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Polymerization Agents

Phosphinoyl and Thiophosphinoylcarbodithioates: Synthesis, Molecular Structure, and Application as New Efficient Mediators for RAFT Polymerization**

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Abstract: New phosphinoyl and thiophosphinoylcarbodithioates were synthesized in a one-pot reaction from the corresponding phosphinochalcogenides. Compounds of this new generation of thiocarbonylthio derivatives have been fully characterized by IR as well as ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy and by mass spectrometry. Their solid-state structures reveal that they are isostructural but crystallize in different space groups. These new compounds are highly efficient reversible chain-transfer agents for the reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene (St) and *n*-butyl acrylate (*n*BA), with controlled number-average molecular weights (M_n) and narrow dispersity values ($Đ < 1.3$). The controlled character of the polymerization was further exemplified by MALDI-TOF mass spectrometry and the synthesis of PSt-P(*n*BA) diblock copolymers.

Introduction

After about twenty years of intensive research on reversible deactivation radical polymerization (RDRP),[1] complementary mature synthetic strategies including atom transfer radical polymerization (ATRP),[2] nitroxide-mediated polymerization (NMP),[3] organoheteroatom-mediated polymerization,[4] cobalt-mediated radical polymerization (CoMP),[5] and reversible addition–fragmentation chain transfer (RAFT) polymerization[6] allow an infinite number of options for the preparation of precisely controlled polymers in terms of molar mass, molar mass distribution, end-functionality, and architecture. Among all these technologies, RAFT polymerization has attracted a great deal of attention, in particular because of its high tolerance to functional monomers and its compatibility with waterborne processes. The RAFT process involves the action of compounds bearing a thiocarbonylthio function. These agents of the general formula Z(C=S)SR control the radical polymerization of a large spectrum of vinyl monomers. In addition to conventional steps of radical polymerization, the RAFT mechanism involves two more steps (Scheme 1), in which both the starting agent **I** and the generated macro-agent **III** should possess a reactive C=S double bond. The intermediate radicals **II** and **IV** should fragment rapidly in favor of the products. The R group should give a R$^\bullet$ radical with a stability at least comparable to that of the propagating radical and a suitable reactivity for efficient chain initiation, whereas the Z group dictates the rate of addition of radicals on the C=S bond and the chain-equilibration kinetics. The R[7] and Z[8] groups are then key levers in the reactivity of these agents toward the propagating radicals and their fragmentation rates. Consequently, for a given monomer it appears essential to select both the appropriate radical leaving R but also the Z group to properly adjust the reactivity of the thiocarbonyl bond and the stability of the intermediate radicals. The literature is rich in theoretical[9] and experimental[10–14] studies related to the main families of RAFT agents, which are classified by the atom which is in α position to the thiocarbonyl group, namely dithioesters,[10] dithiocarbamates,[11] trithiocarbonates,[12] and dithiocarbonates[13] (or xanthates, also known as MADIX[14] agents). These four families present a Z group linked by a carbon, a nitrogen, a sulfur or an oxygen atom, respectively. However, the presence of phosphorus in RAFT agents is much less described, in either Z or R groups.

A survey of the literature shows three different categories of phosphorus-containing RAFT agents. Starting with those that involve the phosphorus atom in the R group, phosphine oxide-containing ($R^1R^2P(O)$–) R groups found applications for anchoring RAFT functionalities at the inorganic surface of quantum dots.[15,16] Moreover, phosphonate and bisphosphonate leaving groups in xanthate RAFT agents were efficiently used in RAFT polymerization of vinyl acetate.[17] Another strat-

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[**] RAFT = reversible addition–fragmentation chain transfer.

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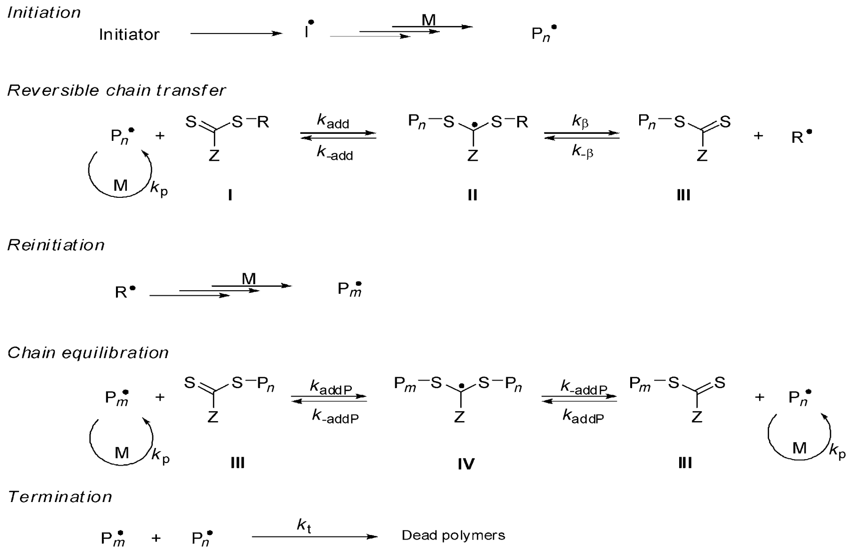


Scheme 1. Mechanism of the RAFT polymerization.

egy consisted in using similar phosphonate esters in order to prepare an α-functional phosphonic acid polymer chain, which gave strong chelation properties for the stabilization of iron oxide nanoparticles.[18] Lastly, phosphine and phosphine-boron complex groups were described to allow the modification of polymer end-groups by means of formation of a peptide bond, leading to biocompatible polymers.[19] Phosphorus can also be part of the Z group, and Destarac et al.[13] showed that phosphonate associated to fluorinated group in the alkoxy part of a xanthate disfavors the conjugation of the oxygen atom and enhances the reactivity of the carbon–sulfur double bond, which was later confirmed by Meiser et al.[20] by means of EPR spectroscopy studies. Finally, a third class concerns RAFT agents that bear a phosphorus atom at the α-position of the thiocarbonylthio group. Recently, Barner-Kowollik et al.[21] used the great ability of phosphonated dithioesters to undergo hetero-Diels–Alder (HDA) cycloaddition reactions for step-growth polymerization of difunctional monomers. But in the RAFT polymerization, after one single example reported in a CSIRO patent,[22] the first detailed studies concerned phosphoryl and (thiophosphoryl)dithioformates[23,24] of the general formula $R\text{-}S\text{-}(C{=}S)\text{-}P(X)(OR')_2$ ($X = O$ or S). However, their behavior in the polymerization of styrene (St), leading to an uncontrolled number-average molar mass (M_n) values and high dispersity ($Đ > 2$), was not conclusive and suggested a contribution of side reactions. Later, Barner-Kowollik et al.[25] generated two low molecular mass poly(2-hydroxyethyl acrylate) polymers with low dispersity ($Đ = 1.13$) mediated by a 2-cyanoprop-2-yl-(diethoxyphosphoryl)dithioformate, for click conjugation with various dienic systems. For these strategies, the same group also reported the use of low molecular mass PSt with low dispersity obtained from a benzyl(diethoxyphosphoryl)dithioformate.[26]

