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Synthesis of Multifunctional Dithioesters Using Tetraphosphorus Decasulfide and Their Behavior as RAFT Agents

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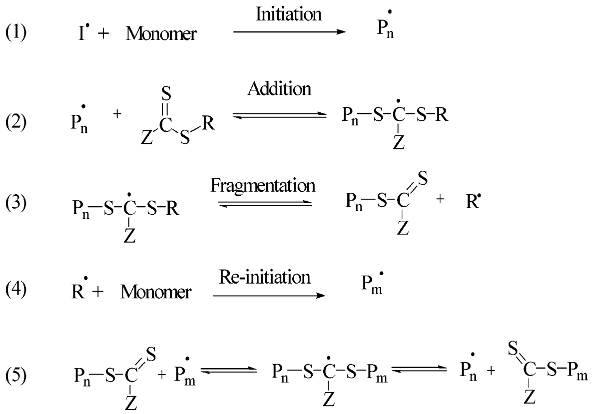
ABSTRACT: The reaction of tetraphosphorus decasulfide (P_4S_{10}) with multicarboxylic acids and benzyl thiol afforded multifunctional dithioesters by a simple experimental procedure. The dithioesters were subsequently used as chain transfer agents to grow poly(*tert*-butylacrylate) and/or polystyrene chains in a controlled fashion by reversible addition-fragmentation chain transfer (RAFT). RAFT polymerizations of styrene were performed thermally at 110 °C either in bulk or in toluene solution, while *tert*-butylacrylate was polymerized at 60 °C in toluene in the presence of AIBN as the radical source. The multifunctional RAFT agents provided good control over the molar masses and polydispersities of the polymers formed, even though the presence of some linear dead chains generated by irreversible terminations could not be avoided. The contribution of the latter reactions was enhanced with the increase of viscosity at high conversion and with the "shielding effect" created by the polymeric arms around the RAFT centers of the core. Better control could be achieved when performing RAFT-mediated polymerizations in toluene solution as compared to bulk experiments. This methodology was applied to synthesize not only linear poly(*tert*-butylacrylate-*b*-styrene-*b*-*tert*-butylacrylate) triblock copolymers, but also three-arm polystyrene stars following an "arm-first" approach.

Introduction

An important development in the area of controlled/living radical polymerization came about with the use of thiocarbonylthio compounds, Z−C(═S)SR, as reversible chain transfer agents (CTAs) in two independently discovered processes.[1−4] These have been named RAFT for reversible addition fragmentation chain transfer[1,2] and MADIX for macromolecular design via interchange of xanthates.[3,4] In these polymerizations (Scheme 1), the CTA first reacts through its C═S double bond with propagating oligomers, leading to a transient radical (step 2). The fate of the latter species depends on both the activating substituent (Z) and the leaving group (R) of the CTA. In the ideal case, this radical intermediate undergoes a β-scission generating a new thiocarbonylthio compound and an expelled R° radical capable of reinitiating the polymerization (steps 3 and 4). Increasing the stability of the radical intermediate may cause the polymerization to be retarded and/or inhibited, in particular when low molar mass polymers are targeted; this is a subject of debate in the current literature.[5−14] A rapid chain-to-chain transfer of the ω-thiocarbonylthio groups between dormant chains and radical active species ensures a controlled/living growth of the chains (step 5). A fast equilibrium relative to the rate of propagation is highly desirable should polymers with narrow molar mass distributions be required. For this purpose, both the activating substituent Z and the R leaving group of the CTA, Z−C(═S)−S−R, should be properly chosen.[1−25]

Since their discovery, significant efforts have been directed at establishing the scope and limitations of RAFT and MADIX processes. These include kinetic and mechanistic investigations,[5−14] their implementations to dispersed media[2,4,26−29] or to homogeneous aqueous solutions,[30−32] and their utilization for macromolecular engineering.[10,33−41]

Scheme 1. Mechanism of the RAFT Process



Among the various types of RAFT agents reported to date, including dithioesters, dithiocarbamates, trithiocarbonates, and xanthates, only a few have been used for star polymer synthesis.[2,36−41] In contrast, numerous reports on the preparation of star polymers by atom transfer radical polymerization (ATRP)[41−43] or, more seldom, by nitroxide-mediated polymerization (NMP)[44,45] can be found in the literature. However, recent reports have shown the possibility to derive multiarm star polymers by RAFT, through the use of multifunctional dithioesters[2,36] or trithiocarbonates.[38−40] Two different types of multifunctional CTAs can be contemplated for use in a RAFT process: those implying an outward growth of arms from the core and those involving the reaction of linear chains with the functional core, following the so-called "core-first" and "arm-first" approaches, respectively.[2,36−40]

