Thermolysis of RAFT-Synthesized Polymers. A Convenient Method for Trithiocarbonate Group Elimination

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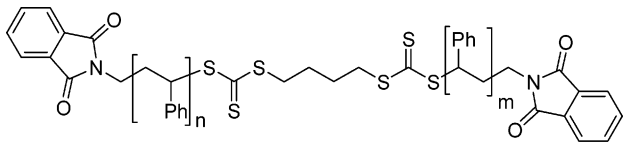
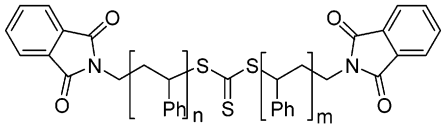
Radical polymerization with thiocarbonylthio RAFT (reversible addition-fragmentation chain transfer) agents[1−4] is arguably one of the most versatile processes for living free radical polymerization displaying superior flexibility with respect to monomers and reaction conditions. A key feature of RAFT polymerization is that the thiocarbonylthio group(s), present in the initial RAFT agent, is (are) retained in the polymeric product(s). The retention of these groups is responsible for the polymers' living character. However, the presence of the thiocarbonylthio groups also means that the polymers are usually colored. The polymers may also, in some cases, be odorous or release an odor over time due to decomposition of the thiocarbonylthio groups and the evolution of volatile sulfur-containing compounds. The presence of such color and odor can be disadvantageous in some applications. Even though some of these issues may be largely mitigated or overcome by more appropriate selection of the initial RAFT agent, there has nonetheless been some incentive to develop effective methods for treatment of RAFT-made polymers to cleave the thiocarbonylthio end-groups postpolymerization.

A variety of methods for removing the thiocarbonylthio groups have been reported. These include radical-induced reduction (to provide a hydrocarbon end-group),[5,6] radical exchange,[7,8] reaction with nucleophiles (e.g., amine,[1,6,9−13] hydroxide,[14,15] borohydride[16,17]—to provide a thiol end-group), treatment with oxidizing agents (e.g., NaOCl,[1] H_2O_2,[1] tBuOOH[18]), and UV irradiation.[19−21] Of these existing processes, only the radical-induced reactions are known to provide desulfurization by complete end-group removal/transfer. These processes require additional reagents and can be complicated by difficult-to-remove byproducts.

In seeking to develop a method for the synthesis of primary amino-functional polymers by way of phthalimido-functional trithiocarbonate RAFT agents (**1, 3, 6**),[6,22] we required a convenient method for trithiocarbonate removal to provide an inert end-group and determined to investigate thermolysis from this perspective. Thermolysis as a means of cleaving thiocarbonylthio compounds has some precedent in ester[23] and xanthate pyrolysis (the Chugaev reaction for synthesizing olefins from alcohols).[24] Thermolysis has the clear advantage over the methods mentioned above in that no chemical treatment is required. It does, however, require that the polymer and any desired functionality are stable to the thermolysis conditions.



1 RAFT agent (n,m=0)
2 Polymer (n,m>0)



3 RAFT agent (n,m=0)
4 Polymer (n=0, m>0)
5 Polymer (n,m>0)

Initially, small-scale thermolysis was carried out using a thermogravimetric balance. Thermolysis of pale yellow polystyrene **7** at 210−250 °C cleanly cleaves the *S*-butyl trithiocarbonate to provide a colorless product (**8**). The thermolysis product was characterized by ^{1}H NMR and GPC. In the thermogram shown in Figure 1a, the mass loss step between 200 and 270 °C corresponds to 7.5% of total mass (9.0% expected for $C_5H_{10}S_3$).

The ^{1}H NMR spectrum of the product of thermolysis of **7** demonstrates the quantitative disappearance of the trithiocarbonate group (the methine hydrogen adjacent to the trithiocarbonate appears as a broad "doublet" at δ 4.7), the formation of a 1,3-diphenylpropenyl end-group (signals at δ 3.1 and 6.1),[2,26−29] and retention of the phthalimido end-group (α-methylene at δ 3.4 and aromatics at δ 7.65 and 7.75) (Figure 2a). The presence of the phthalimido resonances provides a reference peak to simplify end-group quantitation. The electrospray ionization mass spectrum (see Supporting Information) shows a series of peaks at $n \times 104.06$(styrene) + 160.04-(phthalimidomethyl) + 103.05(end-group) + 22.99(Na^+), in accord with the proposed structure **8**. The GPC chromatogram shows the molecular weight distribution to be essentially unchanged (Figure 3a).