At the beginning of our work, we first studied metallophosphorus-based compounds such as Group 6 metal pentacarbonyldiphenyl-phosphinocarbodithioates ($M(CO)_5PPh_2CS_2R$, with $M = W$, Cr, Mo and $R = -CH_2CN$, $-CH(CH_3)C_6H_5$) as mediators for the RAFT polymerization of St and *n*-butyl acrylate (*n*BA).[27] In parallel, Chen et al. polymerized St and *tert*-butyl acrylate by using tungstenpentacarbonyl derivatives with benzyl and allyl as leaving R groups.[28] Our first results confirmed that these metallophosphorus-based compounds behave as efficient RAFT agents. It appeared that their efficiency was not altered by varying the nature of the metal center. Interestingly, we demonstrated that the chain-transfer reactivity, thermal and chemical stability of phosphino RAFT agents and the resulting polymers could be easily monitored by ^{31}P NMR spectroscopy.[27] The next step was to study the influence of the direct environment around the phosphorus center by using ligands providing more versatile electronic effects. We report here the synthesis and studies in radical polymerization of phosphinoyl and thiophosphinoylcarbodithioates as new organophosphorus-based RAFT agents, namely P-RAFT.

Results and Discussion

Synthesis and characterization of new carbodithioates

In the RAFT polymerization, it is well established that the reactivity of the reversible transfer agent must be adapted to the type of monomer involved. Dithioesters or trithiocarbonates are suitable for controlling the polymerization of styrenic monomers, acrylates, and methacrylates, also called "more-activated" monomers (MAMs), but inhibit the polymerization of "less-activated" monomers (LAMs), such as vinyl acetate or *N*-vinylpyrrolidone. In contrast, agents suitable for controlling the polymerization of LAMs, such as dithiocarbamates and xanthates, tend to be ineffective with MAMs, because of the very low rate of addition of the propagating radical to the C═S double bond. Taking these features into consideration, Rizzardo and coworkers proposed a few years ago an elegant alternative with a reversible protonation of a dithiocarbamate, which could lead to a switchable RAFT agent compatible with monomers of highly disparate reactivities.[29] Thus, they were able to synthesize narrow dispersity poly(MAM)-*block*-poly(LAM).

As the reactivity of these universal dithiocarbamates is linked to the mobility of the nitrogen lone pair, their phosphorus-based analogs may show a similar behavior. By moving down in Group 15 we expect more switching modes. Phosphorus differs from nitrogen in its lower electronegativity and also by its ability to coordinate to a wider range of substrates and complexants to trap its lone pair. The major remaining obstacle is the synthesis of a phosphinodithioester,[30] with a phosphine group adjacent to the thiocarbonylthio. Our alternative is to prepare a phosphinoyl or a thiophosphinoyl RAFT agent and later, after an initial polymerization, modify its reactivity by removing or replacing the chalcogenide (oxygen or sulfur) to give either the phosphinodithioester or another phosphorus-based complex.

As we reviewed in the introduction, phosphorylated dithioesters have scarcely been described in the polymerization literature. In organic chemistry, phosphoryl and (thiophosphoryl)dithioformates have not been so much studied. Only a few articles have focused on the reactivity of the $C{=}S$ bond. Some examples, which have been related in the literature, are additions to thiols leading to diacetal derivatives,[31] pericyclic reactions with unsaturated systems,[32] or radical addition, showing that these compounds are efficient radical traps.[33]

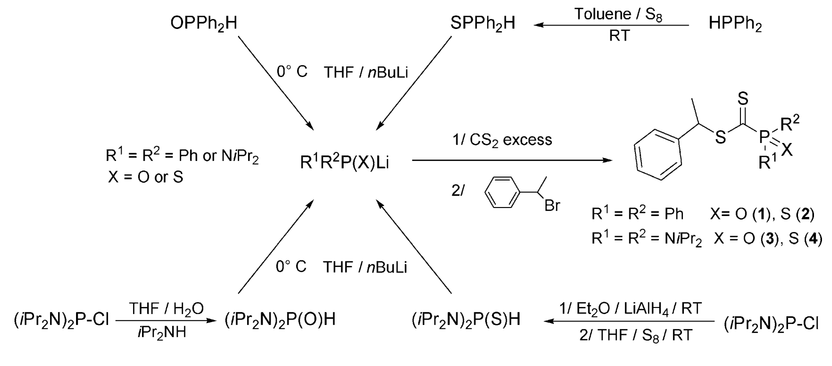
The present work deals with phosphinoyl and thiophosphinoyl carbodithioates of the general formula $R^1R^2P(X)CS_2R$ ($X = O, S$; R^1 and $R^2 =$ alkyl or aryl groups). These compounds have been briefly studied by organic chemists, but never applied to polymerization. The first reports were published by Dahl and Larsen in the 1960s,[30] who described the synthesis of potassium phosphinodithioformate salts and six related thiophosphinoyldithioformates. Two other derivatives were later reported with cyclohexyl groups on the phosphorus,[34,35] and studied as ligands to get stable η^2-CS-bonded platinum complexes. Concerning the oxygen analogs, a few heterocyclic structures were related with amino substituents on the phosphorus.[36,37] These compounds were synthesized from 1,3,2-benzodiazaphosphorine compounds (cyclic $N_2P(O)H$), which were deprotonated with sodium hydride and then allowed to react with carbon disulfide, followed by addition of an alkyl halide at room temperature. An interesting phosphoranimide dithioformate ester, as a red-violet liquid, was obtained by decomposition of a silylated aminophosphonium dithioformate salt, and presented good thermal stability.[38]

Our general synthetic route presents a one-pot reaction from diphenyl or bis(diisopropylamino) phosphine chalcogenides (Scheme 2). Bis(diisopropylamino)phosphine was obtained as described in the literature.[39]

Such secondary phosphine oxides or sulfides are quite acidic. Initial deprotonation with *n*-butyllithium takes place at 0 °C, followed by nucleophilic addition to carbon disulfide. The intermediate lithium dithioformate salt is detected immediately by the appearance of a characteristic red coloration of the THF solution. The first step of the reaction was also monitored by ^{31}P NMR spectroscopy and showed quantitative formation of the intermediate prior to the final alkylation with 1-bromoethylbenzene, which takes place at the sulfur atom. After work up and purification by column chromatography, the phosphinoyl (**1**, **3**) and thiophosphinoyl (**2**, **4**) carbodithioate esters were isolated as pink-dark red oils. Recrystallization from a dichloromethane/pentane mixture (1:10) led to crystalline products. Compounds **1**–**4** have a good solubility in polar and nonpolar solvents, such as pentane, toluene, or cyclohexane.

