Fast and Complete Neutralization of Thiocarbonylthio Compounds Using Trialkylborane and Oxygen: Application to Their Removal from RAFT-Synthesized Polymers

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S Supporting Information

ABSTRACT: A rapid and efficient method to remove thiocarbonylthio end groups from polymers prepared by reversible addition–fragmentation chain transfer (RAFT) is described. The elimination process is obtained in less than 1 min by treating the solution of RAFT-synthesized polymers with 5 equiv of trialkylborane (TAB) in the presence of oxygen under an ambient temperature. The versatility of this method was checked on the most relevant families of thiocarbonylthio chain transfer agents (CTA), including dithioesters, trithiocarbonates, dithiocarbamates, and xanthates, carried by the corresponding RAFT-synthesized polymers. UV, NMR, and MALDI-TOF MS characterization results all confirm the complete removal of their terminal CTA groups.

Reversible addition–fragmentation chain transfer (RAFT) is one of the most versatile controlled/living radical polymerization techniques;¹ it enables the controlled synthesis of a wide range of homo/copolymers with various functionalities and architectures.^{2–4} In RAFT polymerizations, the growing macroradical undergoes repeatedly degenerate transfer in the presence of thiocarbonylthio chain transfer agents (CTA), such as dithioesters (DTE), trithiocarbonates (TTC), dithiocarbamates (DTC), and xanthates (XAN), becoming dormant before being active again upon activation by another entering radical. Although these groups are responsible for the controlled/living growth of the chains, their presence in service conditions for commercial applications is often undesirable as they impart to the polymers that carry them their color and toxicity. The elimination of these thiocarbonylthio moieties and their related toxic sulfur residues entails an extra cost that has been in some instances a real obstacle for the commercialization of the RAFT technology.^{5,6} Several strategies have been considered to remove these sulfur-containing end groups from the RAFT-prepared polymers.^{7–9} As summarized in Scheme 1A, these groups can be displaced by nucleophilic,^{10–12} Diels–Alder,¹³ and radical-induced reactions,^{14–26} as well as by thermolysis.^{27–30} The first two methodologies do not result in the desulfurization of the polymer, but in the transformation of the end groups into other sulfur-containing functional groups, which may serve for further reactions. Thermolysis appears to be a powerful method for a complete end-group removal, but it necessitates high temperatures (120–200 °C) and a long time, and it results in unsaturated end groups that may further undergo side reactions.²⁸

Radical-induced reactions also provide an effective and complete elimination of the thiocarbonylthio end groups, as detailed in Scheme 1B; the radicals generated from AIBN,^{15–17} hydrogen peroxide,²³ elemental Fe or Cu,^{31,32} alkoxyamine,¹⁹ or light^{24–26} induce the cleavage of the C–S bond upon addition to the thiocarbonylthio end group. In most cases, H-donor additives, such as tributyltin hydride,³³ tris(trimethylsilyl)silane,¹⁸ and N-ethylpiperidine hypophosphite,²⁶ had to be added to promote the cleavage reaction and generally require either high temperature or a long reaction time to achieve the end group removal from the RAFT-synthesized polymers.

In this Letter, we unveil a simple, highly efficient, and almost instantaneous procedure to remove the thiocarbonylthio end groups from RAFT-synthesized polymers using trialkylborane (TAB) in open air (O₂). The method described here (Scheme 2) is actually applicable to all families of RAFT-synthesized polymers, unlike some of the methods reported before. In fact, TAB has long been known to be a radical generator in radical polymerization^{34,35} when used in conjunction with O₂: using TAB/O₂ free radicals can be generated at any temperature. Recently Pan,³⁶ Magenau,³⁷ and their co-workers utilized the TAB/O₂ system to initiate RAFT polymerization. The same TAB/O₂ system is leveraged in this work to neutralize the terminal CTA groups after the completion of RAFT-controlled polymerizations. Our discovery takes advantage of the unique property of TAB to react with O₂ and generate very reactive