Chain cleavage (by thermolysis) and GPC analysis can provide useful information regarding the mechanism of RAFT polymerization. For polystyrene **2**, which is prepared from the bis-trithiocarbonate **1**, the TGA weight loss curve is more complex. Nonetheless, the ^{1}H NMR spectrum of the colorless thermolysis product is similar. The GPC trace (Figure 3b) confirms a decrease in molecular weight of 50% for both low and high molecular weight/conversion samples (4.4% conversion, $\bar{M}_n$ 4980 g/mol, $\bar{M}_w/\bar{M}_n$ 1.68, after thermolysis $\bar{M}_n$ 2030 g/mol, $\bar{M}_w/\bar{M}_n$ 1.15; see Figure 3a for 87% conversion data). This indicates that the two polystyrene chains of **2** are equivalent (i.e., $n \sim m$) and therefore that the two trithiocarbonate groups of the bis-RAFT agent have equal reactivity during polymerization.

In contrast, low-conversion polystyrenes synthesized with RAFT agent **3** show little change in molecular weight ($n \ll m$) or molecular weight distribution on thermolysis, and only high-conversion samples show the expected ∼50% reduction in molecular weight (5.1% conversion, $\bar{M}_n$ 4900 g/mol, $\bar{M}_w/\bar{M}_n$ 1.46, after thermoly-

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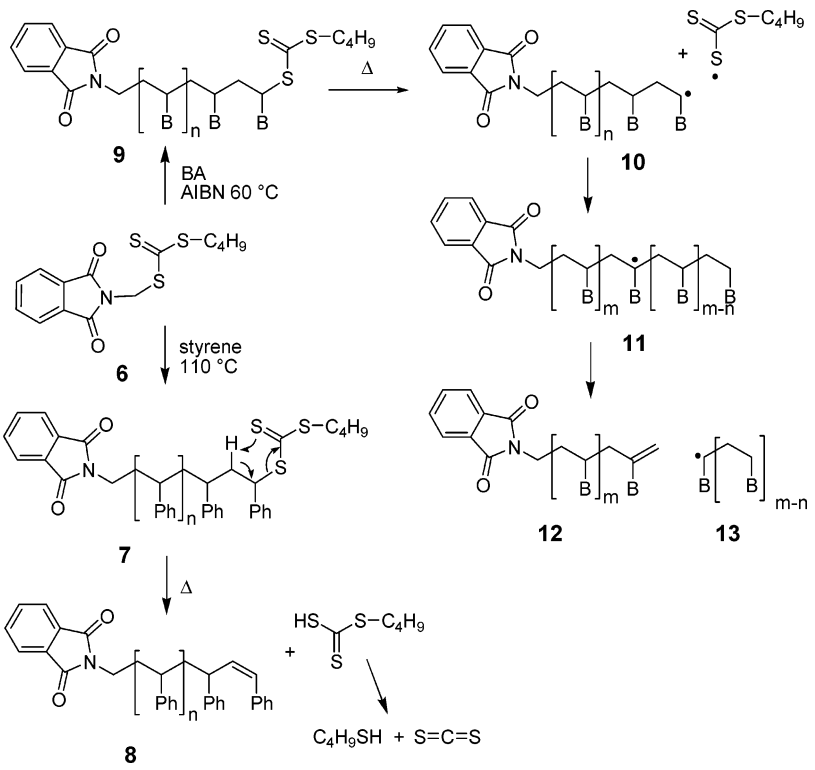
Scheme 1[a]



[a] B = $CO_2C_4H_9$.