None of these compounds are air-sensitive in the solid state or in solution, which is an advantageous feature for further use in free-radical polymerization. Satisfactory spectroscopic and analytical data of these compounds were collected. Chemical-ionization mass spectrometry (CI-MS/NH_3) revealed the peak assigned to the $[M+H]^+$ ion in all cases. By using electron impact ionization mass spectrometry, fragmentation becomes more effective with mainly cleavage of the $P{-}C({=}S)$ and $S{-}CH$ bonds. The ^1H NMR spectra (Figures S-1 to S-4 in the Supporting Information) show characteristic deshielded signals for the CH groups connected to the sulfur with chemical shifts in the range from $\delta = 5.23$ to 4.80 ppm. The multiplicity is a double quartet, which confirms that this proton is correlated both to the methyl group in the α-position ($^3J(H,H) = 7.20$–6.90 Hz) and to the phosphorus ($^4J(H,P) = 2.40$–1.70 Hz). The ^{13}C NMR spectra exhibit characteristic resonances for the carbon atom of the CS_2 group around $\delta = 230$ ppm for compounds **1** and **2** and $\delta = 240$ ppm for compounds **3** and **4**, associated with the corresponding $^1J(C,P)$ from 54 to 126 Hz, the highest values correspond to compounds **3** and **4**. The ^{31}P NMR values obtained for these dithioesters show a more pronounced difference in chemical shift, varying from $\delta = 24.82$ (**1**) to 49.60 ppm (**2**) and from $\delta = 14.65$ (**3**) to 62.45 ppm (**4**). The IR spectra exhibit characteristic stretching bands for the thiocarbonyl bonds at $\tilde{\nu} = 1097$ (**1**) and 1092 cm^{-1} (**3**), whereas the corresponding values are much lower in the case of the thiophosphinoyl compounds, at $\tilde{\nu} = 1071$ (**2**) and 1067 cm^{-1} (**4**). These stretching vibration bands are in the range of expected values for $C{=}S$ bonds involved in a free CS_2 group,[27,30,34] and are strongly dependent on the nature of the chalcogenide. The $P{=}O$ bonds also provide strong vibration as expected at $\tilde{\nu} = 1190$ (**1**) and 1218 cm^{-1} (**3**), whereas the $P{=}S$ bands absorb at lower wave numbers of $\tilde{\nu} = 722$ (**2**) and 687 cm^{-1} (**4**).

These compounds were designed to be used in radical polymerization, which occurs in most cases above ambient temperature. A study of their thermal stability, under typical polymerization conditions of solvent, concentration, and temperature, was necessary prior to more investigations. We followed the



Scheme 2. Synthesis of phosphinoyl and thiophosphinoylcarbodithioates (P-RAFT).

evolution by ^{31}P NMR {^1H} spectroscopy, a solution of 20 nm of the agent in deuterated toluene at 60 °C (see for example compound **2**, Figure S-5 in the Supporting Information). The results indicate that compounds **1**–**4** are totally stable at 60 °C, as no additional signals were detected over a period of 48 h. Moreover, the pink-red color of the solution was unchanged, which is a good indication of the stability of the chain end during polymerization.

The crystallographic data of compounds **1**–**4** are summarized in Table 1 and molecular views of all four structures are shown in Figures 1 and 2. Each of these derivatives presents a different space group, unlike the Cr-RAFT and Mo-RAFT agents previously studied,[27] which were isostructural in the triclinic $P\bar{1}$ space group, showing no effect of the nature of the coordinating metal. Here, comparing compounds **1** and **2**, or compounds **3** and **4**, moving from oxygen to sulfur induces a change in the crystalline system, but does not significantly affect the geometry. The sums of the angles around the phosphorus atoms, $\Sigma P = 319.09$ (**1**), 315.60 (**2**), 324.27 (**3**), and 315.37° (**4**), are in the same range and indicate that the pyramidality of the phosphine moiety is not greatly affected by the substituent. The structures are very similar: the P=O bonds in compounds **1** and **3** and the P=S bonds in compounds **2** and **4** are almost identical, as are the C=S bonds of the thiocarbonyl groups.

Table 1. Crystallographic data for compounds **1**–**4**.

	1	2	3	4
chemical formula	$C_{21}H_{19}OPS_2$	$C_{21}H_{19}PS_3$	$C_{21}H_{37}N_2OPS_2$	$C_{21}H_{37}N_2PS_3$
M_r	382.45	398.54	428.62	444.71
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	Cc	$P2_12_12_1$
a [Å]	8.7336(2)	12.0111(2)	10.8007(12)	8.9843(1)
b [Å]	9.8162(2)	9.0388(2)	31.284(3)	9.8307(1)
c [Å]	12.3448(3)	20.230(5)	7.6073(9)	27.8402(4)
α [°]	67.926(1)	90	90	90
β [°]	85.391(1)	116.982(16)	107.924(4)	90
γ [°]	80.037(1)	90	90.00	90
V [Å^3]	965.83(4)	1957.2(6)	2445.7(5)	2458.90(5)
Z	2	4	4	4
ρ_{calcd} [g cm^{-3}]	1.315	1.352	1.164	1.201
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	193(2)	193(2)	193(2)	193(2)
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.364	0.462	0.296	0.376
crystal size [mm^3]	0.42×0.26×0.10	0.24×0.14×0.12	0.15×0.15×0.10	0.40×0.28×0.14
GOF on F^2	1.023	1.044	1.004	1.037
R ($I > 2\sigma(I)$)	0.0417	0.0344	0.0431	0.0304
wR^2 ($I > 2\sigma(I)$)	0.1031	0.0800	0.0722	0.0761
largest difference peak [e Å^{-3}]	0.586	0.395	0.193	0.355
hole [e Å^{-3}]	−0.419	−0.285	−0.230	−0.161

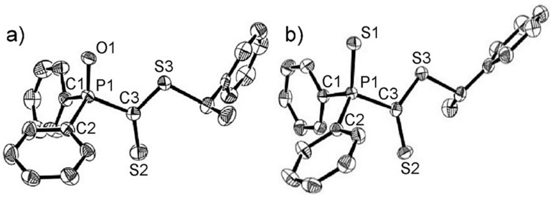


Figure 1. Molecular structure of a) compound **1** and b) compound **2** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms and disordered phenyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: compound **1**: P1–O1 1.489(1), P1–C1 1.802(1), P1–C2 1.800 (2), P1–C3 1.848(2), C3–S2 1.635(2), C3–S3 1.710(2); C1-P1-C2 107.73(7), C2-P1-C3 104.37(7), C1-P1-C3 106.99(7). Compound **2**: P1–S1 1.947(1), P1–C1 1.817(2), P1–C2 1.809(2), P1–C3 1.869(2), C3–S2 1.632(2), C3–S3 1.718(2); C1-P1-C2 108.40(8), C2-P1-C3 104.97(8), C1-P1-C3 102.23(8).

