S1−S30. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00329.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: destarac@chimie.ups-tlse.fr.

Notes

The authors declare no competing financial interest.

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