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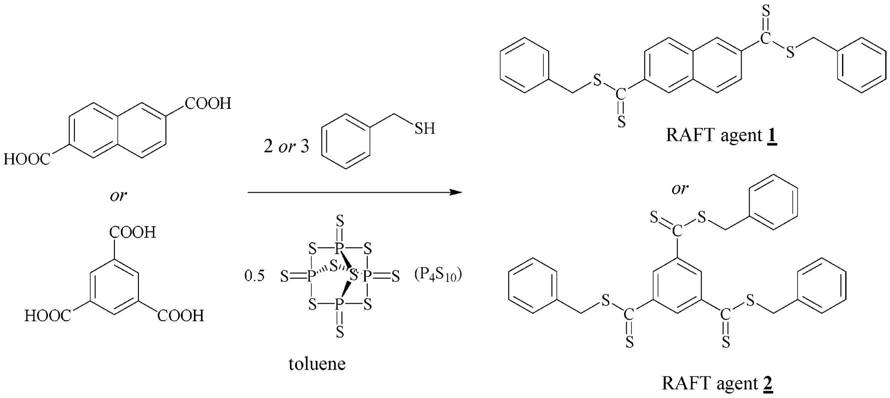
Scheme 2. Synthesis of the Di- and Trifunctional RAFT Agents



Generally speaking, the procedures for synthesizing RAFT agents, including multifunctional ones, suffer from some disadvantages, such as the use of toxic reagents (e.g., iodine, carbone disulfide) or procedures that are not tolerant of functional groups.[46−53] Here, we demonstrate that the use of cheap and mild reactants such as cyclic tetrathiophosphates (P_4S_{10} and Davy reagents) for the synthesis of a di- and a trifunctional dithioester can substantially prevent some of the shortcomings associated with the synthesis of RAFT agents. P_4S_{10} and Davy reagents have been employed for the thionation of carbonyl groups and the preparation of thioamides, thiopeptides, thiolactames, and dithioesters.[46−53] We have recently shown that dithioesters can be obtained in just one step from the reaction of P_4S_{10} (or Davy reagents) with a carboxylic acid in the presence of an alkyl bromide − or radical source − and can be used in situ to control free-radical polymerizations by a RAFT-type mechanism.[54] This report describes (i) the synthesis of multifunctional dithioesters using P_4S_{10}, a thiol (RSH), and a multicarboxylic acid precursor, and (ii) the subsequent utilization of these dithioesters to prepare ABA-type triblock copolymers and three-arm polystyrene stars by RAFT.

Experimental Section

Materials. All reagents were purchased from Aldrich. AIBN (98%) was purified by recrystallization from a methanol solution. All other reagents, P_4S_{10} (97%), benzyl mercaptan (98%), 1,3,5-benzene tricarboxylic acid (98%), 2,6-naphthalene dicarboxylic acid (98%), were used as received. The solvents (toluene, dioxane, 98%) were purified by distillation from calcium hydride prior to use. Styrene (99%) and *tert*-butyl acrylate (99%) were purified by distillation from calcium hydride at reduced pressure and were stored in a glass buret prior to use.

Synthesis of the Difunctional Dithioester (Scheme 2**).** In a three-neck flask equipped with a magnetic stirrer and a reflux condenser, P_4S_{10} (2.05 g, 4.63×10^{-3} mol), 2,6-naphthalene dicarboxylic acid (2 g, 9.25×10^{-3} mol), benzyl mercaptan (2.29 g, 1.85×10^{-2} mol), and toluene (100 mL) were introduced, and the mixture was heated at 110 °C for 24 h. After filtration and concentration, CH_2Cl_2 was added to the crude compound. The mixture was filtered and then purified by two successive columns chromatography on silica gel (one using CH_2Cl_2 as the eluent, the other one using a mixture of 90% hexane and 10% CH_2Cl_2 as the eluting system). The product crystallized at room temperature in CH_2Cl_2 (yield = 19%). ^{1}H NMR: δ 7.2−8.5 ppm (16H, m, **Ar**); 4.6 ppm (4H, s, 2 × CSSC$\mathbf{H}_2$Ph). ^{13}C NMR: δ 43.1 ppm (S**C**H_2Ph); 126−143 ppm (**Ar**); 227.2 ppm (**C**═S). MS: 460 (23%); 337 (32%); 214 (10%); 170 (64%); 126 (20%); 91 (100%).

Synthesis of the Trifunctional Dithioester (Scheme 2). A procedure similar to the one used for the synthesis of the difunctional dithioester was followed except that benzene tricarboxylic acid as a trifunctional precursor and dioxane as a solvent were employed (yield = 23%). ^{1}H NMR: δ 7.1−8.8 ppm (18H, m, **Ar**); 4.6 ppm (6H, s, 3 × CSSC$\mathbf{H}_2$Ph). ^{13}C NMR: δ 43.3 ppm (S**C**H_2Ph); 123−145 ppm (**Ar**); 225 ppm (**C**═S). MS: 476 (18%); 453 (22%); 330 (30%); 207 (60%); 91 (75%); 75 (100%).