RAFT polymerization with P-RAFT agents

RAFT polymerizations of St and *n*BA were realized in toluene at 60 °C in the presence of P-RAFT agents **1**–**4**, and were initiated with azobisisobutyronitrile (AIBN). The reactant concentrations were chosen so that the ratio of monomer to P-RAFT initial concentrations was 300. The main conversion–time data and macromolecular characteristics (M_n, $Đ$) are collected in Table 2. For St, it appears that the nature of the substituent around the phosphorus does not have a significant effect on the overall rate of the polymerization. Styrene polymerization exhibits the common features of a controlled RAFT polymerization, regardless of the nature of the P-RAFT agent. Polymerizations are slower than with the Cr-RAFT and Mo-RAFT agents previously studied.[27]

This is probably related to a more pronounced stability of the intermediate radicals with P-RAFT agents. The possibility of a small fraction of dead PSt chains resulting from irreversible termination of intermediate radicals[40] cannot be ruled out, and could contribute, together with classically terminated chains due to AIBN initiation; to the presence of a small but visible shoulder at around twice the molar mass of the main peak of the SEC chromatograms (Figure 3 b). For the P-RAFT agents **1** and **2**, St polymerization (Table 2, Entries 1–8; Figure 3 a) showed an increase of M_n proportional to the monomer conversion that matches the values predetermined by the $[St]_0$-to-$[P\text{-}RAFT]_0$ ratio and, therefore, demonstrates the efficiency of these P-RAFT agents. A slight downward curvature in the M_n evolution profile for the highest reaction times is noticeable (Figure 3 a).

This slight deviation is attributed to the contribution of AIBN-derived chains that are no longer negligible during the second half of the polymerization, when considering the rate of decomposition of the initiator under the chosen reaction conditions. When using the P-RAFT agents **3** and **4** for the

Table 2. RAFT polymerization of St and *n*BA in toluene with P-RAFT **1-4**, initiated with AIBN at 60 °C.

Entry	P-RAFT	M	*t* [h]	$M_{n\,th}$[a]	M_n[b]	Đ	Conv. [%][c]
1	**1**	St	10.0	5200	5350	1.06	15.2
2	**1**	St	20.1	9200	8800	1.18	28.2
3	**1**	St	48.1	15 300	15 300	1.25	47.8
4	**1**	St	96.1	21 500	18 900	1.27	67.7
5	**2**	St	10.0	6600	6800	1.06	19.7
6	**2**	St	20.1	10 050	10 350	1.17	30.6
7	**2**	St	48.0	16 700	15 950	1.22	52.2
8	**2**	St	96.1	24 900	21 200	1.25	78.3
9	**3**	St	10.0	5450	6200	1.08	17.0
10	**3**	St	20.0	9550	10 350	1.12	31.0
11	**3**	St	48.0	16 650	17 400	1.16	55.0
12	**3**	St	93.3	22 550	20 300	1.16	75.0
13	**4**	St	10.1	5900	5650	1.06	17.6
14	**4**	St	20.0	9950	9750	1.13	30.3
15	**4**	St	48.0	17 800	16 900	1.19	55.4
16	**4**	St	96.2	24 900	22 300	1.15	78.2
17	**3**	*n*BA	0.6	3950	4560	1.48	9.0
18	**3**	*n*BA	1.0	11 850	13 860	1.34	29.0
19	**3**	*n*BA	2.0	21 300	25 630	1.25	53.0
20	**3**	*n*BA	3.3	28 750	31 100	1.27	72.0
21	**4**	*n*BA	0.6	9300	9800	1.26	23.0
22	**4**	*n*BA	1.0	19 950	21 050	1.19	50.7
23	**4**	*n*BA	2.0	27 600	29 100	1.25	70.9
24	**4**	*n*BA	3.3	33 950	35 850	1.29	87.2

[a] $M_{n\,th} = ([M]_0/[\text{P-RAFT}]_0) \times (\text{Conv.}) \times M_w(M) + M_w(\text{P-RAFT})$. [b] Determined by size-exclusion chromatography (SEC) in THF based on PSt standards for PSt. For P(*n*BA) samples, M_n was determined by SEC in THF based on PSt standards by using the Mark–Houwink–Sakurada parameters of PSt and P(*n*BA). [c] Determined by ^{1}H NMR spectroscopy.

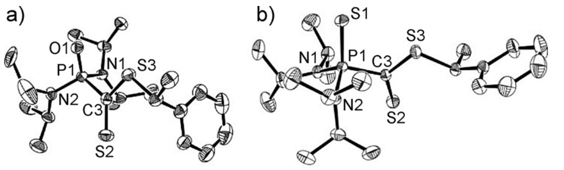


Figure 2. Molecular structure of a) compound **3** and b) compound **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: compound **3**: P1–O1 1.475(2), P1–N1 1.655(2), P1–N2 1.641(2), P1–C3 1.868(3), C3–S2 1.634(3), C3–S3 1.720(3); N1-P1-N2 111.56(11), N2-P1-C3 109.62(11), N1-P1-C3 103.09(11). Compound **4**: P1–S1 1.948 (1), P1–N1 1.668(1), P1–N2 1.655(1), P1–C3 1.883(1), C3–S2 1.638(1), C3–S3 1.730(1); N1-P1-N2 107.00(6), N2-P1-C3 103.89(6), N1-P1-C3 104.51(6).

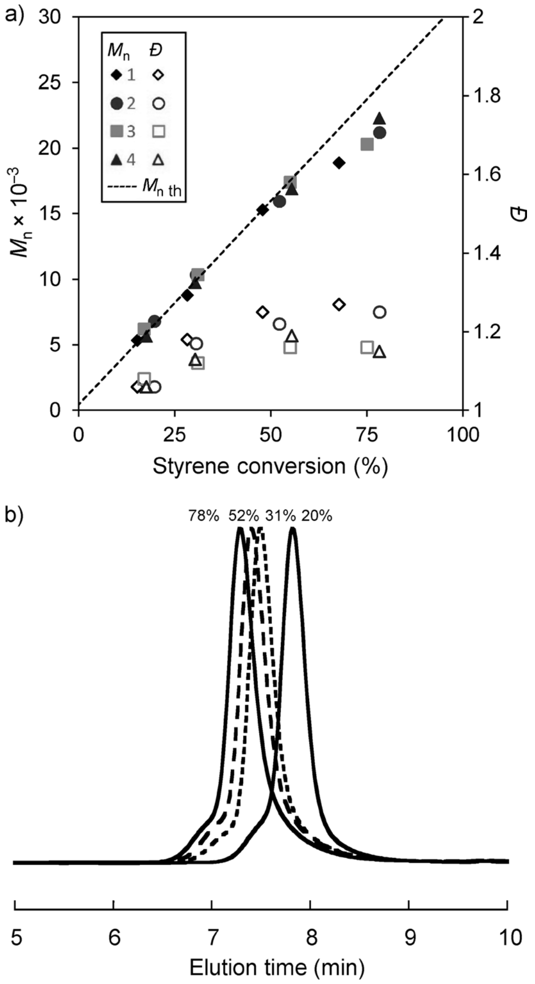


Figure 3. a) Evolution of number-average molar-mass values and the dispersity during St polymerization mediated by the P-RAFT agents **1**–**4** and b) overlay of the SEC chromatograms for the St polymerization in the presence of the P-RAFT agent **2**.

