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Multiblock copolymer synthesis via controlled radical polymerization in aqueous dispersions. Part 1: Synthesis of *S-tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamates

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Abstract—In a novel two- or three-step synthetic route, *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) is reacted at low temperature with various alkyl chloroformates to form various *S-tert*-alkyl-*N*,*N*-alkoxycarbonylmethyl-dithiocarbamate RAFT agents. Also an alternative and novel synthetic route towards *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate), is proposed.

1. Introduction

In a forthcoming series of papers, the synthesis of multiblock copolymers via controlled radical polymerization in aqueous dispersions will be discussed. These polymers can be used, for example, as compatibilizers for polymer blends and composites, or as pressure-sensitive adhesives, which can be applied to the substrates directly from the waterborne latex. Various techniques have been reported in literature for the synthesis of (multi)block copolymers, for example, anionic polymerization,[1] polycondensation of telechelic polymers,[2,3] the iniferter method[4,5] and more recently several techniques allowing controlled (or 'living') radical polymerization.[6–10] However, of these techniques only the RAFT process allows the well-controlled synthesis of (multi)block copolymers in aqueous dispersions.[9,11–14] Therefore, the RAFT process has been utilized in this work. The number of polymerization steps needed to create multiblock copolymers is dependent on the number of RAFT moieties per controlling molecule/polymer chain. Most of the research in block copolymer synthesis via the RAFT process has been performed employing mono- and bifunctional RAFT agents.[15–24] The concept of this work, however, has been to employ multifunctional RAFT agents, which allow the synthesis of multiblock copolymers in one or two polymerization steps, depending on the nature of the Z group (see Fig. 1). If Z in compounds **1** (dithiocarboxylate) or **2** (trithiocarboxylate) is a low molecular weight moiety (e.g., butyl), then two polymerization steps are required to obtain a (multi)block copolymer. If Z is a macromolecular moiety, then only one polymerization step is required. Recently, the synthesis of sequence ordered polystyrene via compound **2** was reported by Motokucho.[25] However, these authors reported that the synthesis of

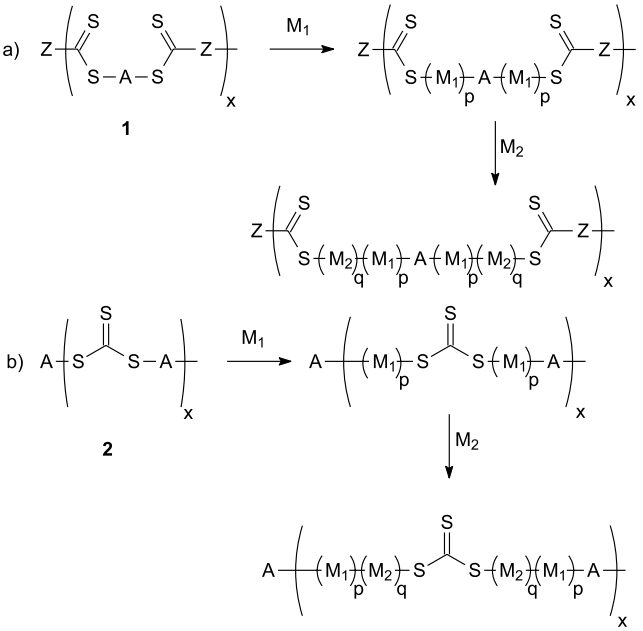

Figure 1. Multiblock copolymer synthesis via a multifunctional RAFT agent. (a) Multiblock copolymer synthesis starting from a symmetrical, multifunctional RAFT agent **1**. (b) Multiblock copolymer synthesis starting from a symmetrical multifunctional trithiocarbonate **2**.

Keywords: Block copolymer synthesis; Alkyl chloroformates; Dithiocarbamates; Living radical polymerization.
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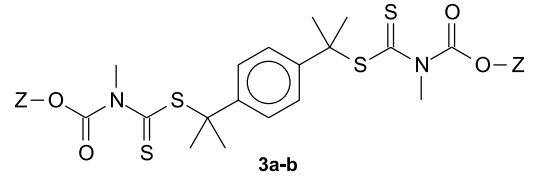
compound **2** is cumbersome. Moreover, only primary alkyl leaving groups have been used, leading to relatively high polydispersities of the resulting polymers.

In this work, the *S*-alkyl-*N*,*N*-alkoxycarbonylmethyldithiocarbamate RAFT moiety has been employed, for three major reasons. The first reason is that this type of RAFT agent has a high transfer constant.[25–32] The second reason involves the incorporation of a macromolecule into the RAFT agent during synthesis: the classical synthetic routes towards RAFT agent synthesis[10,33,34] imply the incorporation of a macromolecule into the RAFT agent during the first synthesis step. Since RAFT agent synthesis generally involves three reaction steps, this renders purification of the macromolecular RAFT agent extremely difficult. However, in this paper a novel synthetic route towards *S*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamate RAFT agents is reported that allows the incorporation of macromolecules during the final reaction step. The third reason for choosing the *S*-alkyl-*N*,*N*-alkoxycarbonylmethyldithiocarbamate moiety is related to the synthesis of multifunctional RAFT agents: the classical synthetic routes towards RAFT agents generally involve low to medium yield reaction steps, which subsequently implies a low final yield. The synthetic route that is reported in this paper allows the synthesis of a linear, symmetrical multifunctional RAFT agent, via the step-growth polymerization principle.

