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Reversible Addition−Fragmentation Chain Transfer Polymerization: End Group Modification for Functionalized Polymers and Chain Transfer Agent Recovery

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In the past few years, free radical polymerization has seen a renewal of interest with the rise of living radical polymerizations (LRP).[1−5] Among the LRP techniques reported to date, reversible addition−fragmentation chain transfer (RAFT)[4,6] and macromolecular design by interchange of xanthates (MADIX)[5] are the most versatile techniques and show great promises for scale-up reactions. RAFT and MADIX are both based on a radically induced degenerative chain transfer reaction between a thiocarbonyl−thio containing compound and a propagating radical, following the principle of degenerative chain transfer first reported by Zard's group in the late 1980s.[7] RAFT and MADIX permit to produce a variety of polymeric architectures with predictable molecular weight and narrow molecular weight distribution, from a wide range of vinyl monomers.[5,8−12] Furthermore, the simple process governing the polymerization offers great potential for large-scale reactions. However, the polymeric chains formed via RAFT/MADIX polymerization contain the thiocarbonyl−thio compound as the end group, and therefore the chain transfer agent not only confers color and a certain degree of toxicity to the polymeric product but also it is not recovered at the end of the process.[8] As the syntheses of these RAFT/MADIX agents are usually costly and require multistep reactions,[13−16] the loss of polymerization mediator throughout the process may be an issue when scaling-up the process. We propose in this communication a simple reaction that leads to (a) the full removal of the thiocarbonyl−thio end group from the polymeric chains, (b) the introduction of a wide range of chain-end functionalities on the polymers, and (c) the recovery of the chain transfer agent.

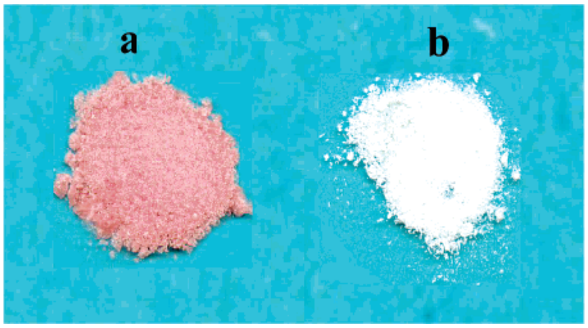

Figure 1. Picture of poly(methyl methacrylate) (PMMA) synthesized by the RAFT process (a) before and (b) after reaction with AIBN.

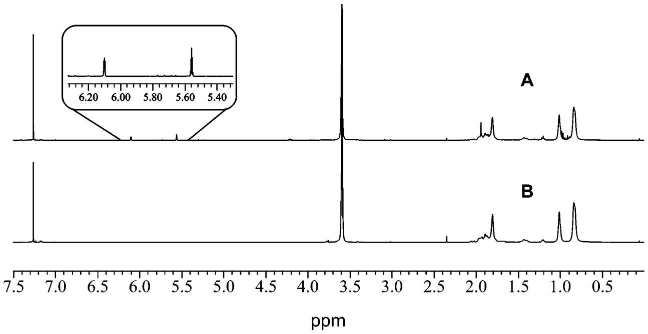

Figure 2. ^{1}H NMR spectra of poly(methyl methacrylate) chains reacted with AIBN in ratio AIBN:PMMA = 10:1 (A) and 20:1 (B). Note the appearance of vinyl protons' peaks at 5.56 and 6.10 ppm when a ratio AIBN:PMMA = 10:1 is used.

Methyl methacrylate was mixed with *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) and α,α′-azobis(isobutyronitrile) (AIBN) in a ratio 500:1:0.1, and the solution was heated at 60 °C. After 8 h, a sample was taken to determine the monomer conversion (34%), and the polymer was isolated by precipitation in cold hexane to yield a powder with the characteristic pink color (Figure 1) of polymers obtained by the RAFT process (due to the dithiobenzoate moiety present at the end of the polymeric chain which absorbs at 510 nm). The molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) (M_n = 13 500 g/mol, PDI = 1.18). The PMMA was redissolved in toluene, and AIBN was added to the solution in a ratio PMMA:AIBN = 1:20. After purging the solution with nitrogen gas, the temperature was raised to 80 °C for 2.5 h (AIBN half-life time at 80 °C is 80 min). After the reaction with AIBN, the polymer was precipitated in cold hexane, and a white powder was isolated by filtration (Figure 1) along with a pink filtrate. The filtrate was evaporated in vacuo to afford a pink oily product. The product was analyzed by ^{1}H NMR spectroscopy and gas chromatography−mass spectroscopy (GC−MS). The ^{1}H NMR spectrum showed the characteristic peak at 1.54 ppm for tetramethylsuccinonitrile, formed from the recombination reaction of the cyanoisopropyl radicals. GC−MS showed the presence of two peaks in the gas chromatogram, with retention times of 7.5 and 22.2 min. On-line mass spectrometry confirmed the peak at 7.5 min was tetramethylsuccinonitrile and the peak at 22.2 min was cyanoisopropyl dithiobenzoate (CPDB).