St polymerization (Table 2, Entries 9–16; Figure 3 a), the M_n conversion profile matches the theory similarly to that of compounds **1** and **2**, but lower values of Đ (<1.2) were obtained at the end of the polymerization.

For all the agents, the Đ profile, which is quite constant over the second part of the polymerization, indicates the chemical stability of the polymer chain end for long reaction times, with Đ values up to 1.27–1.25 for compounds **1** and **2** and 1.16–1.15 for compounds **3** and **4**. These features are characteristic of a controlled RAFT polymerization and are illustrated in Figure 3 b, which shows an overlay of the size-exclusion chromatograms of P(St)s (Table 2, Entries 5–8) during a polymerization mediated by the P-RAFT agent **2**.

As expected, polymerizations of *n*BA (Table 2, Entries 17–24) showed appreciably reduced reaction times compared with those for St because of the intrinsic greater reactivity of the acrylate monomers. For both P-RAFT agents **3** and **4**, the evolution of M_n is proportional to the conversion and fits well to the theoretical values.

These results show quantitative consumption of the P-RAFT agents and a negligible fraction of AIBN-derived chains even for high *n*BA conversions. The Đ value remains low throughout the polymerization and increases slightly at high *n*BA conversion (Đ < 1.3). For Table 2, Entry 17, the high dispersity value is explained by the low conversion and the significant contribution of the oligomers. These features are also characteristic of a controlled RAFT polymerization. For the studied P-RAFT agents **1**–**4**, the controlled M_n values and the quite low Đ values observed even at low monomer conversions for both St and *n*BA polymerizations suggest that both the chain transfer to the P-RAFT agent and the interchain transfer are fast relative to the propagation step. A fast transfer to the P-RAFT agent **3** was confirmed by ^{31}P NMR spectroscopy for both St and *n*BA polymerizations, with a complete conversion of compound **3** before 17% for St and 9% for *n*BA (see Figure S-7 in the Supporting Information). As expected for a controlled RAFT polymerization, the ^{31}P NMR spectra showed the presence of the phosphorylated polymer chain ends.

To further confirm the controlled character of the polymerizations mediated by this new generation of RAFT agents, and the integrity of the polymer chain ends, a diblock copolymer of St and *n*BA was prepared. To do so, a PSt macro-RAFT agent (PSt-**4**) was synthesized in the presence of compound **4** in toluene at 60 °C and isolated. Characterization indicates a M_n of 1100 g mol^{-1} and a $Đ$ of 1.13 (Table S-1, Entry 25, in the Supporting Information). Compound PSt-**4** was analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). As shown in Figure 4 (and Figure S-6 in the Supporting Information), the spectrum displays the main population (1), which is in complete agreement with the expected PSt bearing P-RAFT **4** groups at both ends, with R as the α end-group and the thiocarbonylthio moiety as the ω terminus; $m/z = 105+104n+339+23$ (Na$^+$), where *n* is the degree of polymerization. The difference in *m/z* between the peaks corresponds to the molar mass of one styrene unit. The main population corresponds to intact dormant chains; this is a very relevant point, which indicates the high stability of the polymer chain-end functionality. Indeed, the loss of the thiocarbonylthio moiety in MALDI-TOF MS analysis of RAFT polymers, which originates under the experimental conditions of the ionization, is well known in the literature. The chain-end functionalities of PSt-RAFT cannot usually be characterized by MALDI-TOF MS,[41,42] especially in the presence of salts,[43] whereas the integrity of the chain end is better conserved with polyacrylates or polyvinyl esters for example.[17,43,44] Three other minor populations can be distinguished, noted (2), (3), and (4). Series (2) corresponds to a PSt population with unsaturated termination, whereas series (3) is related with PSt chains initiated with AIBN. Series (1), (2), and (3) are cationized with sodium. Series (4), which is cationized with a proton, is attributed to PSt chains ω terminated with a thiol group. It is worth mentioning that no side population originating from coupling between growing chains was observed for this low molar mass PSt-**4** sample obtained at low St conversion (≈8%).

The resulting PSt-**4** was subsequently used as a macro-RAFT agent for the AIBN-initiated polymerization of *n*BA in toluene