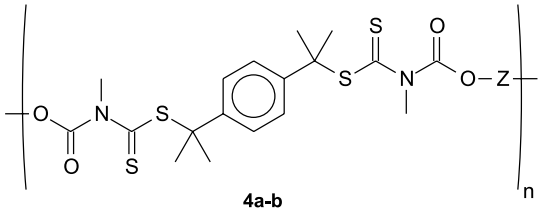
The RAFT agents that have been used in our study on the polymerization of acrylic monomers are depicted in Figure 2. Bifunctional RAFT agents **3** [*S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*,*N*-alkoxycarbonylmethyldithiocarbamate)] were synthesized because the mini-emulsion polymerization of acrylic monomers mediated with an *S*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamate RAFT agent has not yet been described. These polymerizations



3a-b

3a: Z = -$CH_2CH_2CH_2CH_3$

3b: Z = poly(ethylene-*co*-butylene)- (Kraton L1203)



4a-b

4a: Z = -$(CH_2)_{10}$-

4b: Z = -poly(ethylene-*co*-butylene)- (Kraton L2203)

Figure 2. Bi- and multifunctional *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamates studied in this work. Bifunctional RAFT agents **3**, with varying length of the Z group are used to study the viability of the *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamate moiety to control polymerization of various acrylates in solution and emulsion. RAFT agents **4**, either with a low molecular weight or a macromolecular Z group are studied on their ability to synthesize multiblock copolymers.

will be discussed in two forthcoming papers. Compounds **4** [poly(*S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*,*N*-alkoxycarbonylmethyldithio-carbamate))] are the multifunctional RAFT agents. The synthesis of multiblock copolymers with this compound will be discussed in two future papers. These compounds do not suffer from the disadvantages of the traditional RAFT agents. Whereas the more classical RAFT agents exhibit a dark red to pink color and an extremely bad smell, the *S*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamates described in this work are only slightly yellow and have a faint, sweet smell.

The novel, extremely versatile synthetic route is based on two bifunctional precursors, which upon condensation form the RAFT moiety. This approach avoids the cumbersome three-step reaction towards most RAFT agents and reduces the total number of synthetic steps needed. Moreover, this synthetic route allows the incorporation of a tertiary leaving group in high yield. The novel synthetic route is based on the route proposed by Allainmat et al.,[35] which implies the reaction of a chloroformate with a primary *S*-alkyl dithiocarbamate. This route is depicted in Figure 3, applied to the RAFT agents that have been synthesized in this work. Employing this route, the synthesis of a macromolecular or a multifunctional RAFT agent can be performed in a maximum of three convergent reaction steps: the synthesis of bifunctional dithiocarbamate **5**, the synthesis of chloroformates **6b** and **7a–b** (**6a**, that is, butyl chloroformate, is commercially available), and the (poly)condensation reaction of dithiocarbamate **5** with chloroformates **6a–b** or **7a–b**. Unfortunately, Allainmat et al.[35] only reported the use of primary *S*-alkyl dithiocarbamates, and not of tertiary *S*-alkyl dithiocarbamates in this synthetic route. In the following sections the syntheses of compound **5**, **6b** and **7a–b** are described in detail. Then, the synthetic route proposed by Allainmat et al.[35] is modified and applied to the synthesis of *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamates.

Two of the RAFT agents, of which the synthesis is described in this paper, are based on either Kraton® L-1203 or on Kraton® L-2203. Kraton is the trade name of fully hydrogenated, linear poly(butadiene), carrying primary hydroxyl groups on either one (L-1203) or both (L-2203) chain ends. The number average molar mass of both polymers, according to the manufacturer, is 4000 g mol^{-1}. Both non-crystalline Kraton grades have a glass transition temperature below −50 °C, and, because of their low molar masses, both compounds are viscous liquids.

2. Results and discussion

2.1. Synthesis of *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate)

For the synthesis of *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate), that is, compound **5**, the route reported by Monde et al.[36] was employed. Using this method, sodium alkylthiolate salts were reacted with various isothiocyanates, resulting in excellent yields while short reaction times were employed. To the best of our knowledge, however, no reports are available on the reaction of tertiary thiolate salts with isothiocyanates.