The recovered polymer was analyzed by ^{1}H NMR spectroscopy. Figure 2 (top spectrum) shows the characteristic spectrum of PMMA in CDCl$_3$, and we observe the disappearance of the peaks at 7.30, 7.38, and 7.93 ppm, characteristic of the dithiobenzoate moiety. To prove further the complete removal of the dithiobenzoate moiety from the end of the polymeric chain, elemental analysis was performed on the PMMA, and no traces of sulfur were found, confirming a reaction of 99+%. A UV/vis spectrum was also taken of the PMMA before and after AIBN treatment, resulting in the loss of the characteristic peak of the dithiobenzoate. Finally, the polymer was analyzed by SEC, and no difference between the polymeric chains before and after treatment was observed. Details of analyses are supplied in the Supporting Information.

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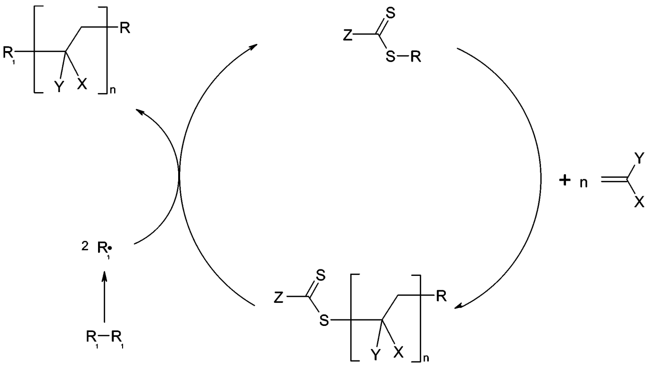
In solution, AIBN decomposes to form two cyano isopropyl radicals, which react on the reactive C=S of the thiocarbonyl−thio moiety present at the chain end of the polymer. The addition of the cyano isopropyl radical to the reactive C=S bond of the thiocarbonyl−thio group leads to the formation of an intermediate radical. This intermediate has then the possibility to fragment either back to the original attacking radical or to free the leaving group (R group). In the presence of an excess of cyano−isopropyl radicals, the equilibrium is displaced toward the formation of the R group radical, which can then combine irreversibly with free cyano isopropyl radicals present in solution, thus forming dead polymeric chains, capped by the cyano−isopropyl group.

The ratio of AIBN to polymer chain as well as the temperature and the length of the reaction are important parameters to consider in order to fully remove the thiocarbonyl−thio end group from the polymeric chains. To attain complete conversion, the length of the reaction should follow the half-life time of the radical initiator. Furthermore, excess of AIBN relative to polymer needs to be used. Indeed, in our initial attempts, a lower ratio of AIBN to PMMA (10:1) led to disproportionation reactions between polymeric chains.[17] Figure 2 (lower spectrum) shows the appearance of singlets at 5.7 and 6.2 ppm, characteristic of vinyl protons of the unsaturated PMMA chains formed through disproportionation termination reactions. By increasing the concentration of free radicals in solution (ratio AIBN:PMMA = 20:1), we avoided such side reactions. However, disproportionation may be wanted in order to introduce a certain amount of double bond end groups on methacrylate polymeric chains.