General Procedure for Polymerization Experiments. All polymerizations were performed in a Schlenk apparatus under homogeneous conditions. The required concentrations of the RAFT agent, the monomer, and the initiator were mixed with the solvent. The solutions were degassed by three freeze−pump−thaw cycles and placed in a thermostated oil bath prior to the polymerization. After a given time, unconverted monomer was removed by evaporation under vacuum without heating, and the residue was analyzed directly by SEC. In a typical experiment, 10 mg (2.17×10^{-5} mol) of the difunctional RAFT agent, 3 mL (2.05×10^{-2} mol) of *tert*-butyl acrylate, and 1.5 mg (9.15×10^{-6} mol) of AIBN were dissolved in 3 mL of toluene. After degassing, the solution was heated at 60 °C for 7 h under nitrogen atmosphere. The polymer was obtained with 10% of conversion, M_n = 10 500 g mol^{-1}; PDI = 1.12. The polymer compound (215 mg, 2.04×10^{-5} mol) was subsequently used as a macro-CTA for chain extension by adding styrene (1 mL, 8.74×10^{-3} mol) and 4 mL of toluene. After degassing, the solution was heated at 110 °C for 17 h under nitrogen atmosphere. Conversion of the obtained polymer was 20% with M_n = 20 200 g mol^{-1}; PDI = 1.20 (Figure 7).

Characterization. NMR spectra were obtained using a Bruker AC200 NMR spectrometer. Apparent molar masses of homopolymers and block copolymers were obtained by SEC using a refractive index detector (Varian). SEC analysis was performed in THF at 25 °C at a flow rate of 1 mL/min using a refractometer (Varian) and a UV−visible spectrophotometer (Varian) operating at 254 nm, and either 4 TSK columns G5000HXL (9 μm), G4000HXL (6 μm), G3000HXL (6 μm), and G2000HXL (5 μm) or a PSS column (SDV linear M 5μ 8 × 300 mm). Calibration was performed using linear polystyrene standards. The actual molar masses of some samples (entries 10 and 11 in Table 1) were drawn from the response of a multiangle laser light scattering detector (Wyatt Technology, ASTRA Software) that was connected to the SEC line with a laser source (He−Ne) operating at 633 nm. It was assumed that the d*n*/d*c* values for polystyrene stars were the same as that of linear polystyrene (d*n*/d*c* = 0.183 cm^3/g).[43]

Results and Discussion

To design novel multifunctional RAFT agents from which star polymers could be grown, we resorted to a synthetic methodology based on the use of P_4S_{10} which was first described by Davy et al.[51] and subsequently applied by Levesque et al.[52] and Benicewicz et al.[53] P_4S_{10} (see its chemical structure in Scheme 2) is a mild and versatile sulfunation agent of carbonyl groups.[46−54] To the best of our knowledge, however, there is only one

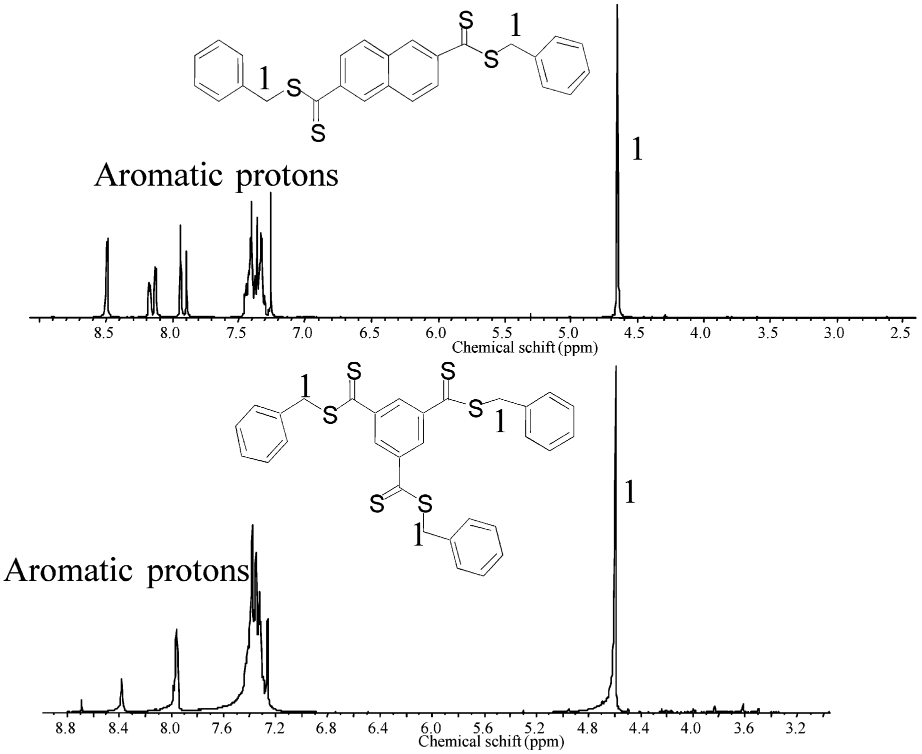


Figure 1. ^1H NMR spectrum ($CDCl_3$; 200 MHz) of (a) RAFT agent **1** and (b) RAFT agent **2**.