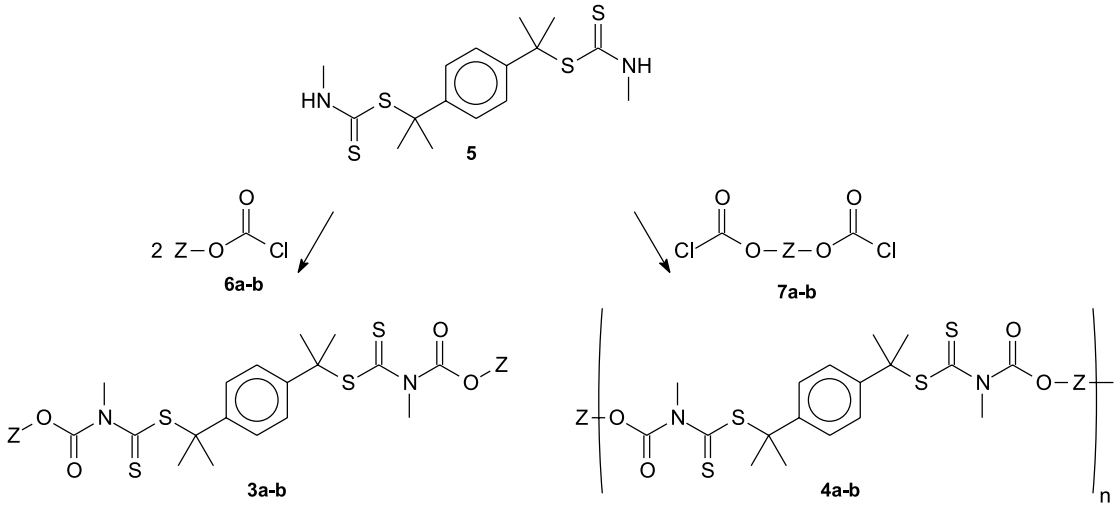


Figure 3. Allainmat's synthetic route applied to the RAFT agents that have been studied in this work. Bifunctional dithiocarbamate **5** is reacted with monofunctional chloroformate **6a–b** to form bifunctional RAFT agents **3a–b**. By using a bifunctional chloroformate **7a–b**, a polycondensation reaction of this compound with bifunctional dithiocarbamate **5** allows the synthesis of multifunctional RAFT agent **4a–b**.

However, we successfully modified Monde's route, thereby enabling it to synthesize tertiary *S*-alkyl dithiocarbamates. This method, however, requires the use of tertiary sodium thiolate salts. These compounds were synthesized according to the procedure reported by Lee et al.[37] This procedure involves the reaction of a tertiary alkyl alcohol with thiourea, and subsequent hydrolysis to form the sodium thiolate salt.

The entire synthetic route towards compound **5** is depicted in Figure 4. In the first reaction step, diol **8**, thiourea and hydrobromic acid were reacted according to the procedure reported by Lee et al.,[37] to form bifunctional dithiouronium salt **9**. The method reported by Lee et al.,[37] then implies the hydrolysis of bifunctional dithiouronium salt **9** to the dithiol with 2 equiv of aqueous sodium hydroxide. However, as was mentioned above, the route proposed by Monde et al.,[36] implies the addition of a sodium thiolate salt to an alkyl isothiocyanate. The tertiary dithiol, formed via Lee's procedure,[37] should therefore be hydrolyzed to dithiolate salt **10** in a separate reaction step. We found that it was also possible to hydrolyze dithiouronium salt **9** directly to dithiolate anion **10**, using 6 equiv of aqueous sodium hydroxide. Moreover, a methanolic solution of methyl isothiocyanate could be added to the dithiolate anion **10** solution without isolating the dithiolate sodium salt first. After addition of methyl isothiocyanate to the reaction mixture, dithiocarbamate **5** readily precipitated out of the solution and could be collected easily by filtration. After recrystallization, the product was pure and compound **5** was obtained in an overall yield of 60%. With this approach, we thus succeeded in reducing the number of reaction steps required for this synthesis from three to two.

2.2. Chloroformate synthesis

In this work, we opted for the use of a phosgene solution in toluene. To ensure safe reaction conditions, all reactions involving a phosgene solution were performed under strict exclusion of air by having a stream of argon passing through the reaction mixture at all times. All gases that left the reactor were passed through a solution of sodium hydroxide in order to destroy phosgene and hydrogen chloride passing along with the argon. Various mono- and bifunctional (macromolecular) alcohols were treated with a 20% phosgene solution in toluene. The reaction mechanism and the various synthesized chloroformates are depicted in Figure 5. It should be noted that the formation of the

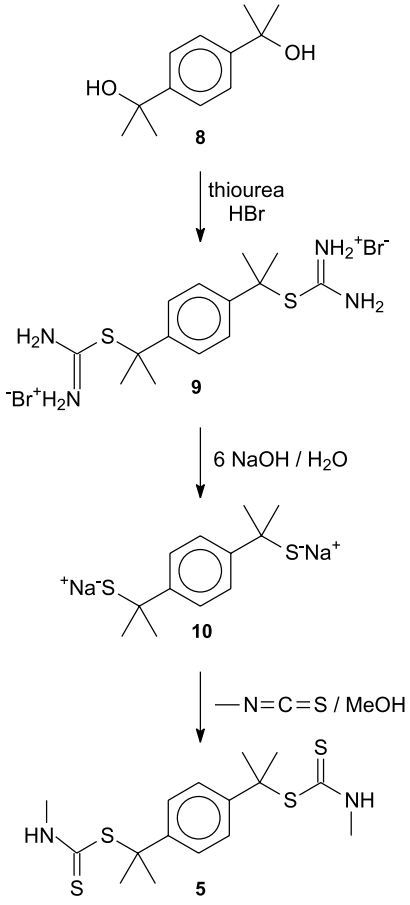


Figure 4. Novel synthetic route towards *S-tert*-alkyl-*N*-alkyldithiocarbamates.