To assess the activity of the recovered chain transfer agent (CTA) and to test the recovery cycle, a similar reaction as that described above was undertaken, with a ratio of MMA:MCPDB:AIBN = 100:1:0.2 in toluene. The temperature was raised to 80 °C for 24 h (98% conversion). The polymer was precipitated by dropwise addition into hexane and characterized by SEC (M_n = 16 300 g/mol, PDI = 1.23). The polymer was dissolved in toluene, and a second batch of AIBN was added to cleave the dithiobenzoate moiety from the polymeric chains. After a further 2.5 h at 80 °C, the solution was cooled, and the poly(methyl methacrylate) was precipitated by dropwise addition of the solution into hexane. The polymer was filtered off and characterized by SEC (M_n = 16 000 g/mol, PDI = 1.25). The filtrate was evaporated to dryness, and the pink product was added to a clean dry ampule together with methyl methacrylate, AIBN, and toluene using the exact amounts as for the first reaction. The solution was degassed with N_2 for 10 min and then heated to 80 °C for 60 h. The solution was cooled, and the poly(methyl methacrylate) was precipitated by dropwise addition of the solution into hexane. The polymer was filtered off and characterized by SEC to reveal a similar molecular weight and polydispersity as those of the previous product (M_n = 16 300 g/mol, PDI = 1.17). The polymer was dissolved in toluene, and a second batch of AIBN was added to cleave the dithiobenzoate moiety from the polymeric chains. After a further 2.5 h at 80 °C, the solution was cooled, and the poly(methyl methacrylate) was precipitated by dropwise addition of the solution into hexane. The polymer was filtered off and characterized by SEC to reveal a similar molecular weight and polydispersity as those of the previous cleaved product (M_n = 16 500 g/mol, PDI = 1.24). The reproducibility of the polymerization and end group removal reaction confirms that the CTA is almost quantitatively recovered and with virtually no loss to its activity. Scheme 1 summarizes the recovery cycle for the process.

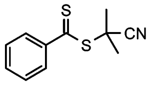
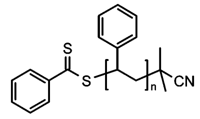
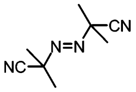
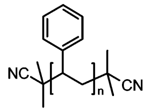
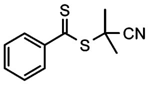
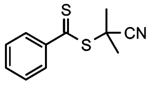
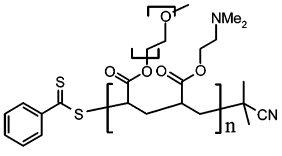
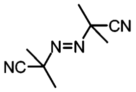
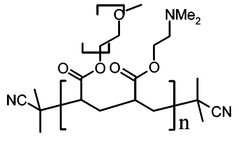
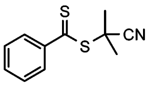
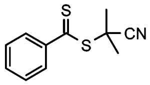
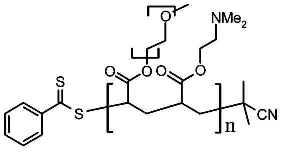
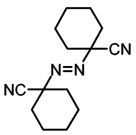
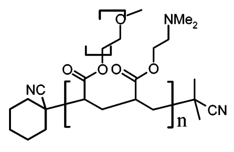
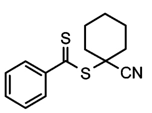
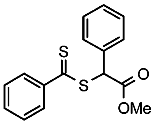
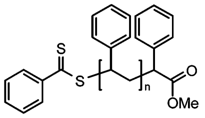
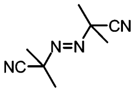
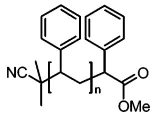
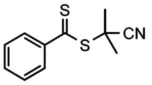
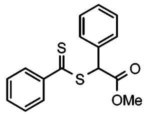
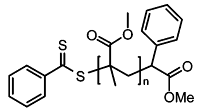
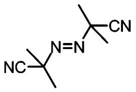
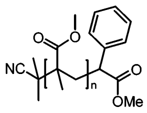
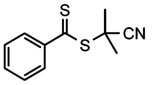
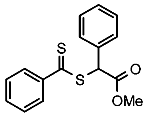
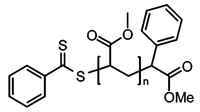
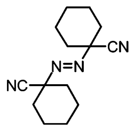
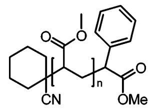
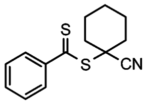
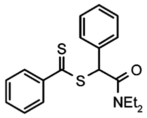
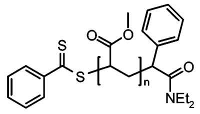
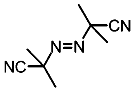
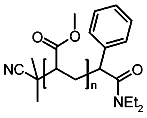
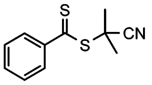
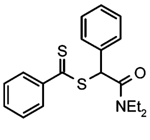
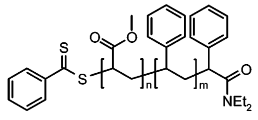
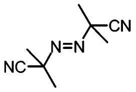
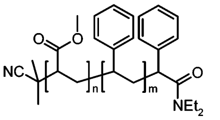
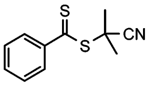
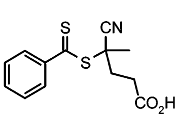
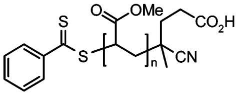
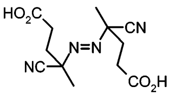
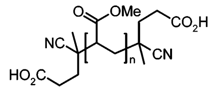
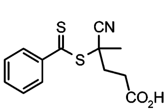
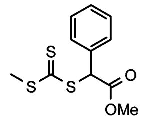
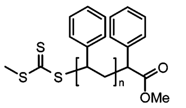
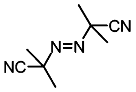
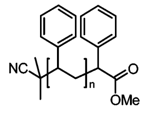
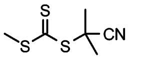
Scheme 1. Reaction Cycle To Produce Chain-End Functional Polymers via Reversible Addition−Fragmentation Chain Transfer Polymerization with Recovery of the Chain Transfer Agent