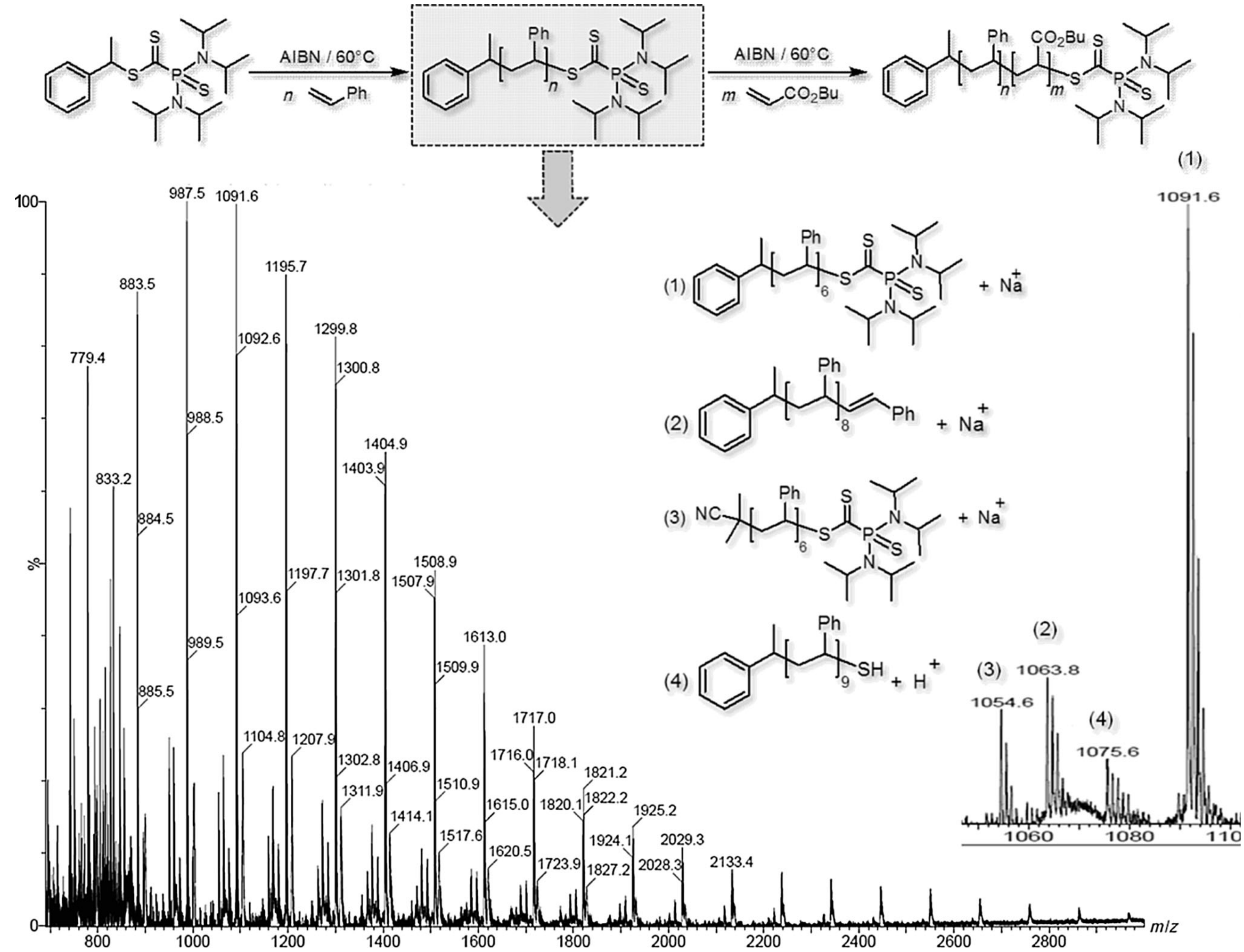


Figure 4. MALDI-TOF mass spectrum of PSt-**4** realized with a 4-(4-nitrophenylazo)resorcinol matrix in presence of trifluoroacetic acid (TFA)-Na in THF.

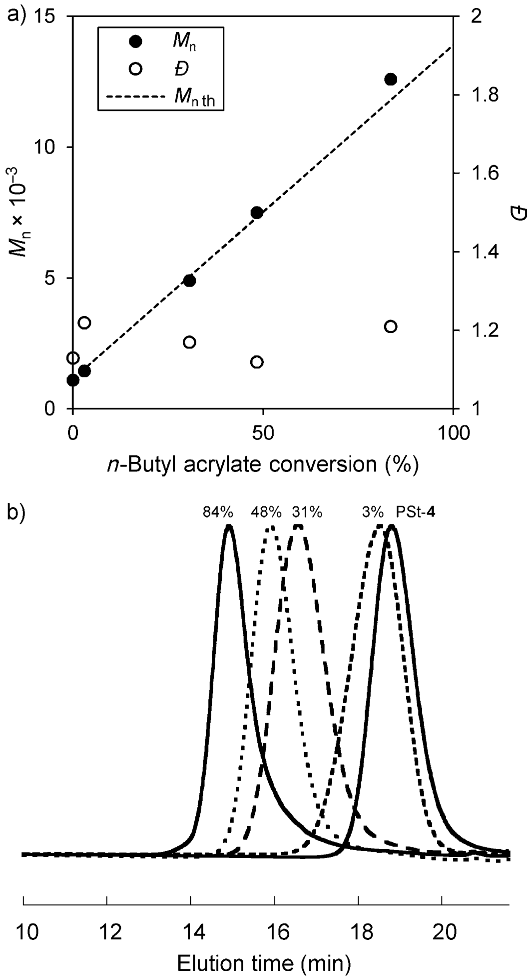


Figure 5. Evolution of number-average molar-mass values and dispersity values with conversion of a) *n*BA and b) overlay of the SEC chromatograms during *n*BA polymerization mediated by PSt-**4**.

at 60 °C. Figure 5 a shows the controlled growth of the P(*n*BA) block as indicated by the increase of M_n with values fitting perfectly to theoretical ones for block copolymerization. The Đ value remained quite low with a slight increase at high conversion due to the contribution of dead chains from the initiator. Figure 5 b is an overlay of the size-exclusion chromatograms during *n*BA polymerization mediated by PSt-**4**. The results summarized in Table S-1 of the Supporting Information (Entries 26–29) allowed us to conclude that the PSt-**4** precursor acted as an efficient macro-RAFT agent leading to the corresponding diblock copolymers PSt-P(*n*BA)-**4**.

Conclusion

New phosphinoyl and thiophosphinoylcarbodithioates (P-RAFT) were synthesized in a one-pot reaction from the corresponding phosphinochalcogenides. Their complete characterization by spectroscopic and spectrometric methods is described, including X-ray analyses. The structures obtained are very similar and the pyramidality of the phosphine moiety does not appear to be affected by varying the substituent. This new generation of phosphorylated compounds presents a strong thermal stability in toluene and was found to mediate efficiently the RAFT polymerization of St and *n*BA. The St polymerization exhibits the common features of a controlled RAFT polymerization, regardless of the nature of the P-RAFT agent. However, slower polymerizations potentially attributed to a small fraction of irreversible termination involving intermediate radicals were observed in comparison with previously reported organometallic phosphinocarbodithioate RAFT agents. The *n*BA polymerization proceeds with an excellent control over the M_n values and low dispersity values. The increase of M_n is proportional to the monomer conversion and matches the predetermined theoretical values, whereas the dispersity values are quite low ($Đ < 1.3$). The high chain-transfer reactivity of the P-RAFT agents and the fast formation of P-RAFT-capped polymer chains was evidenced by ^{31}P NMR spectroscopy. To extend the controlled character of polymerization of this new generation of RAFT agents, and to confirm the integrity of the polymer chain-ends, a diblock copolymer of St and *n*BA was prepared. To this end, PSt-RAFT was isolated and characterized by MALDI-TOF mass spectrometry, which revealed the presence of both end groups of the starting P-RAFT agent. The following growth of the P(*n*BA) block was realized in a highly controlled manner. This work is the beginning of a wider study of phosphorus-based RAFT agents. Continuing the modulation of the environment at the phosphorus atom will help us to identify the spectrum of efficiency of these agents, in terms of monomers. Later, in situ changes in the functionalities at the phosphorus atom may lead to novel P-based switchable RAFT agents.

Experimental Section

General: The syntheses of the P-RAFT agents **1**–**4** were carried out by using standard Schlenk and high-vacuum line techniques under an argon atmosphere. The RAFT polymerizations were performed in glass tubes that were sealed under vacuum after three freeze–evacuate–thaw cycles. NMR spectra were recorded by using a Bruker AVANCE-300 spectrometer for the samples in $CDCl_3$. IR spectra were recorded by using a Thermo Fischer Nexus 6700 FTIR spectrometer in the ATR mode. Melting points were measured with a sealed capillary by using the Stuart automatic melting point SMP40 apparatus. Mass spectra were recorded by using a Nermag R10-10H or Hewlett Packard 5989A mass spectrometer. MALDI-TOF MS measurements were performed by using a MALDI Micro MX (Waters). This instrument is equipped with a nitrogen laser ($\lambda =$ 337 nm, 4 ns pulse), a delayed extraction, and a reflector. It was operated at an accelerating potential of 12 kV in the reflectron mode. The matrix used was 4-(4-nitrophenylazo)resorcinol. Number-average molar mass (M_n) values and dispersity values (Đ) of the polymer samples were determined by size-exclusion chromatography (SEC). The SEC analysis was conducted by using a Waters 712 WISP and R410 differential refractometer with a Styragel column (HR4E) in tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1} (35 °C). The column system was calibrated with narrow PSt standards, obtained from Polymer Laboratories, ranging from 400 to 10^5 g mol^{-1}. Values of M_n are reported in PSt equivalents by using the Mark–Houwink–Sakurada parameters of PSt and P(*n*BA). The St and *n*BA conversions were determined gravimetrically or by ^{1}H NMR spectroscopy.