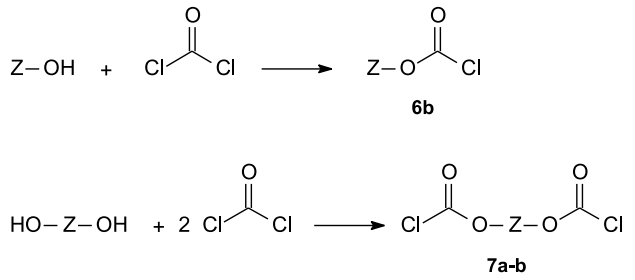


Figure 5. Chloroformate synthesis employing a 20% phosgene solution in toluene. A slight excess of phosgene must be used in order to prevent the reaction between the chloroformate and the alcohol to form a carbonate.

respective carbonates or polycarbonates, formed by a reaction of two alcohol molecules with one phosgene molecule, cannot be entirely avoided, since for safety reasons only a slight excess of phosgene was used. After the reaction, in all cases the yields were close to 100%. In the case of Kraton® chloroformate **6b**, a minor amount of di(Kraton®) carbonate was found after the reaction with GPC analysis. However, this is only a few percent, and could not be observed in the ^{1}H NMR and ^{13}C NMR spectra, due to the low end-group concentration in the sample. The reaction of various alcohols with a phosgene solution was performed with and without the use of a proton trap, but no differences could be observed in reaction yield or product purity.

2.3. Synthesis of *S*-alkyl-*N*,*N*-alkoxycarbonyl-methyldithiocarbamates

After describing the synthesis of all the required compounds for the (poly)condensation reaction between bifunctional dithiocarbamate **5** and various mono- and bifunctional chloroformates, we will focus on the condensation reaction itself. As was reported earlier, Allainmat et al., only used primary *S*-alkyl-*N*-alkyldithiocarbamates in this reaction.[35] Although not much difference in reactivity towards chloroformates was expected between primary and tertiary *S*-alkyl-*N*-alkyldithiocarbamates, we found that the reaction pathway did require some optimization, especially in the reaction of dithiocarbamate **5** with bifunctional chloroformates.

The synthetic route towards bifunctional *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylmethyl-dithiocarbamates is depicted schematically in Figure 6, together with the optimal reaction conditions. Dithiocarbamate **5** was reacted with monofunctional chloroformates **6a**–**b** to form bifunctional RAFT agents **3a**–**b**. In this reaction, triethylamine was used to trap the hydrogen chloride that is formed upon reaction. Triethylamine hydrochloride precipitated from the solution, thus forcing the reaction equilibrium towards the reaction products. The highest yield (85–90%) was obtained when performing the reaction at −20 °C in THF for 48 h, using 5 equiv of triethylamine as the proton trap. The remaining 10–15% of the obtained crude reaction mixture was compound **11a**–**b**, which resulted from addition of only one chloroformate molecule to dithiocarbamate **5**. The extended reaction times that were required can be explained by the fact that the reaction in Figure 6 proceeds via intermediate *N*-alkoxycarbonyl triethylammonium chloride, which is formed by the reaction of triethylamine with a chloroformate, and in which the carbonyl group is activated for reaction with **5**. The *N*-alkoxycarbonyl triethylammonium chloride salt is only moderately soluble in tetrahydrofuran, and precipitated partially out of the solution. This salt gradually redissolved and thus ensured complete reaction.

The full potential of the synthetic route introduced above is shown when it is applied to the synthesis of multifunctional RAFT agents. As was mentioned earlier, it is possible to synthesize multifunctional RAFT agents starting from *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) **5**, and bifunctional chloroformates **7a**–**b** via a polycondensation reaction. The reaction scheme is presented in Figure 7. In a first series of experiments, equimolar quantities of 1,4-butanediol bischloroformate

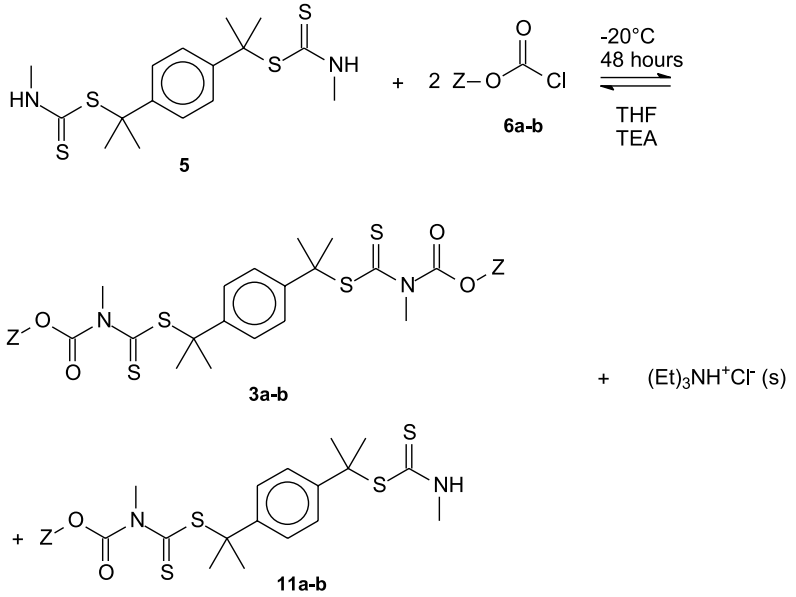


Figure 6. Synthesis of bifunctional RAFT agents. The reaction proceeds optimally when performed at −20 °C over 48 h, employing 5 equiv of the proton trap.