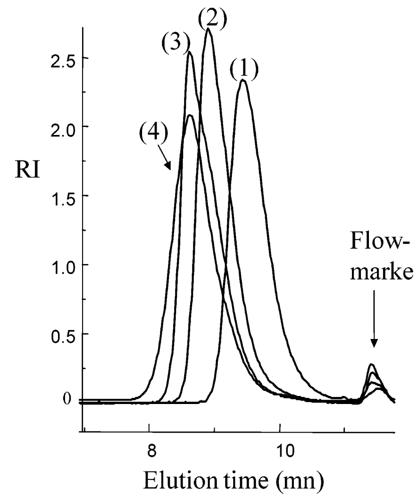


Figure 2. SEC traces of PS samples obtained by polymerizing styrene in bulk at 110 °C in the presence of the difunctional RAFT agent **1** (entries 1−4 in Table 1).

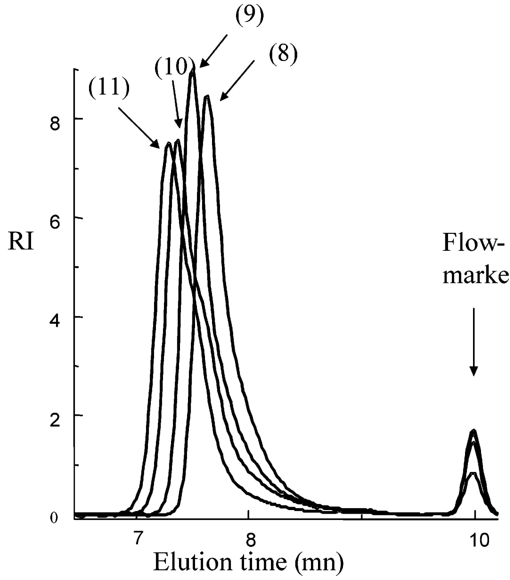


Figure 3. SEC traces of three-arm star PS obtained by polymerization of styrene in toluene at 110 °C in the presence of RAFT agent **2** (entries 8−11 in Table 1).

reported example of multifunctional dithioesters being synthesized by this procedure. This was described by Levesque et al.[52] who used P_4S_{10}, methanol, and difunctional carboxylic acids. The difunctional dithioesters thus obtained have not been used for RAFT polymerizations but in a step growth process for the preparation of polythioamides. For the synthesis of our dithioesters, we employed benzyl thiol, rather than methanol as did Levesque et al.,[52] and reacted it with P_4S_{10} in the presence of either a di- or a tricarboxylic acid because benzyl dithiobenzoate derivatives thus formed are better RAFT agents than their methyl version.[2] In a RAFT process, indeed, such compounds expel benzyl radicals after fragmentation ($Z = -CH_2Ph$ in Scheme 1): as compared to primary methyl radicals, benzyl radicals are not only substantially better leaving groups but they also initiate styrene and acrylate polymerization more efficiently,[55] which is crucial for a successful RAFT polymerization.[2] Thus, benzyl thiol was reacted with P_4S_{10} in the presence of either 2,6-naphthalene dicarboxylic acid or 1,3,5-benzene tricarboxylic acid (Scheme 2). Purification by column chromatography afforded the dithioesters with moderate yields and a high chemical purity, as evidenced by ^1H and ^{13}C NMR and mass spectroscopy. As an illustration, the ^1H NMR spectra of the di- and trifunctional dithioesters and their assignments are given in Figure 1.

In employing these di- and trifunctional RAFT agents, one can expect that each of the thiocarbonylthio groups serves as a transfer center for the growing radicals and retains them to form either a linear difunctional chain or a three-arm star polymer, respectively. A similar

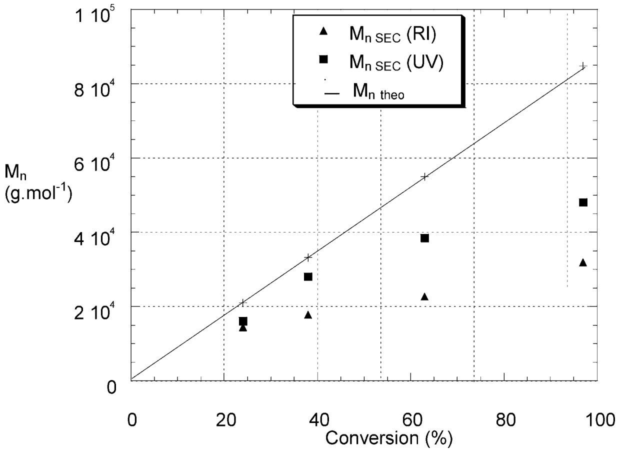


Figure 4. Evolution of molar masses with conversion for the polymerization of styrene in the presence of RAFT agent **2** (entries 8−11 in Table 1).