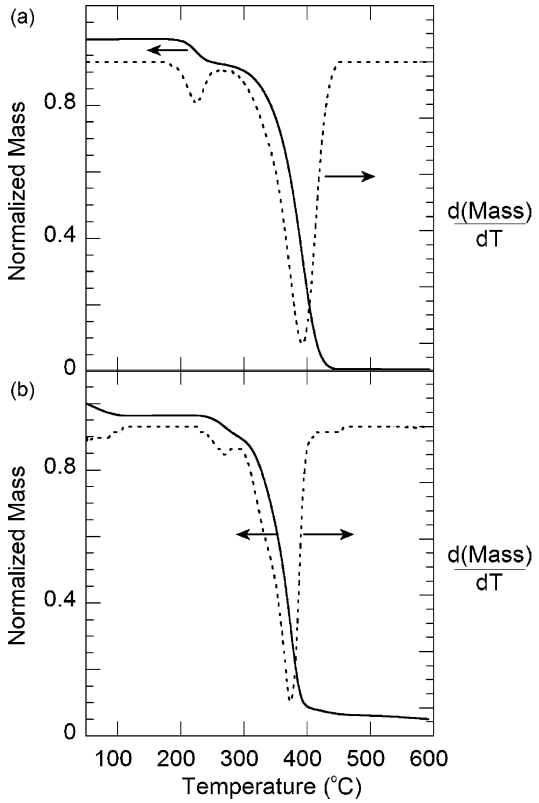


Figure 1. Normalized mass loss (—) and first derivative of mass loss (arbitrary units) (- - -) (a) for polystyrene **7** with number-average molecular weight ($\bar{M}_n$) 1850 g/mol and polydispersity ($\bar{M}_w/\bar{M}_n$ 1.20) and (b) for poly(*n*-butyl acrylate) **9** with $\bar{M}_n$ 6830 g/mol and $\bar{M}_w/\bar{M}_n$ 1.17. Samples were heated at 2 °C/min under nitrogen in an alumina crucible (Mettler TGA/SDTA521 thermobalance).[25]

sis $\bar{M}_n$ 4630 g/mol, $\bar{M}_w/\bar{M}_n$ 1.36; 96% conversion, $\bar{M}_n$ 50 100 g/mol, $\bar{M}_w/\bar{M}_n$ 1.25; after thermolysis $\bar{M}_n$ 31 200 g/mol, $\bar{M}_w/\bar{M}_n$ 1.18). This is attributed to the polystyryl chain being a better homolytic leaving group than the phthalimidomethyl group in the polymeric RAFT agent **4**. Our thermolysis methodology has very recently been applied in characterization of poly(styrene-*alt*-maleic anhydride)-*block*-styrene ABA triblocks prepared by RAFT polymerization.[31]

Poly(*n*-butyl acrylate) (**9**) synthesized with RAFT agent **6** shows quite different thermolysis behavior from the analogous polystyrene samples (Figure 1b). The ^{1}H NMR spectrum (Figure 2b) shows no signals for the direct elimination product but rather signals at δ 5.55 and 6.1, which are characteristic of a methacrylate end-group **10** (Scheme 1). The corresponding ^{13}C NMR signals appear at δ 127 and 138. Two-dimensional NMR (HMBC, HSQC) proved the assignments. The ratio of phthalimide chain ends to unsaturated chain ends was estimated by integration of the ^{1}H NMR as ~10:6. The product is similar to that formed by backbiting β-scission during high-temperature polymerization of butyl acrylate[32] or by copolymerization of butyl acrylate in the presence of a methacrylate and a catalytic chain transfer agent.[2,29,33] The GPC trace for a low molecular weight sample indicates some broadening of the molecular weight distribution and the formation of oligomeric products (Figure 3c). Thermolysis of a higher molecular weight poly(*n*-butyl acrylate) sample ($\bar{M}_n$ 23 900 g/mol, $\bar{M}_w/\bar{M}_n$ 1.07) gave a relatively unchanged molecular weight yet with some oligomer formation evident (overall $\bar{M}_n$ 20 890 g/mol, $\bar{M}_w/\bar{M}_n$ 1.09, with the major component $\bar{M}_n$ 20 900 g/mol, $\bar{M}_w/\bar{M}_n$ 1.08 and oligomer component $\bar{M}_n$ 1320 g/mol, $\bar{M}_w/\bar{M}_n$ 1.20). A plausible mechanism for poly(*n*-butyl acrylate) thermolysis is shown in Scheme 1. The C−S bond undergoes homolysis to a poly(*n*-butyl acrylate) propagating radical which decays by intramolecular (or, to a lesser degree, intermolecular) transfer and β-scission.[34] Thermal degrada-