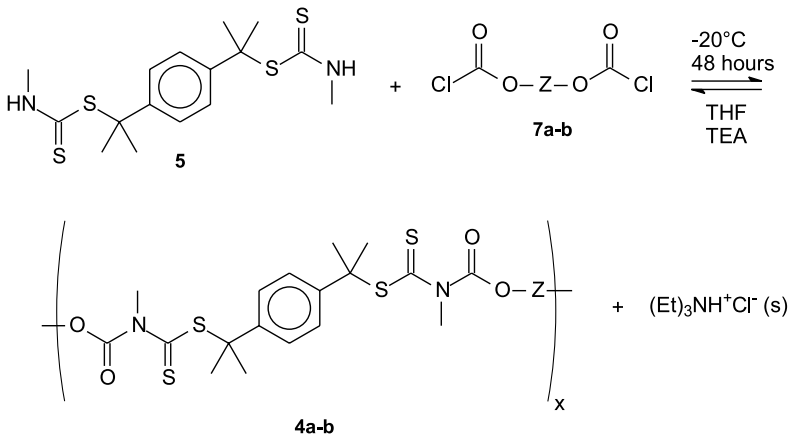


Figure 7. Synthesis of multifunctional RAFT agents. The reaction proceeds optimally when performed at −20 °C over 48 h, employing 5 equiv of the proton trap. However, the chain length of the Z group has a major influence on the conversion of the functional groups.

(commercially available) and bifunctional dithiocarbamate **5** were reacted at −20 °C, together with a sixfold excess of triethylamine. However, after 48 h, no reaction had taken place. Here, the bifunctional *N*-alkoxycarbonyl triethylammonium dichloride salt was formed as an intermediate of this reaction, but this compound was virtually insoluble in tetrahydrofuran. Thus, the reaction was fully inhibited, due to the absence of activated bischloroformate in the solution. However, by employing 1,10-decanediol bischloroformate **7a** instead, a polycondensation reaction occurred. In this reaction again the dichloride salt was formed, but in this molecule the *N*-alkoxycarbonyl triethylammonium moieties were further separated from each other, and the more apolar character of this compound enhanced its solubility in tetrahydrofuran. Therefore, solubility was less affected, and only partial precipitation took place. The dichloride salt derived from 1,10-decanediol bischloroformate **7a** gradually redissolved during the reaction, allowing the synthesis of a multifunctional RAFT agent.

In a similar fashion, macromolecular multifunctional RAFT agent poly(Kraton®-RAFT) was synthesized from Kraton® L-2203 bischloroformate **7b** and bifunctional dithiocarbamate **5**. Here also, a dichloride salt was formed upon reaction of Kraton® bischloroformate **7b** with triethylamine, but this was not a problem here, due to the small influence the end-groups had on the solubility of the macromolecule in the reaction medium.

3. Conclusions

Employing the RAFT process always implies the synthesis of the organic chain transfer agents that are necessary to mediate the RAFT polymerization. However, for the objective of this work, the classical synthetic routes towards RAFT agents were not useful. It was shown that there is one type of RAFT moiety which can be synthesized in a different way than the classical synthetic routes towards RAFT agents, allowing the introduction of a macromolecule in the chain, and allowing the synthesis of a multifunctional RAFT agent: the versatile *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamate moiety. We have successfully developed a two- or three-step synthetic route (depending on the targeted compound) towards these compounds, based on a procedure reported by Allainmat et al.[35] We have modified this procedure in such a way that it now allows the synthesis of *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylalkyldithiocarbamates. Also, we have developed a novel synthetic route towards *S*-*tert*-alkyl-*N*-alkyldithiocarbamates, as the synthetic routes reported in literature were only suitable for the synthesis of primary and secondary *S*-alkyl-*N*-alkyldithiocarbamates. This novel route successfully combines the synthetic route towards tertiary thiols reported by Lee et al.,[37] with the synthetic route towards primary *S*-alkyl-*N*-alkyldithiocarbamates reported by Monde et al.,[36] to synthesize *S*-*tert*-alkyl-*N*-alkyldithiocarbamates in two steps with a good overall yield. These compounds are intermediates in the synthesis of *S*-*tert*-alkyl-*N*,*N*-alkoxycarbonylmethyldithiocarbamates.

4. Experimental

4.1. Materials and methods

Thiourea, α,α,α′,α′-tetramethyl-1,4-benzenedimethanol, HBr 48% in water, sodium hydroxide, methylisothiocyanate, a 20% phosgene solution in toluene, 1,10-decanediol, triethylamine and *n*-butyl chloroformate were purchased from Aldrich, and were used as received. Kraton® L-1203 and L-2203 were purchased from Kraton BV, Amsterdam and were used as received. All solvents were purchased from Biosolve BV, and were dried and purified before use over a Grubbs apparatus, that is, an apparatus in which the solvent is passed under pressure over an alumina catalyst in order to dry and deoxygenate the solvent, except for methanol, which was used as received. Dichloromethane was used as received for column chromatography. All glassware was dried overnight at 150 °C before use, except in the synthesis of *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate).

NMR analysis was performed on a Varian Gemini-2000 300 MHz or a Varian Mercury-Vx 400 MHz spectrometer. Samples of the various compounds were dissolved in deuterated chloroform (Cambridge Isotope Laboratories).

GPC analysis was carried out using a Waters model 510 pump, a model 410 refractive index detector (at 40 °C) and a model 486 UV detector (at 254 nm) in series. Injections were done by a Waters model WISP 712 autoinjector, using an injection volume of 50 μL. The columns used were a PLgel guard (5 μm particles) 50×7.5 mm column, followed by two PLgel mixed-C or mixed-D (5 μm particles) 300×7.5 mm columns at 40 °C in series. Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 mL min^{-1}. Calibration has been done using polystyrene standards (Polymer Laboratories, $\bar{M}_n = 580$ to 7.1×10^6 g mol^{-1}). Data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software. Before injection, the samples were filtered over a 13 mm×0.2 μm PTFE filter, PP housing (Alltech).