The precipitation of polymers is an easy technique to separate the chain-end functionalized polymer and recovered CTA for laboratory scale experiments, but it is less appropriate for scale-up processes. Alternative methods of recovering the CTA, more practical for large-scale processes, include (a) increase of temperature toward the end of the polymerization to recover the CTA by distillation or sublimation; (b) following the reaction with excess AIBN, the recovered CTA and end-functionalized, nonreactive, polymeric chains can be kept in solution, and a new batch of monomer may be added to restart polymerization. In the latter technique, a new batch of polymeric chains is therefore formed in the presence of the previous batch of product, with similar molecular weight and polydispersity; the same CTA is therefore reused to produce a similar material. However, the time for reaction of the polymer with AIBN when removing the thiocarbonyl−thio group must be sufficiently long for complete decomposition of the AIBN. These alternative processes are currently being tested in our laboratories.

The process we report here not only is a simple and effective method to recycle a RAFT or MADIX agent but also has great potential to introduce specific chain-end functionalities to both ends of a polymeric chain with an efficiency of nearly 100%. Indeed, the careful choice of the initial CTA followed by free radical initiator, from the breadth of free radical initiators available commercially, to remove the thiocarbonyl−thio group will allow the production of polymers with specific functionalities at both ends, with known molecular weight and low polydispersity. To illustrate further this technique, we applied this process to a variety of methacrylate, acrylate, acrylamide, and styrenyl polymers and a choice of free radical initiators (see Table 1). Among these results, sample **i** is noteworthy, as it demonstrates the one-step synthesis of a telechelic poly(methyl acrylate) of M_n = 32 600 g/mol and PDI = 1.27, with a carboxylic acid functionality at both chain ends, useful as a building block for methacrylate resins. Further modification of the end group functionalized polymers can be achieved using classical synthetic organic chemistry, an example of which has been successfully achieved by tagging sample **d** with a fluorescent marker. Reduction

Table 1. Examples of End Functional Polymers and Recovered Chain Transfer Agents

	CTA	Polymer	Cleavage initiator	Modified Polymer	Recycled CTA
a		 Mn = 19 750, PDI = 1.18		 Mn = 19 700, PDI = 1.17	
b		 Mn = 36 000, PDI = 1.23		 Mn = 35 700, PDI = 1.23	
c		 Mn = 36 000, PDI = 1.23		 Mn = 35 900, PDI = 1.23	
d		 Mn = 12 800, PDI = 1.10		 Mn = 12 700, PDI = 1.08	
e		 Mn = 13 450, PDI = 1.18		 Mn = 13 350, PDI = 1.17	
f		 Mn = 8 800, PDI = 1.10		 Mn = 8 800, PDI 1.10	
g		 Mn = 48 500, PDI = 1.21		 Mn = 48 300, PDI = 1.20	
h		 Mn = 42 000, PDI = 1.27		 Mn = 41 750, PDI = 1.25	
i		 Mn = 34 700, PDI = 1.26		 Mn = 32 600, PDI = 1.27	
j		 Mn = 30 700, PDI = 1.08		 Mn = 30 550, PDI =1.07	

of the end group methyl ester with sodium borohydride by dissolving cyanoisopropyl poly(styrene) methyl ester in tetrahydrofuran and following addition of $NaBH_4$, under N_2 for 18 h at room temperature, afforded the corresponding alcohol (see Supporting Information). The cyanoisopropyl−hydroxymethyl poly(styrene) was further reacted with 9-fluorenone-4-carbonyl chloride at 50 °C for 18 h to produce a fluorenone-tagged polystyrene.

A UV/vis spectrum showed the formation of a band at 400 nm (see Supporting Information).[18]

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Supporting Information Available: All experimental procedures, selected GC chromatograms, MS spectra, ^{1}H NMR spectra, GPC chromatograms, and UV/vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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