Materials: THF, toluene, and carbon disulfide were purified by conventional methods before use. Diphenylphosphinesulfide,[45] bis(*N*,*N*-diisopropylamino)phosphine,[39] chloro-bis(*N*,*N*-diisopropylamino)phosphine,[39] and bis(*N*,*N*-diisopropylamino)phosphine oxide[46] were prepared following literature methods. Diphenylphosphine oxide (Aldrich, 97 %), diphenylphosphine (Acros, 97 %), *n*-butyllithium (Aldrich, 1.6 M solution in hexane), and (1-bromoethyl)benzene (Aldrich, 97 %) were used as received. Styrene (Aldrich, 99 %) was distilled over calcium hydride under reduced pressure and *n*BA (Acros, 99 %) were passed through a column filled with basic alumina prior to use. AIBN was obtained from Janssen Chimica and purified by triple recrystallization from methanol.

Synthesis of bis(*N*,*N*-diisopropylamino)phosphine sulfide: A solution of bis(*N*,*N*-diisopropylamino)phosphine[38] (5.99 g, 25.82 mmol) and S_8 (0.91 g, 28.43 mmol) in THF (90 mL) was stirred at room temperature during 30 min. After removal of the solvent under reduced pressure, the product was obtained as a white solid (6.35 g, 93 %). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 31.76$ ppm.

General synthetic procedure for 1–4: The solution of the corresponding phosphine chalcogenide (6.40 mmol) in THF (20 mL) was treated with a stoichiometric amount of *n*-butyllithium (4.0 mL, 1.6 M in hexane) at 0 °C and the yellow mixture was stirred for 60 min. Then a large amount (excess) of CS_2 (2 mL, 33 mmol) was added dropwise at 0 °C to yield a red solution. The mixture was allowed to warm up to room temperature and stirred for 30 min. (1-Bromoethyl)benzene (1.75 g, 9.45 mmol) was added, and the dark red solution was stirred for additional 2 h at 10–15 °C. After removal of the solvent under reduced pressure, the residual product was subjected to column chromatography (silica gel, cyclohexane/diethyl ether (1:4 v/v)). All compounds were obtained as oily pink-red materials. Recrystallization from a dichloromethane/pentane mixture (1:10) led to the crystalline compounds. The ^1H NMR spectra of compounds **1**–**4** are shown in the Supporting Information (Figures S-1 to S-4).

Compound 1: α-Methylbenzyl-(diphenylphosphinoyl)carbodithioate (0.538 g, 22 %); m.p: 122–124 °C; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 24.87$ ppm; ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.74$ (dd, $^3J(H,H) = 7.20$, $^5J(H,P) = 0.90$ Hz, 3 H; CH_3), 5.23 (qd, $^3J(H,H) = 7.20$, $^4J(H,P) = 2.10$ Hz, 1 H; CH), 7.25–7.37 (m, 5 H; C_6H_5), 7.41–7.61 (m, 6 H; C_6H_5), 7.78–7.91 ppm (m, 4 H; C_6H_5); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.41$ (s, CH_3), 49.20 (s, CH), 127.86 (s, C_m- C_6H_5), 127.99 (s, C_p-C_6H_5), 128.36 (d, $^3J(C,P) = 12.45$ Hz, C_m-C_6H_5), 128.69 (s, C_o- C_6H_5), 130.19 (d, $^1J(C,P) = 104.98$ Hz, C_{ipso}-C_6H_5), 132.35 (s, C_p- C_6H_5), 132.50 (d, $^2J(C,P) = 7.32$ Hz, C_o- C_6H_5), 140.12 (s, C_{ipso}-C_6H_5), 234.95 ppm (d, $^1J(C,P) = 76.08$ Hz, CS_2); IR (neat): $\tilde{\nu} = 1190$ (P=O), 1097 m^{-1} (C=S); MS (CI-NH_3): *m/z*: 383 $[M+H^+]$; MS (EI, 70 eV): *m/z*: 245 $[M^+ - SCH(C_6H_5)CH_3]$, 201 $[M^+ - CS_2CH(C_6H_5)CH_3]$, 105 $[M^+ - PO(C_6H_5)_2CS_2]$.

Compound 2: α-Methylbenzyl-(diphenylthiophosphinoyl)carbodithioate (0.764 g, 30 %); m.p. 112–114 °C; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 49.60$ ppm; ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.73$ (dd, $^3J(H,H) = 7.20$, $^5J(H,P) = 1.20$ Hz, 3 H; CH_3), 5.08 (qd, $^3J(H,H) = 6.90$, $^4J(H,P) = 2.40$ Hz, 1 H; CH), 7.26–7.36 (m, 5 H; C_6H_5), 7.39–7.58 (m, 6 H; C_6H_5), 7.76–7.91 ppm (m, 4 H; C_6H_5); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.27$ (s, CH_3), 51.08 (s, CH), 127.94 (s, C_m-C_6H_5), 127.96 (s, C_p-C_6H_5), 128.27 (d, $^3J(C,P) = 12.90$ Hz, C_m-C_6H_5), 128.63 (s, C_o-C_6H_5), 131.27 (d, $^1J(C,P) = 87.16$ Hz, C_{ipso}-C_6H_5), 132.03 (s, C_p-C_6H_5), 132.46 (d, $^2J(C,P) = 15.54$ Hz, C_o-C_6H_5), 140.17 (s, C_{ipso}-C_6H_5), 233.19 ppm (d, $^1J(C,P) = 54.57$ Hz, CS_2); IR (neat): $\tilde{\nu} = 1071$ (C=S), 722 cm^{-1} (P=S); MS (CI-NH_3): *m/z*: 399 $[M+H^+]$; MS (EI, 70 eV): *m/z*: 293 $[M^+ - CH(C_6H_5)CH_3]$, 217 $[M^+ - CS_2CH(C_6H_5)CH_3]$, 105 $[M^+ - PS(C_6H_5)_2CS_2]$.