HPLC-ESI MS analysis was carried out on an Agilent Technologies 1100 series system, using a G1311A quaternary pump, a G1313A autosampler, a G1315B UV-DAD detector at 254 nm and an Agilent MDS type SL G1946D mass spectrometer with atmospheric pressure electrospray ionization. All data were processed with HP Chemstation software. The column used was a Supersphere 100RP-18E; 150×3 mm; dp 4 μm (Bischoff) using a methanol (HPLC grade, Biosolve)/water 50:50 to methanol gradient in 25 min at a flow of 0.4 mL min^{-1} at 25 °C. Samples were dissolved in methanol (HPLC grade, Biosolve) at a concentration of 10 mg mL^{-1}. Typical injection volumes were 1 μL.

MALDI-TOF MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile, which was synthesized according to the procedure reported by Ulmer et al.[38] Sodium, potassium or lithium trifluoroacetate (Aldrich, 98%) was added to the compounds as cationic ionization agent at a typical concentration around 1 mg mL^{-1}. The matrix was dissolved in THF (Biosolve) at a concentration of 40 mg mL^{-1}. In a typical MALDI experiment, the matrix, salt and polymer solution were premixed in the ratio: 5 μL sample: 5 μL matrix: 0.5 μL salt. Approximately, 0.5 μL of the obtained mixture was hand spotted on the target plate. All the spectra were acquired on the Voyager DE-STR in the reflector mode.

4.1.1. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) (5). Thiourea (17.2 g, 0.23 mol) and α,α,α′,α′-tetramethyl-1,4-benzenedimethanol (20.0 g, 0.10 mol) were mixed and added slowly with stirring to HBr 48% (41.7 g, 0.25 mol) in a 250 mL flask. The slurry was heated to 50 °C with an oil bath for 5 min, after which the slurry solidified. The white solid was cooled down, filtered, washed with a 0.1 M aqueous HBr solution, and dried under vacuum. The solid was then crushed to powder. A solution of NaOH (24.7 g, 0.62 mol) in water (50 mL) was prepared in a 250 mL three-necked flask, and heated to 40 °C with an oil bath. The white powder was added to the NaOH solution and was left to stir at 40 °C for 2 h. After this, the solution had become clear and red. The solution was filtered over a Büchner funnel and the filtrate was transferred to a 250 mL three-necked flask under Ar atmosphere, equipped with a dropping funnel and a cooler, and the solution was cooled to 5 °C using an ice bath. Methyl isothiocyanate (15.8 g, 0.22 mol) was dissolved in the minimum amount of methanol needed, and this solution was added dropwise to the red thiolate solution. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) **5** readily precipitated out as a white solid. The resulting slurry was left to stir for 1 h to ensure complete reaction, and was then filtered over a Büchner funnel and washed with cold water. The white solid was recrystallized twice from ethanol and dried under vacuum. The overall yield was 60%. ^{1}H NMR: δ 1.83 (s, 12H, C–(CH_3)$_2$), 2.95 (d, J=4.7 Hz, 6H, NH–CH_3), 6.65 (s broad, 2H, N–*H*), 7.64 (s, 4H, aromatic H). ^{13}C NMR: δ 29.92 (C–CH_3), 33.18 (NH–(CH_3)$_2$), 54.37 (C–(CH_3)$_2$), 127.27 (aromatic, 2-, 3-, 5-, 6-C), 143.96 (aromatic, 1-, 4-C), 196.01 (C=S). LC–MS (ESI): m/z calcd for $(M+Na)^+$ $C_{16}H_{24}N_2S_4Na$ 395.07; found 395.01.

4.1.2. Kraton® chloroformate (6b). A 250 mL three-necked flask was equipped with a stirrer, a 100 mL dropping funnel with stopper and 2 septa equipped with needles. The flask was placed under Ar atmosphere through the first septum, and the second septum was connected to a washing bottle containing a 1 M aqueous NaOH solution, to destroy all phosgene escaping from the reaction vessel. Phosgene solution (2.5 g, 5.2 mmol) was injected into the flask through the septum, using a 10 mL syringe. The flask was then cooled to 0 °C with an ice bath. Monohydroxyfunctional Kraton® L-1203 ($\bar{M}_n = 4000$ g mol^{-1}, 20.0 g, 5 mmol) was dissolved in toluene (30 mL) and the solution was brought into the dropping funnel, and slowly added to the phosgene solution. The mixture was left to stir at 0 °C for 4 h. The mixture was then purged with Ar for 2 h to remove the excess phosgene. Toluene was removed under reduced pressure. Kraton® chloroformate was used without further purification. Yield 98% (calculated from ^{1}H NMR). ^{1}H NMR: δ (ppm) 0.80–1.80 (m, polymer chain H), 4.36 (t, J=7.0 Hz, –CH_2–O(CO)Cl). ^{13}C NMR: δ 10.60–39.20 (polymer chain C), 71.16 (–CH_2–O(CO)Cl), 151.10 (C=O).