Received: May 15, 2019

Accepted: May 20, 2019

Scheme 1. Main Reported Processes of RAFT End-Group Removal or Transformation (A), and RAFT End-Group Removal Based on Radical-Induced Reactions (B)

Scheme 2. Synthesis of RAFT Polymers and the Removal of the Respective End Groups from PMMA-DTE, PS-TTC(CN), PMA-TTC(CO₂H), PVAc-DTC, and PNVP-XAN

alkyl free radicals, which in turn add to the thiocarbonylthio (DTE, TTC, DTC, or XAN) end groups carried by RAFT-synthesized polymers and remove them from the main chain in just seconds and at room temperature. The simplest TAB, triethylborane (TEB), was first utilized to test the efficiency of end group removal from RAFT-synthesized polymers. PMMA-DTE was first synthesized by RAFT polymerization with 2-cyano-2-propyl benzodithioate as transfer agent and AIBN as radical generator. After completion of the polymerization, 5 equiv of TEB were added into the pink solution of PMMA-DTE in the presence of O₂. The strong pink color, typical of the DTE end group, gradually became lighter and

totally faded in less than 1 min (see the [video in SI](#)). After precipitation, the white recovered polymer treated by TEB/O₂ (denominated as PMMA-T) was submitted to UV–visible, ¹H NMR, and MALDI-TOF MS characterization. The strong UV–visible signal at 309 nm, due to the DTE group, totally disappeared after treatment, indicating the complete removal of DTE (Figure 1A). The ¹H NMR spectra also confirm the

Figure 1. (A) UV–vis absorption spectra and (B) ¹H NMR spectra of PMMA-DTE before and after treatment with TEB and O₂.

disappearance of the terminal DTE group, as no signal due to the aromatic protons could be seen in the spectrum of the PMMA-T sample (Figure 1B), which is consistent with UV spectroscopic results. As for the GPC analysis of PMMA-T, it exhibits exactly the same profile of molar mass and polydispersity as that of the PMMA-DTE precursor (Figure S1A, entry 1, in Table 1). These results suggest that, during the TEB/O₂ treatment, the original polymer backbone was untouched and chain–chain couplings did not occur.

To identify the group standing at the chain-end after the TEB/O₂ treatment, PMMA-DTE and PMMA-T were characterized by MALDI-TOF MS mass spectrometry. In the case of PMMA-DTE (Figure 2A), the main population is fitted with a DTE group, and its main peak shows a molar mass of 5047 (*m/z*) corresponding to (100.12)₄₈ + 221.34 + 23, where 100.12, 221.34, and 23 are the molar mass values of the PMMA monomeric unit, of DTE, and of sodium, respectively. A small population not capped with DTE (PMMA-H) is also detected, with a main peak of molar mass 5096 (*m/z*) corresponding to the following structure: (100.12)₅₀ + 68.10 + 1 + 23, where 100.12 represents the molar mass of the PMMA monomeric unit, 68.10 is that of 2-cyanoprop-2-yl, 1 being the mass of hydrogen, and 23 is that of the sodium. An incomplete

Table 1. Results of Radical-Induced Reaction of RAFT-Synthesized Polymers with Trialkylborane and O₂