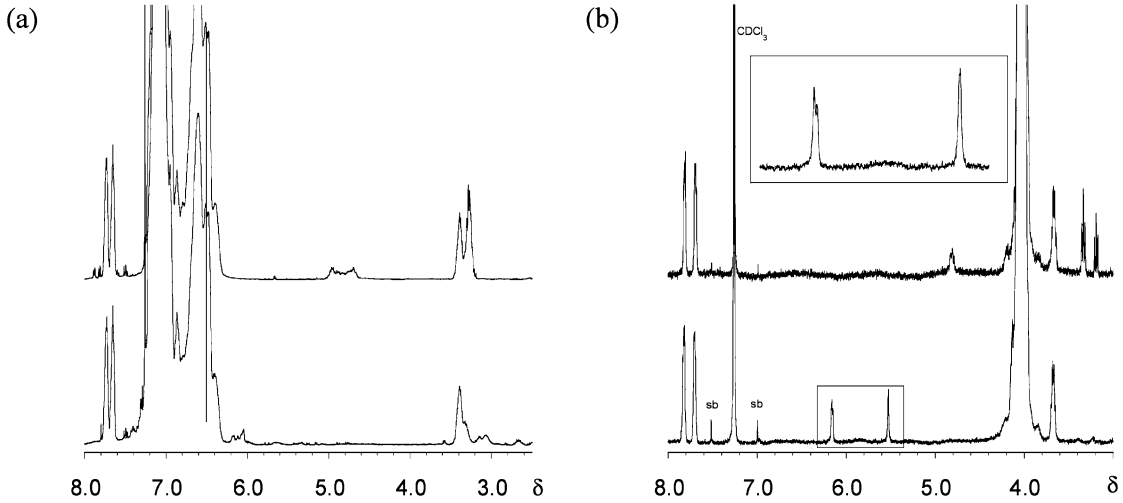


Figure 2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): (a) polystyrene **7** with $\bar{M}_n$ 1850 g/mol ($\bar{M}_n^{NMR}$ 1950 g/mol), $\bar{M}_w/\bar{M}_n$ 1.20 (upper) and thermolysis product **8** with $\bar{M}_n$ 1740 g/mol ($\bar{M}_n^{NMR}$ 1860 g/mol), $\bar{M}_w/\bar{M}_n$ 1.18 (lower); (b) poly(*n*-butyl acrylate) **9** with $\bar{M}_n$ 6830 g/mol ($\bar{M}_n^{NMR}$ 6220 g/mol), $\bar{M}_w/\bar{M}_n$ 1.17 (upper) and thermolysis product **12** with $\bar{M}_n$ 4500 g/mol ($\bar{M}_n^{NMR}$ 6160 g/mol), $\bar{M}_w/\bar{M}_n$ 1.67 (lower), prepared under isothermal conditions.[30] Inset shows expansion of region δ 5.4−6.2 showing olefinic resonances.