4.1.3. 1,10-Decanediol bischloroformate (7a). A 250 mL three-necked flask was equipped with a stirrer, a 100 mL dropping funnel with stopper and 2 septa equipped with needles. The flask was placed under Ar atmosphere through the first septum, and the second septum was connected to a washing bottle containing a 1 M aqueous NaOH solution, to destroy all phosgene escaping from the reaction vessel. Phosgene solution (33.0 g, 67 mmol) was injected into the flask through the septum, using a 50 mL syringe. The flask was then cooled to 0 °C with an ice bath. 1,10-Decanediol (5.8 g, 33 mmol) was dissolved in a minimum amount of THF and the solution was brought into the dropping funnel, and slowly added to the phosgene solution. The mixture was left to stir at 0 °C for 4 h. The mixture was then purged with Ar for 2 h to remove the excess phosgene. Toluene was removed under reduced pressure. 1,10-Decanediol bischloroformate was used without further purification. Yield 98% (calculated from ^{1}H NMR). ^{1}H NMR: δ 1.20–1.90 (m, –CH_2–(CH_2)$_8$–CH_2–), 4.38 (t, J=6.7 Hz, –CH_2–(CH_2)$_8$–CH_2–). ^{13}C NMR: δ 25.36–29.13 (–CH_2–(CH_2)$_8$–CH_2–), 72.22 (–CH_2–(CH_2)$_8$–CH_2–), 150.44 (C=O).

4.1.4. Kraton® bischloroformate (7b). A 250 mL three-necked flask was equipped with a stirrer, a 100 mL dropping

funnel with stopper and 2 septa equipped with needles. The flask was placed under Ar atmosphere through the first septum, and the second septum was connected to a washing bottle containing a 1 M aqueous NaOH solution, to destroy all phosgene escaping from the reaction vessel. Phosgene solution (5.4 g, 11 mmol) was injected into the flask through the septum, using a 10 mL syringe. The flask was then cooled to 0 °C with an ice bath. Bishydroxyfunctional Kraton® L-2203 ($\bar{M}_n = 4000$ g mol^{-1}, 20.0 g, 5 mmol) was dissolved in toluene (30 mL) and the solution was brought into the dropping funnel, and slowly added to the phosgene solution. The mixture was left to stir at 0 °C for 4 h. The mixture was then purged with Ar for 2 h to remove the excess phosgene. Toluene was removed under reduced pressure. Kraton® bischloroformate was used without further purification. Yield 98% (calculated from ^{1}H NMR). ^{1}H NMR: δ 0.80–1.80 (m, polymer chain H), 4.36 (t, $J=7.0$ Hz, –CH_2–O(CO)Cl). ^{13}C NMR: δ 10.60–39.20 (polymer chain C), 71.16 (–CH$_2$–O(CO)Cl), 151.10 (C=O).

4.1.5. Butyl-RAFT agent (3a). Butyl-RAFT agent will be further used as the common name for *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*,*N*-butoxycarbonylmethyldithiocarbamate).

N-Butyl chloroformate (3.1 g, 23 mmol) was dissolved in THF (10 mL) in a 100 mL double enveloped flask, equipped with a stirrer and a 50 mL dropping funnel, and placed under Ar atmosphere. The mixture was cooled to −20 °C using a cryostate. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) (4.0 g, 11 mmol) and triethylamine (5.4 g, 54 mmol) were dissolved in a minimum amount of THF. This solution was added dropwise to the *n*-butyl chloroformate solution with stirring. This mixture was left to stir at −20 °C for 48 h, after which the mixture was brought to room temperature. Triethylamine hydrochloride was filtered off, and THF was removed under reduced pressure. The resulting yellow oil was purified by column chromatography using dichloromethane as the eluent and yielded butyl-RAFT **3a** as a yellow solid. Yield 85%. ^{1}H NMR: δ 0.92 (t, $J=7.3$ Hz, 6H, –CH_2–CH_2–CH_2–CH_3), 1.43 (m, 4H, –CH_2–CH_2–CH_2–CH_3), 1.70 (m, 4H, –CH_2–CH_2–CH_2–CH_3), 1.88 (s, 12H, C–$(CH_3)_2$), 3.51 (s, 6H, N–CH_3), 4.26 (t, $J=6.6$ Hz, 4H, –CH_2–CH_2–CH_2–CH_3), 7.40 (s, 4H, aromatic H). ^{13}C NMR: δ 13.64 (–CH_2–CH_2–CH_2–CH_3), 19.12 (–CH_2–CH_2–CH_2–CH_3), 28.83 (C–$(CH_3)_2$), 30.52 (–CH_2–CH_2–CH_2–CH_3), 38.35 (C–$(CH_3)_2$), 56.15 (N–CH_3), 67.42 (–CH_2–CH_2–CH_2–CH_3), 126.05 (aromatic, 2-, 3-, 5-, 6-C), 142.84 (aromatic, 1-, 4-C), 153.97 (C=O), 202.97 (C=S). LC–MS (ESI): *m*/*z* calcd for $(M+Na)^+$ $C_{26}H_{40}N_2S_4O_4Na$ 595.84; found 595.76. HRMS (MALDI-TOF MS): *m*/*z* calcd for $(M+K)^+$ $C_{26}H_{40}N_2S_4O_4K$ 611.151; found 611.135.

4.1.6. Kraton®-RAFT agent (3b). Kraton®-RAFT agent will be further used as the common name for *S*-(1,4-phenylenebis(propane-2,2-diyl)) bis(*N*,*N*-Kratoncarbamoylmethyldithiocarbamate).