entry	RAFT-synthesized polymer ^a	[RAFT polymer]/[TAB] ^c	solvent	M_n ($\times 10^3$)/PDI ^b	M_n ($\times 10^3$)/PDI after treatment	M_p (MALDI-TOF)		end group removal ^d	content of P-H ^e (%)
						before	after		
1	PMMA-DTE	1:5 (TEB)	THF	5.2/1.18	5.1/1.24	5147	5095	complete	81.0
2	PMMA-DTE	1:5 (TEB)	THF	26.2/1.10	25.5/1.17			complete	
3	PS-TTC(CN)	1:5 (TEB)	THF	3.0/1.15	3.4/1.25	2941	2497 4994	complete	13.0
4	PMA-TTC(CO ₂ H)	1:5 (TEB)	THF	5.4/1.14	5.7/1.21	4778	4415	complete	49.7
5	PVAc-DTC	1:5 (TEB)	THF	5.8/1.22	5.9/1.26	4292	3938	complete	78.1
6	PNVP-XAN	1:5 (TEB)	THF	8.6/1.20 ^f	9.2/1.24 ^f	2790	2789	complete	63.3
7	PMMA-DTE	1:5 (TBB)	THF	5.2/1.15	5.1/1.22	4653	4402	complete	34.0
8	PMMA-DTE	1:5 (TiBB)	THF	5.2/1.15	5.2/1.18	4845	4694	complete	45.1
9	PMMA-DTE	1:5 (TEB)	toluene	5.0/1.18	5.3/1.21	4652	4298	complete	51.9
10	PMMA-DTE	1:5 (TEB)	benzene	5.0/1.18	5.3/1.20	4652	4498	complete	52.8

^aPMMA-DTE: poly(methyl methacrylate) with a dithiobenzoate; PS-TTC(CN): poly(styrene) with trithiocarbonate; PMA-TTC(CO₂H): poly(methyl acrylate) with trithiocarbonate; PVAc-DTC: poly(vinyl acetate) with dithiocarbamate; PNVP-XAN: poly(vinylpyrrolidone) with xanthate. ^bDetermined by GPC using tetrahydrofuran as the eluent and polystyrene as the standard. ^cThe TAB treatment with RAFT polymer were performed at 25 °C for 1 min. TEB: triethylborane; TBB: tributylborane; TiBB: triisobutylborane. ^dThe extent of end group removal is characterized by ¹H NMR, MALDI-TOF MS, and UV–visible spectroscopy. ^eEstimated by MALDI-TOF MS spectrometry. ^fDetermined by GPC using DMF as the eluent and polystyrene as standard.

Figure 2. MALDI-TOF MS spectra of RAFT synthesized polymer PMMA-DTE before (A) and PMMA-T after TEB/O₂ treatment (B).

showed an increased thermal stability whose degradation starts only above 180 °C. In contrast, PMMA-DTE exhibits initial degradation at 84 °C, losing up to 15 wt % at 180 °C.

After succeeding to remove the DTE group from the RAFT-synthesized PMMA, we prepared four other polymer samples by the RAFT methodology using three different type of CTAs, each of them suited to the monomer to polymerize: polystyrene, poly(methyl acrylate), poly(vinyl acetate), and poly(vinylpyrrolidone) samples were thus derived using TTC(CN) [PS-TTC(CN)], TTC(CO₂H) [PMA-TTC(CO₂H)], DTC (PVAc-DTC), and XAN (PNVP-XAN) as RAFT agents (Scheme 2). These different CTAs are indeed reported to allow excellent control of molar mass and to afford samples of narrow polydispersity for these four families of polymers (Table 1). The same reaction conditions, as those described above, were applied to check the versatility of TEB-oxygen based chemistry for chain end removal. In all cases, the color of the solutions submitted to TEB/O₂ treatment disappeared in less than 1 min as in the PMMA-DTE case after treatment with TEB in the presence of air. All the recovered polymers were respectively characterized by UV, NMR, GPC, MALDI-TOF MS, and the results are summarized in Table 1. Based on the full characterization data provided in Table S1 and Figures S2–S6, the end terminal CTA groups were totally removed in all cases, and colorless polymers were eventually isolated. Except for PS-T, all samples maintain their original molar mass distributions.