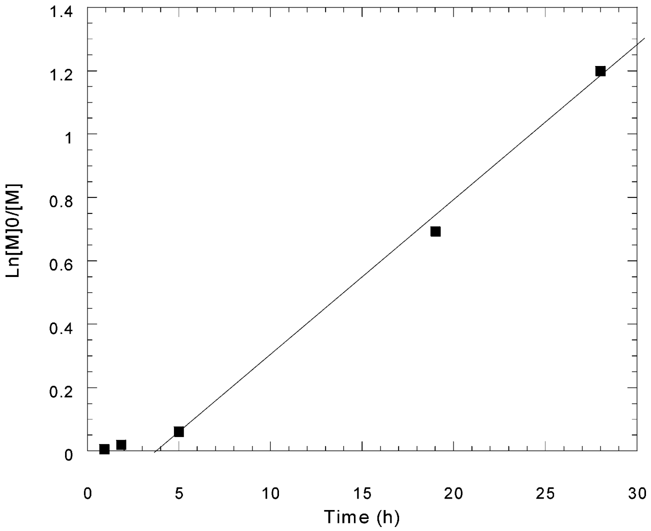


Figure 5. Ln[M]$_0$/[M] as a function of time for the polymerization of *tert*-butylacrylate in toluene at 60 °C in the presence of the difunctional RAFT agent **1** (entries 12−15 in Table 1).

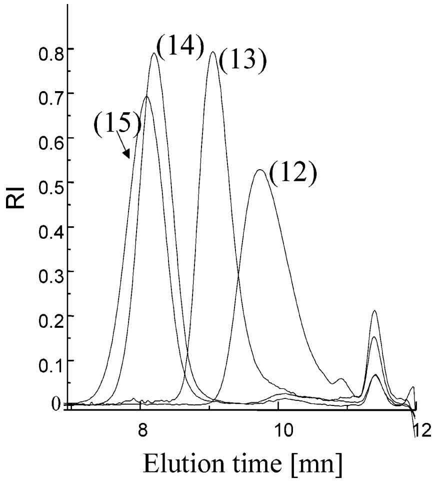


Figure 6. SEC traces of P*t*BA samples obtained by polymerization of *tert*-butylacrylate in toluene at 60 °C controlled by the difunctional RAFT agent **1** (entries 12−15 in Table 1).

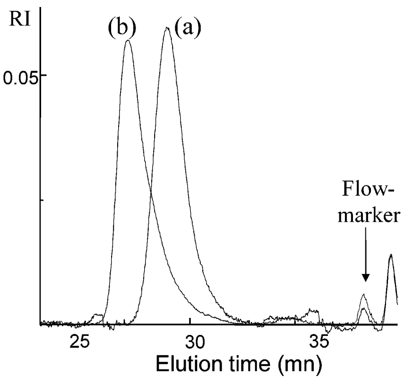


Figure 7. SEC traces of (a) a P*t*BA sample [M_{nSEC} = 10 500 g mol^{-1} PDI = 1.12] obtained by polymerization of *tert*-butylacrylate in toluene at 60 °C in the presence of the difunctional RAFT agent **1** and (b) a P*t*BA-*b*-PS-*b*-P*t*BA sample [M_{n} = 20 200 g mol^{-1}; PDI = 1.20] obtained by polymerization of styrene in toluene at 110 °C in the presence of a macro-RAFT agent.

approach to generate multiarm stars and star-block copolymers has recently been reported by the Rizzardo and the Davis groups. These authors synthesized tetrakis-(trithiocarbonate)[40] and a heptakis(trithiocarbonate)[39] CTA using CS$_2$-based chemistry to derive their multifunctional cores. One main advantage of the arm-first strategy is that complications seen in the core-first synthesis[40−45] such as star−star and star−linear chain couplings can be ruled out here as shown in Scheme 3. Addition of an oligomer chain (P_n°) onto one of the dithioester groups of **2** results in an intermediate radical that will release a benzyl radical upon fragmentation, allowing a new linear chain to be initiated. The latter will eventually become one of the arms of a given star after undergoing an addition-fragmentation transfer reaction to its core. Thus, such arm-first stars only contain branches in a dormant form. Samples prepared under these conditions, however, include dead chains produced by termination reactions, in this case α-benzyl linear polymers, and their proportion can largely vary with the conditions used. Such dead chains do not contain any thiocarbonylthio group.