Compound 3: α-Methylbenzyl-[bis(N,N-diisopropylamino)phosphinoyl]carbodithioate (2.33 g, 85 %); m.p. 47–46 °C; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 14.65$ ppm; ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.13$ (d, $^3J(H,H) = 6.80$ Hz, 24 H; CH_3), 1.61 (d, $^3J(H,H) = 7.20$ Hz, 3 H; CH_3), 3.35–3.65 (m, 4 H; CH), 4.98 (qd, $^3J(H,H) = 7.20$, $^4J(H,P) = 1.70$ Hz, 1 H; CH), 7.11–7.30 ppm (m, 5 H; C_6H_5); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.09$ (s, CH_3), 23.08 (d, $^3J(C,P) = 2.80$ Hz, $NCHCH_3$), 47.05 (d, $^2J(C,P) = 2.80$ Hz, $NCHCH_3$), 48.23 (d, $^3J(C,P) = 2.10$ Hz, CH), 127.35 (s, C_m-C_6H_5), 127.89 (s, C_p-C_6H_5), 128.29 (s, C_o-C_6H_5), 141.25 (s, C_{ipso}-C_6H_5), 242.60 ppm (d, $^1J(C,P) = 126.23$ Hz, CS_2); IR (neat): $\tilde{\nu} = 1218$ (P=O), 1092 cm^{-1} (C=S); MS (CI-NH_3): *m/z*: 429 $[M+H^+]$; MS (EI, 70 eV): *m/z*: 323 $[M^+ - CH(C_6H_5)CH_3]$, 247 $[M^+ - CS_2CH(C_6H_5)CH_3]$, 105 $[M^+ - (iPr_2N)_2P(O)CS_2]$.

Compound 4: α-Methylbenzyl-[bis(N,N-diisopropylamino)thiophosphinoyl]carbodithioate (0.568 g, 20 %); m.p. 110–112 °C; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 62.45$ ppm; ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.18$ (d, $^3J(H,H) = 6.90$ Hz, 24 H; CH_3), 1.65 (dd, $^3J(H,H) = 7.20$, $^5J(H,P) = 1.20$ Hz, 3 H; CH_3), 3.74 (sept, $^3J(H,H) = 6.90$ Hz, $^3J(H,P) = 2.10$ Hz, 4 H; CH), 4.80 (qd, $^3J(H,H) = 7.20$, $^4J(H,P) = 2.40$ Hz, 1 H; CH), 7.09–7.31 ppm (m, 5 H; C_6H_5); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.20$ (s, CH_3), 23.55 (d, $^3J(C,P) = 2.26$ Hz, $NCHCH_3$), 48.02 (d, $^2J(C,P) = 3.47$ Hz, $NCHCH_3$), 50.96 (d, $^3J(C,P) = 2.11$ Hz, CH), 127.43 (s, C_m-C_6H_5), 128.11 (s, C_p-C_6H_5), 128.26 (s, C_o-C_6H_5), 141.26 (s, C_{ipso}-C_6H_5), 240.61 ppm (d, $^1J(C,P) = 95.10$ Hz, CS_2); IR (neat): $\tilde{\nu} = 1067$ (C=S), 687 cm^{-1} (P=S); MS (CI-NH_3): *m/z*: 445 $[M+H^+]$; MS (EI, 70 eV): *m/z*: 339 $[M^+ - CH(C_6H_5)CH_3]$, 263 $[M^+ - CS_2CH(C_6H_5)CH_3]$, 105 $[M^+ - (iPr_2N)_2PSCS_2]$.

Crystallographic data collection and structure determination for 1–4: The data were collected at low temperature on a Bruker-AXS SMART APEX II diffractometer (for compounds **1**, **2**, and **4**) or on a Bruker-AXS APEX II QUAZAR diffractometer (compound **3**) equipped with a 30 W air-cooled microfocus source by using $Mo_K\alpha$ radiation ($\lambda = 0.71073$ Å). Phi- and omega-scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[47] The structures were solved by direct methods (SHELXS-97)[48] and refined by using the least-squares method on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions by using a riding model.

CCDC 952380 (**1**), CCDC-952381 (**2**), CCDC-952382 (**3**), and CCDC-952383 (**4**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General polymerization procedures: A stock solution that contained the monomers, the P-RAFT agents **1**–**4**, AIBN, and toluene was prepared in the following concentrations, respectively: $[St]_0 = 6.33$ mol L^{-1}, $[P\text{-}RAFT]_0 = 21$ mmol L^{-1}, $[AIBN]_0 = 7.4$ mmol L^{-1}; $[nBA]_0 = 5.33$ mol L^{-1}, $[P\text{-}RAFT]_0 = 17.8$ mmol L^{-1}, $[AIBN]_0 = 6.2$ mmol L^{-1}. Aliquots (4 mL) were transferred to four tubes, degassed with three freeze–evacuate–thaw cycles and the tubes were sealed under vacuum. The sealed tubes were heated at 60 °C for the requisite times in an oil bath equipped with a thermostat. The sealed tubes were removed at given intervals and cooled rapidly. An aliquot of the reaction mixture was taken, the excess amount of monomer and solvent was removed by evaporation at ambient temperature under vacuum and the residues was analyzed by using SEC.

Synthesis of PSt-4: A solution that contained AIBN, RAFT agent **4**, St, and toluene ($[St]_0 = 6.32$ mol L^{-1}, $[\mathbf{4}]_0 = 0.062$ mol L^{-1}, $[AIBN]_0 =$

0.021 mol L^{-1}) was prepared, transferred to a tube, degassed, and the tube was sealed. The solution was heated at 60 °C for 15 h. The PSt-**4** was isolated by evaporation of the residual monomer under reduced pressure (737 mg, 7.8% conversion, M_n = 1100 g mol^{-1}, $Đ$ = 1.13 (Table S-1, Entry 25, in the Supporting Information).

Synthesis of PSt-*b*-P(*n*BA) copolymers: PSt-**4** (737 mg) was prepared as described above, *n*BA (8.57 g), AIBN (36.24 mg), and toluene (2.6 mL) were transferred to a glass tube and the tube was sealed and heated at 60 °C for the requisite times. Volatile material was removed under reduced pressure to give the PSt-*b*-P(*n*BA) copolymers (Table S-1, Entries 26–29, in the Supporting Information).

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Keywords: diblock copolymers · phosphinoylcarbodithioates · radicals · RAFT polymerization · thiophosphinoylcarbodithioates

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FULL PAPER

Polymerization Agents

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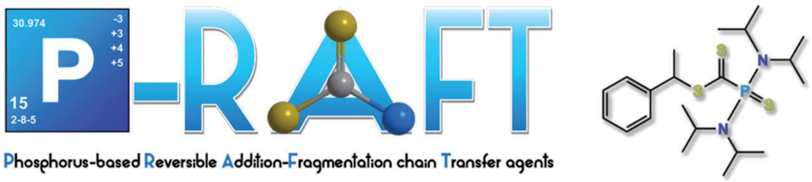
Phosphinoyl and Thiophosphinoylcarbodithioates: Synthesis, Molecular Structure, and Application as New Efficient Mediators for RAFT Polymerization



Phosphorus RAFTing: Novel phosphinoyl and thiophosphinoylcarbodithioates have been synthesized and were fully characterized, including by X-ray analysis. They are efficient transfer agents for the reversible addition–fragmentation chain transfer polymerization of styrene and *n*-butyl acrylate, and related block copolymerization (see figure).