In the case of PS-T, a high molar mass bump is indeed seen in the GPC traces (entry 3, Table 1 and Figure S2B), corresponding to the double of the original molar masses which was also detected by MALDI-TOF MS (Figure S6); this is indicative of the occurrence of some polymer–polymer coupling during TEB/O₂ treatment. Indeed, more stable secondary polystyrene radicals are known to undergo such polymer–polymer coupling, unlike tertiary methacrylate radicals. Besides the peak due to PS–PS coupling (m/z 4994), the MALDI-TOF MS spectrum of PS-T shows three other populations: (1) PS-CH₂CH₃ (m/z 2913), (2) PS-OO-CH₂CH₃ (m/z 2930), and (3) PS-H (m/z 2981), which

correspond to (1) the recombination of Et[•] radicals with PS[•] radicals, (2) the recombination of the peroxy radical with the PS[•] radical, and (3) the dismutation of PS[•] with the above radicals, respectively. In contrast the MALDI-TOF MS spectrum of PS-TTC(CN) exhibited only one single population, the peak at 2941 (*m/z*) representing the expected PS terminated with TTC(CN) group. As for the MALDI-TOF MS spectrum (Figure S3C) of PMA-TTC(CO₂H) prepared with a similar TTC-type transfer agent –TTC(CO₂H)–, two main populations corresponding to PMA chains terminated with TTC(CO₂H) (*m/z* 4778, PMA-TTC-CO₂H) and its sodium salt (*m/z* 4800, PMA-TTC-CO₂Na), along with a minor population of deactivated terminal hydrogen (*m/z* 4846, PMA-H) can be seen. After treatment with TEB/O₂, the MALDI-TOF MS spectrum of the obtained PMA-T three populations similar to those of PS-T afforded the following (Figure S3D): PMA-CH₂CH₃ (*m/z* 4788), PMA-OO-CH₂CH₃ (*m/z* 4820), and PMA-H (*m/z* 4845). In the case of PVAc-DTC, the MALDI-TOF MS spectrum shows two populations, a major one filled with the DTC end group (*m/z* 4206, Figure S4C) and a minor one terminated with a (CH₃)₂-C-CN (initiating fragment from AIBN) and H at two ends (*m/z* 4139, NC-C(CH₃)₂-PVAc-H). After TEB/O₂ treatment, the PVAc-T submitted in MALDI-TOF MS analysis showed one main population confirming the complete removal of the DTC thiocarbonylthio group (*m/z* 4197, PVAc-H, Figure S4D), and one minor population corresponding to the recombination of the polymeric radical PVAc[•] with the ethyl radical (*m/z* 4224, PVAc-CH₂-CH₃). Finally, in the case of PNVP-XAN, the MALDI-TOF MS spectrum (Figure S5C) exhibits two main populations corresponding to the following two structures: PNVP-XAN (*m/z* 2798) and PNVP-H (*m/z* 2790). After TEB/O₂ treatment the MALDI-TOF MS spectrum of resulting polymer showed one major population corresponding to PNVP-H (*m/z* 2789, Figure S5D) and one small population corresponding to the coupling of the polymeric radical PNVP[•] with ethyl radical: PNVP-CH₂-CH₃ (*m/z* 2819).

One additional experiment was carried out with a high molar mass sample PMMA-DTE (25.5 kg/mol, entry 2 in Table 1) to check the validity and efficiency of this method of neutralization of thiocarbonylthio end groups over a large spectrum of molar masses. As shown in ¹H NMR and UV characterization results DTE group is completely removed from the PMMA sample of 25.5 kg/mol (Figure S7).

All the cleavage reactions described above were carried out in THF and in the absence of H-donor additives; on the hand THF is known to behave as a H-donor under certain conditions.¹⁶ Intrigued by the fact that all of our cleavage experiments resulted in the formation of mostly H-terminated chains and to a lesser extent of chains fitted with Et and EtOO moieties, generated by recombination with the corresponding radicals, we tried other TABs than TEB and thus used tributylborane (TBB) and triisobutylborane (TiBB) as cleaving agents in the presence of O₂.