Another potential problem from such an arm-first approach is the accessibility to the dithioester groups carried by the core. As recently emphasized by Davis et al.,[39] the star core can be shielded by its polymeric arms, its access by linear growing chains being limited as the star arm grows. Consequently, linear chains will experience a higher probability of termination, thus increasing the concentration of dead polymers. This was demonstrated in the case of the heptafunctional cyclodextrin-based RAFT agent used by Davis et al.[39] One can however anticipate less complications with our di- and trifunctional dithioesters.[56]

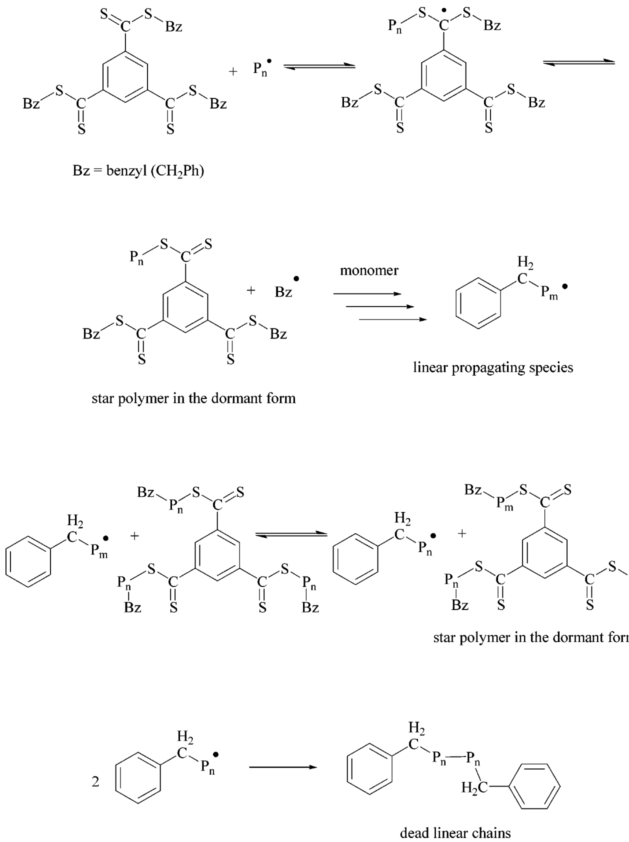
The data pertaining to the polymerizations of styrene and *tert*-butylacrylate in the presence of the di- and the trifunctional RAFT agents are summarized in Table 1. Styrene was polymerized thermally at 110 °C (with no added initiator), first in bulk, then in a toluene solution; the polymerization of *tert*-butylacrylate was performed in toluene solution at 60 °C, using AIBN as the radical source. Figure 2 shows the refractometric response of the SEC traces for polystyrene samples prepared in bulk with the difunctional RAFT agent **1**, at different reaction times. The molar masses increase with the monomer conversion. The SEC traces show a symmetrical and narrow molar mass distribution for moderate monomer conversions and its broadening at higher conversions. As discussed above, this is likely due to the continuous build-up of the concentration of dead chains induced by the increasingly hindered access to RAFT groups carried by the naphthalene moiety. Similar

Table 1. Data for Polymers Obtained by Polymerization of Styrene or *tert*-Butylacrylate in the Presence of Compound 1 or 2[a]

entry	RAFT agent (mol L^{-1})	monomer,[b] °C (in toluene, mol L^{-1})	initiator[c] (mol L^{-1})	time (h)	conv.[d] (%)	M_{ntheo}[e] (g mol^{-1})	M_{nSEC}[f] (g mol^{-1})	PDI[f]
1	**1**[g] (2.1 × 10^{-3})	St, 110 (bulk)	thermal	3.2	9	3930	3200	1.25
2				8.5	27	11 800	7420	1.29
3				21.8	50	21 800	10 800	1.41
4				45.5	82	35 900	15 600	1.57
5	**2** (7.5 × 10^{-3})	St, 110 (bulk)	thermal	4	30	36 300	22 300	1.19
6				22	61	74 000	42 600	1.45[h]
7				46	93	113 000	53 200	1.52[h]
8	**2**[i] (5.2 × 10^{-3})	St, 110 (4.37)	thermal	14.5	24	21 000	14 500	1.20
9				24	38	33 200	17 800	1.30
10				43.7	63	55 000	22 700	1.29
11				78	97	84 800	31 900	1.19
12	**1**[j] (4.1 × 10^{-3})	*t*BA, 60 (4.35)	AIBN (2.2 × 10^{-3})	1.8	2	1840	1820	1.36
13				5	6	5520	6600	1.21
14				19	50	46 000	41 500	1.28
15				28	70	64 500	54 900	1.31