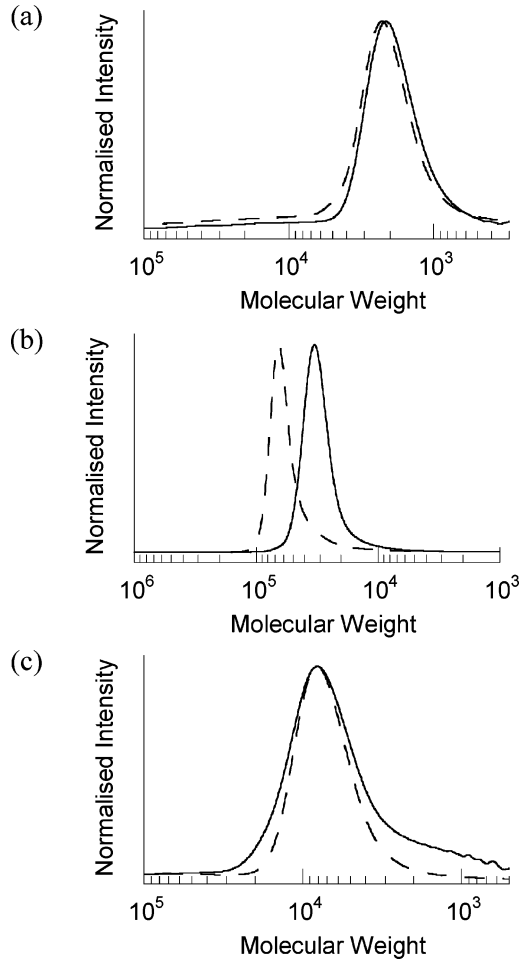


Figure 3. GPC traces for the precursor polymer (- - -) and reaction products (—) which arise from thermolysis: (a) monopolystyrene trithiocarbonate **7** (precursor $\bar{M}_n$ 1850 g/mol, $\bar{M}_w/\bar{M}_n$ 1.20; product $\bar{M}_n$ 1740 g/mol, $\bar{M}_w/\bar{M}_n$ 1.17), (b) bis-(polystyrene) trithiocarbonate **2** (precursor $\bar{M}_n$ 52 900 g/mol, $\bar{M}_w/\bar{M}_n$ 1.13; product $\bar{M}_n$ 27 100 g/mol, $\bar{M}_w/\bar{M}_n$ 1.17), and (c) mono-poly(*n*-butyl acrylate) trithiocarbonate **9** (precursor $\bar{M}_n$ 6830 g/mol, $\bar{M}_w/\bar{M}_n$ 1.17; product $\bar{M}_n$ 4500 g/mol, $\bar{M}_w/\bar{M}_n$ 1.67).

tion of poly(*n*-butyl acrylate) and other polyacrylates usually occurs at significantly higher temperatures (304−370 °C).[35−37] β-Scission following backbiting is known[32] to strongly favor formation of the polymeric macromonomer (**12**) and "dimer" radical (**13**, $m - n = 1$). If β-scission takes the alternate pathway, the polymeric product will be a new radical **10** with chain length shortened by 3 units. This **10** can then decay by the same path. On the basis of this mechanism, we predict good end-group purity. Thermolysis of RAFT-made poly(*n*-butyl acrylate) may provide a route to relatively narrow polydispersity macromonomers.

We anticipate that thermolysis should also be appropriate for removing other forms of RAFT agent residues such as dithioester and xanthate chain ends. Similarly, the method may be applied to other polymers, the only proviso being that the polymer and any desired functionality are stable to the conditions used for thermolysis. However, temperature required may vary according to the specific structure of the polymer and the RAFT agent used.

Thermolysis of polystyrene **7** was scaled successfully to ~300 g by conducting the thermolysis in a Kügelrohr operating at 200 °C under vacuum. Thermolysis was also successful by reactive extrusion under nitrogen, with vacuum venting. The thermolysis byproducts, butanethiol and carbon disulfide, are odorous, and appropriate safety precautions should be implemented. In conclusion, thermolysis provides a simple and efficient way of removing trithiocarbonate group from polystyrene and poly(butyl acrylate).

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Supporting Information Available: ESI mass spectrum of polystyrene **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) RAFT polymerizations were are carried out as follows: RAFT agent **6** (0.285 g, 8.757×10^{-4} mol) and styrene (1.82 g, 1.747×10^{-2} mol) was transferred to an ampule, degassed with four freeze−pump−thaw cycles, sealed under vacuum, and heated at 110 °C for 24 h when polymerization was quenched by cooling in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ (for GPC or ^{1}H NMR analysis respectively). Samples used for thermolysis were purified by precipitation into methanol.
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