PMMA-DTE served as a model for this part of the investigation, which was carried out under conditions similar to those used with TEB (entries 7 and 8 in Table 1). Interestingly, the rate of decoloration was even faster than that observed with TEB, following this order: TiBB > TBB > TEB. The complete cleavage and the terminal functionalities after treatment of TiBB and TBB were further characterized by MALDI-TOF MS spectrometry. As shown in Figure S8A,B, in both cases, the major population formed is the H-terminated

PMMA-H, along with two minor PMMA populations resulting from recombination of PMMA[•] with iBu[•] or Bu[•]. We then wondered whether the formation of H-terminated PMMA chains could be due to the involvement of THF as H-donor. Two cleavage experiments (entries 9 and 10 in Table 1) were thus carried out in benzene²⁷ and toluene^{18,26} to check the above hypothesis. As seen in Figure S8C,D, the results obtained were essentially the same as those generated in THF, PMMA-H being by far the major population of cleaved chains.

Based on this last result and also the above thorough characterization, especially by MALDI-TOF MS, a straightforward elimination mechanism of CTA using TEB-oxygen is proposed in Scheme 3. In the presence of O₂, TEB undergoes

Scheme 3. Plausible Mechanism of RAFT End Group Removal Using TEB and O₂

autooxidation and produces an ethyl radical (Et[•]) and boron peroxy radical (Et₂BOO[•]).^{36,37,39} The highly active Et[•] radical immediately adds to the –C=S bond of the thiocarbonyl group (1) to generate an intermediate that undergoes fragmentation and produces a polymer radical (2) and a new thiocarbonylthio compound (3). Most of these polymeric radicals P[•] undergo either disproportionation upon reaction with the Et[•] radical to form P–H (5) or recombination with Et[•] and with the peroxy radical EtOO[•] to form P–Et (5') and P–OOEt (5'') as minor populations. The role of THF as the H-donor can thus be excluded since very similar results were obtained in benzene and toluene (entries 9 and 10 in Table 1). For clarifying the disproportionation reaction between polymeric radical and ethyl radical, one cleavage experiment was intentionally carried out in a Young's NMR tube to avoid the evolution of any gaseous product. Indeed, as shown in Figure S9, the disproportionation product, ethylene, is unambiguously detected at 5.31 ppm in the mixture of PMMA-DTE treated with TEB/O₂. In the case of PS-CTA, some PS–PS coupling is also observed (6) due to the recombination of two PS[•]. As for the thiocarbonylthio compound (3) formed upon cleavage from the initial polymer, it undergoes a radical-induced oxidation in the presence of peroxy radical EtOO[•], yielding thioesters (4), a colorless stable sulfur compound.⁴⁰ The formation of such thioesters was further confirmed by GC-MS analysis (Figure S10). In this method, the alkyl radicals generated through autooxidation of TAB first cleave the bond between the polymer and the thiocarbonylthio group, inducing the reaction between the

polymeric radicals produced and the continuous flow of Et[•] and EtOO[•] radicals. The latter reactions result in either disproportionation or recombination as shown by MALDI-TOF MS.

In attempt to obtain exclusively H-terminated polymers a very similar experiment using PMMA-DTE as model was carried out in the presence of tributyltin hydride,³³ which is a well-known H-donor additive. As shown in Figure S11, PMMA-H is the sole formed population in contrast to the case where no H-donor was added, which produced a mixture of three populations of PMMA (PMMA-H, PMMA-Et, and PMMA-OOEt).

In summary, we established a very simple, fast, and efficient method based on TAB/O₂ for the removal of thiocarbonylthio end groups without altering the polymer carrying such end groups. Thanks to the high reactivity of alkyl radicals produced by autoxidation of TAB, this process can indeed completely knock out all types of CTA end groups from RAFT-synthesized polymers in seconds and under mild conditions; in the additional presence of H-donors, only H-terminated polymers are produced. We expect that this method, which can be applied after completion of any RAFT polymerization, be it in solution, emulsion, or suspension, will remove the remaining obstacles for the industrial development of this valuable controlled polymerization technique.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00357.

Experimental details and additional characterization data, including Table S1 and Figures S1–S11 (PDF)

Supporting video (MP4)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research work is supported by KAUST under baseline funding (BAS/1/1374-01-01).

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