[a] All reactions were performed in Schlenk flasks that were placed in an oil bath at the desired temperature, after degassing by three freeze−pump−thaw cycles. [b] St = styrene; *t*BA = *tert*-butylacrylate. [c] AIBN = 2,2′-azobis(2-cyanopropane). [d] Conversions determined by gravimetry after the evaporation of solvent and/or monomer. [e] Theoretical molar mass expressed as follows: M_{ntheo} = [monomer]/[RAFT agent] × conversion(%) × molar mass of the monomer unit. This expression is based on both assumptions that the RAFT agent was entirely consumed at the given conversion of the monomer and that the proportion of chains derived from AIBN is negligible. [f] Experimental molar mass and polydispersity index obtained by SEC in THF using the RI detector (calibration with linear PS standards). [g] See Figure 2. [h] Bimodal distribution. [i] See Figure 3: entry 10, M_{nLLS} = 46 000 g mol^{-1}; entry 11, M_{nLLS} = 68 000 g mol^{-1}. [j] See Figure 6.

Scheme 3. Synthesis of Arm-First Stars Using RAFT Agent 2



observations were made when the trifunctional RAFT agent **2** was employed in the thermal bulk polymerization of styrene (see entries 5−7 in Table 1). The molar mass distribution was multimodal in this case, even at moderate conversion (footnote h, Table 1).

Styrene was then polymerized at 110 °C using toluene as the solvent. We reasoned that the “shielding effect” mentioned above was also due to the increasing viscosity of the polymerization medium, which decreases the chain’s mobility. The solution polymerizations of styrene were more efficient than bulk experiments, in terms of control over the molar masses and polydispersities (PDIs). The linear increase of the molar masses as a function of the monomer conversion and the PDIs around 1.2 are indicative of a controlled growth of the polymer chains (Figure 3). In addition, the core consisting of the chromophoric thiocarbonylthio groups, −S(C═S), could be detected by SEC using a UV detector at 310 nm. At high conversions, however, a tailing attributed to dead linear chains formed by recombination appeared in the low molar mass area. Nevertheless, it was much less pronounced as compared to the samples obtained in bulk, plausibly because of an increased chain mobility due to the dilution. As explained above, these dead chains did not contain any thiocarbonylthio moiety and could not be detected at 310 nm; as they were not taken into account in the calculation of the apparent M_n values delivered by UV, the latter were higher than those obtained with the refractometric detector (see Figure 4). However, both evolve linearly with the conversion of styrene. These experimental molar masses (M_{nSEC})—whether generated by UV or RI—were lower than those determined by laser light scattering (M_{nLLS}). Because of the compactness of star molecules, SEC, when calibrated with linear PS standards, only gives apparent M_n values for stars, in contrast to LLS that allows access to absolute molar masses.[43] However, M_{nLLS} values (see footnote i of Table 1) did not perfectly match the theoretical values (M_{ntheo}) corresponding to the following expression: [monomer]/[CTA] × conversion of the monomer, because of the presence of the aforementioned linear dead chains that decreased the overall molar mass of the star.

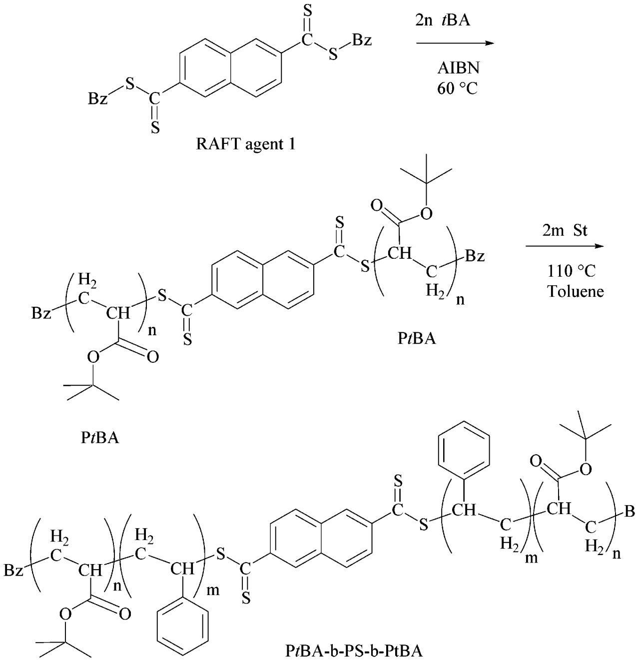
In all experiments, a short inhibition period was noted with both RAFT agents **1** and **2**. A similar observation was made upon polymerizing styrene in the presence of benzyl dithiobenzoate,[2] ($PhC(=S)SCH_2Ph$), which is the monofunctional homologue of **1** and **2**. Opposing explanations have been proposed to account for this phenomenon. Some authors have suggested that the intermediate radical $P_nS-(Z)C^{\bullet}-SP_m$ (Scheme 1) undergoes a slow fragmentation and terminates reversibly, the RAFT agent acting therefore as a radical sink,[8,10−13] whereas others have counterproposed[2,11−12] that $P_nS-(Z)C^{\bullet}-SP_m$ can be captured by propagating species $P_n^{\bullet}$ in irreversible terminations thereby producing three-arm stars. The short duration of the inhibition period observed with our RAFT agents is an argument in favor of a slow fragmentation of the transient radical species. Irreversible terminations with propagating chains would, indeed, have led to byproducts of higher molar masses and would have been easily detected by LS/SEC.