Kraton® chloroformate (20.0 g, 5 mmol) was dissolved in THF (30 mL) in a 250 mL double enveloped flask, equipped with a stirrer and a 50 mL dropping funnel, and placed under Ar atmosphere. The mixture was cooled to −20 °C using a cryostate. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) (0.9 g, 2.5 mmol) and triethylamine (1.3 g, 13 mmol) were dissolved in a minimum amount of THF. This solution was added dropwise to the Kraton® chloroformate solution with stirring. This mixture was left to stir at −20 °C for 48 h, after which the mixture was brought to room temperature. Triethylamine hydrochloride was filtered off, and THF was removed under reduced pressure. Yield 86%. The resulting yellow viscous oil was not further purified and was used as such in polymerizations. ^{1}H NMR: δ 0.80–1.80 (m, polymer chain H), δ 1.96 (s, 12H, C–$(CH_3)_2$), 3.57 (s, 6H, N–CH_3), 4.35 [t, $J=6.9$ Hz, 4H, –O–CH_2–), 7.47 (s, 4H, aromatic H). ^{13}C NMR: δ 10.24–38.77 (polymer chain C, C–$(CH_3)_2$), 56.20 (N–CH_3), 67.78 (–O–CH_2–), 126.10 (aromatic, 2-, 3-, 5-, 6-C), 142.84 (aromatic, 1-, 4-C), 153.98 (C=O), 206.22 (C=S).

4.1.7. Poly(decyl-RAFT) agent (4a). Poly(decyl-RAFT) agent will be further used as the common name for poly(*S*-1,4-phenylenebis(propane-2,2-diyl)) bis(*N*,*N*-1,10-decoxycarbonylmethyl-dithiocarbamate)).

1,10-Decanediol bischloroformate (2.3 g, 11 mmol) was dissolved in THF (10 mL) in a 100 mL double enveloped flask, equipped with a stirrer and a 50 mL dropping funnel, and placed under Ar atmosphere. The mixture was cooled to −20 °C using a cryostate. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) (4.0 g, 11 mmol) and triethylamine (6.7 g, 66 mmol) were dissolved in the minimum amount of THF. This solution was added dropwise to the 1,10-decanediol bischloroformate solution with stirring. This mixture was left to stir at −20 °C for 48 h, after which the mixture was brought to room temperature. Triethylamine hydrochloride was filtered off, and THF was removed under reduced pressure. The resulting viscous yellow oil was further purified by preparative SEC. Yield 70%. ^{1}H NMR: δ 1.20–2.10 (m, –CH_2–$(CH_2)_8$–CH_2–, C–$(CH_3)_2$), 3.51 (s, N–CH_3), 4.25 (t, $J=7.0$ Hz, –CH_2–$(CH_2)_8$–CH_2–), 7.40 (s, aromatic H). ^{13}C NMR: δ 22.63–32.42 (–CH_2–$(CH_2)_8$–CH_2–, C–$(CH_3)_2$), 38.37 (C–$(CH_3)_2$), 56.14 (N–CH_3), 67.39 (–CH_2–$(CH_2)_8$–CH_2–), 126.38 (aromatic, 2-, 3-, 5-, 6-C), 142.97 (aromatic, 1-, 4-C), 154.07 (C=O), 203.12 (C=S). GPC (before purification): $\bar{M}_n = 1800$ g mol^{-1}, PDI = 1.80. GPC (after purification and isolation of the high molecular weight fraction): $\bar{M}_n = 3700$ g mol^{-1}, PDI = 1.59.

4.1.8. Poly(Kraton®-RAFT) agent (4b). Poly(Kraton®-RAFT) agent will be further used as the common name for poly(*S*-(1,4-phenylenebis (propane-2,2-diyl)) bis(*N*,*N*-Kratoncarbamoylmethyldithiocarbamate)).

Kraton® bischloroformate (4.0 g, 1 mmol) was dissolved in THF (20 mL) in a 100 mL double enveloped flask, equipped with a stirrer and a 50 mL dropping funnel, and placed under Ar atmosphere. The mixture was cooled to −20 °C using a cryostate. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) (0.37 g, 1 mmol) and triethylamine (0.51 g, 5 mmol) were dissolved in a minimum amount of THF. This solution was added dropwise to the Kraton® chloroformate solution with stirring. This mixture was left

to stir at −20 °C for 48 h, after which the mixture was brought to room temperature. Triethylamine hydrochloride was filtered off, and THF was removed under reduced pressure. Yield 80% (GPC). The resulting yellow oil was not further purified and was used as such in polymerizations. ^{1}H NMR: δ 0.80–1.80 (m, polymer chain H), 1.95 (s, 12H, C–(CH_3)$_2$), 3.59 (s, 6H, N–CH_3), 4.36 (t, J=7.0 Hz, 4H, –O–CH_2–), 7.45 (s, 4H, aromatic H). ^{13}C NMR: δ 10.20–38.70 (polymer chain C, C–(CH_3)$_2$), 56.21 (N–CH_3), 67.83 (–O–CH_2–), 126.08 (aromatic, 2-, 3-, 5-, 6-C), 142.84 (aromatic, 1-, 4-C), 153.95 (C=O), 206.18 (C=S). GPC: $\bar{M}_n = 21,600$ g mol^{-1}, PDI=1.60.

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