To demonstrate that the samples obtained with the RAFT agent **2** actually exhibit a star-type architecture, one of them (entry 5, Table 1) was subjected to a "core destruction" reaction. This could be achieved by reacting that sample with diethylamine, as reported previously.[2] As expected, this yielded PS chains with a lower molar mass, $M_{\mathrm{n(RI)}} = 13\,000$ g mol^{-1}, than that of the parent sample, $M_{\mathrm{n,RI}} = 22\,300$ g mol^{-1} ($M_{\mathrm{ntheo}} = 36\,300$ g mol^{-1}).

The polymerization of *tert*-butylacrylate was also performed in the presence of RAFT agent **1**, using toluene as the solvent and AIBN as the radical source at 60 °C (entries 12−15 in Table 1). Free-radical polymerizations of alkylacrylates carried out in the presence of benzyl dithiobenzoate are relatively well-controlled, although dithioesters with a better homolytic leaving group can be selected for this class of monomers.[2,8] With the difunctional benzyl dithiobenzoate derivative **1**, no polymer was produced after 1 h of polymerization. Figure 5 illustrates this inhibition period with the plot of the evolution of $\mathrm{Ln}[M]_0/[M]$ as a function of time. This is consistent with the results of Davis et al. who studied the polymerization of acrylates in the presence of benzyl dithiobenzoate.[8] Again, the inhibition period can be ascribed to a slow fragmentation of the benzyl group during the first equilibrium (Scheme 1), rather than to an inefficient initiation of *tert*-butylacrylate by benzyl radicals or to irreversible terminations. After this inhibition period, however, the molar mass of the samples increased linearly with the monomer conversion and PDIs were lower than 1.3, confirming a controlled growth of the chains (see Figure 6).

These poly(*tert*-butylacrylate) (P*t*BA) samples subsequently served as difunctional macro-RAFT agents for styrene polymerization, generating ABA-type triblock copolymers in this way. This order of addition of the two monomers led to the formation of a PS central block and two P*t*BA external blocks (Scheme 4). The thermal polymerization of styrene at 110 °C in the presence of the macro-RAFT agent was carried out with toluene as the solvent. The SEC traces of this chain extension unambiguously showed the formation of the expected P*t*BA-*b*-PS-*b*-P*t*BA block copolymer (Figure 7): the SEC trace shifted from that of the poly(*tert*-butylacrylate) precursor to the higher molar mass region after polymerization of styrene, meaning that the crossover reaction between the two blocks occurred efficiently. One can note, however, a tailing in the low molar mass area of the SEC of the triblock copolymer, likely due to the formation of dead chains obtained by irreversible termination reactions for the same reasons as those explained above.

Scheme 4. Synthesis of an ABA-type Triblock Copolymer Using RAFT Agent 1



Work is in progress to exemplify this low cost and safe procedure of dithioester synthesis through the preparation of various polymeric structures (block and graft copolymers, organic/inorganic hybrid compounds, hyperbranched polymers) from properly selected carboxylic acid-containing precursors.

Conclusion

In this paper, emphasis was placed on the versatility and simplicity of a new synthetic route to di- and trifunctional thiocarbonylthio compounds based on the reaction of P_4S_{10} with a thiol and a carboxylic acid. The di- and trifunctional dithioesters thus obtained subsequently served as multifunctional RAFT agents for the synthesis of either ABA-type triblock copolymers or three-arm stars. This was achieved following an arm-first approach because the core itself was part of the activating group of the RAFT agents, while the homolytic leaving group generated linear growing chains. This allowed us to overcome the complications of star−star couplings often encountered in star polymer synthesis by the core-first method. However, the accessibility of the RAFT functionalities within the core of the star was impeded in bulk experiments, presumably due to the decreasing mobility of the linear chains as the viscosity of the polymerization medium increased with monomer conversion. This, however, could be minimized by carrying out the polymerizations in toluene solutions.

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References and Notes

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(56) One referee suggested we make use of multifunctional RAFT agents to investigate the origin of retardation and/or inhibition in RAFT polymerization. Indeed, should irreversible termination take place at one of the dithioester moieties of such RAFT agents, the derived molecule would still contain thiocarbonylthio groups that could be detected by UV at 310 nm. This is a subject of ongoing studies in our laboratory.

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